Investigation Into Silicone-Silicate Conversion Due to Atomic Oxygen in the Low Earth Orbit Environment

JUSTIN SELF | MS THESIS DEFENSE

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06 JUNE 2025

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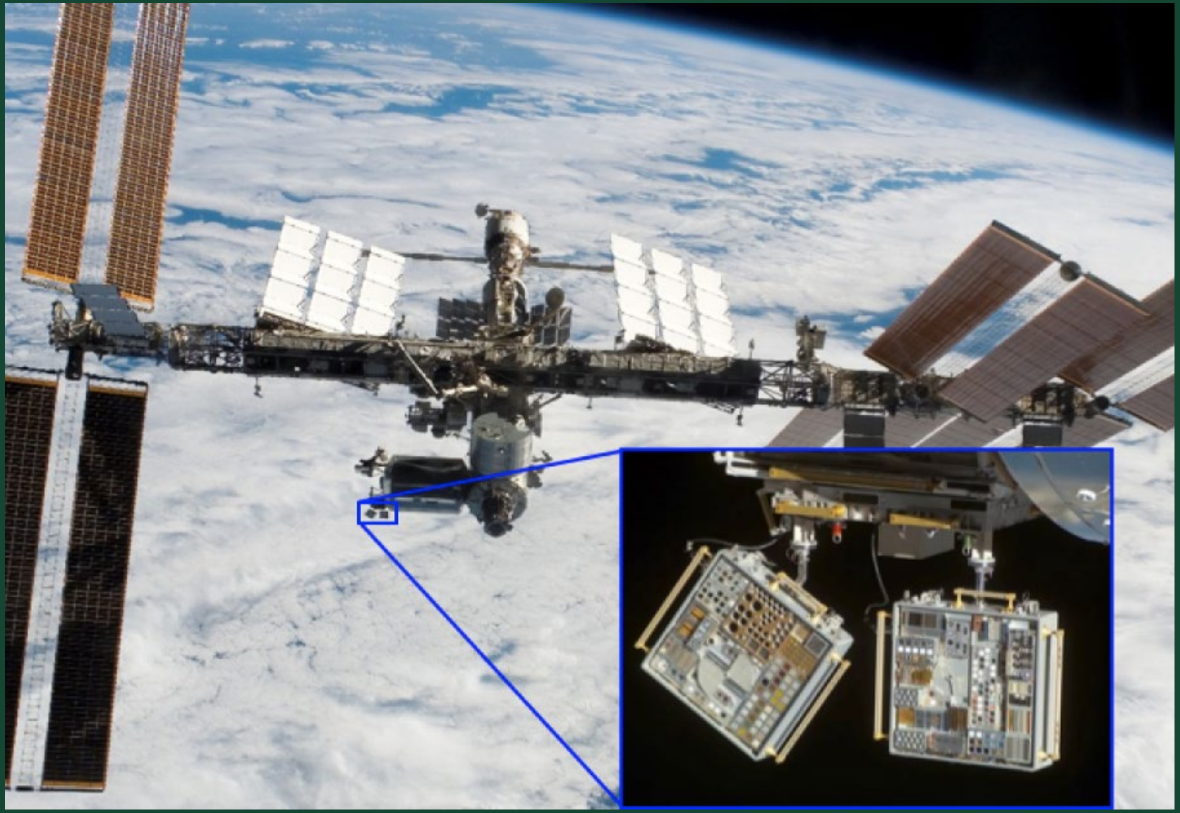
Introduction and Background

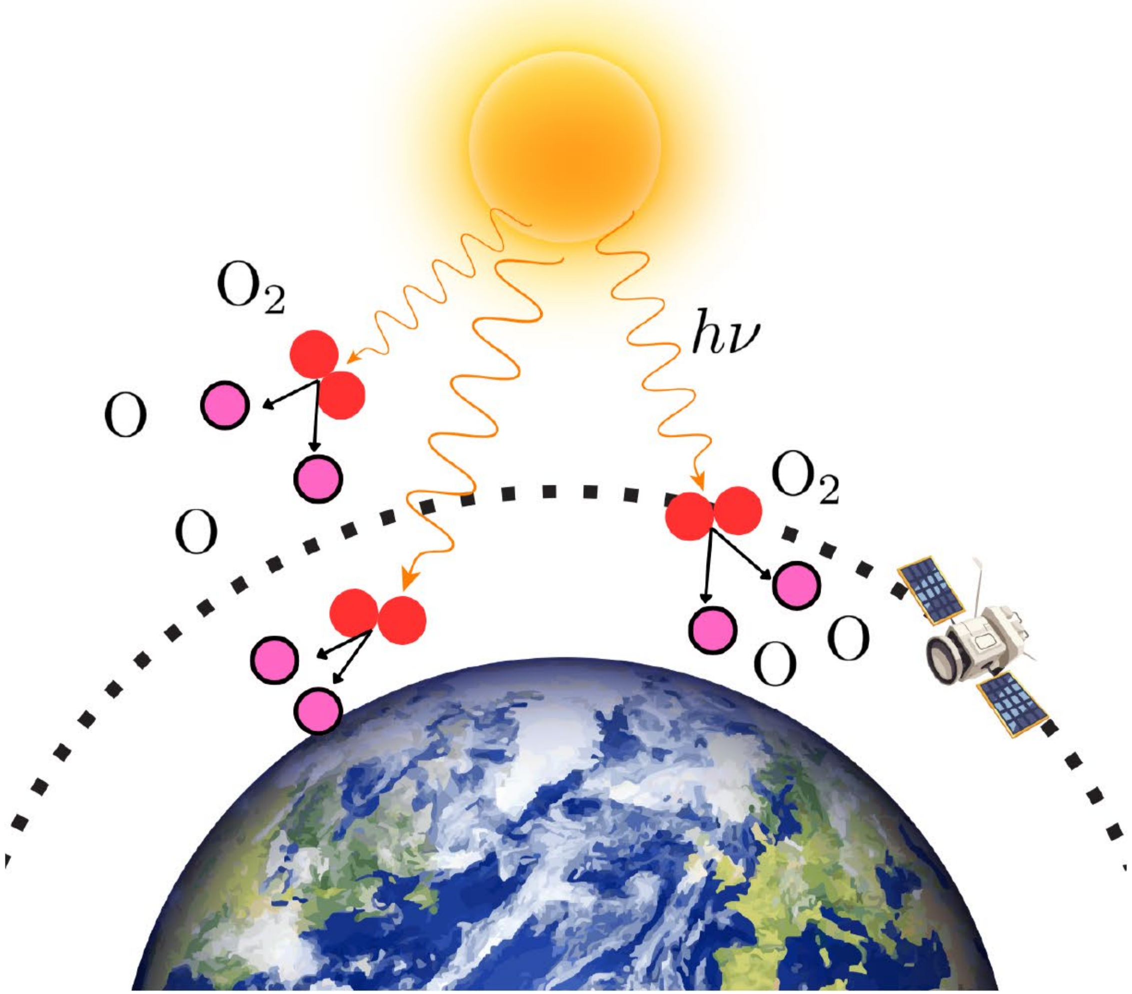
Introduction and Background

The space environment

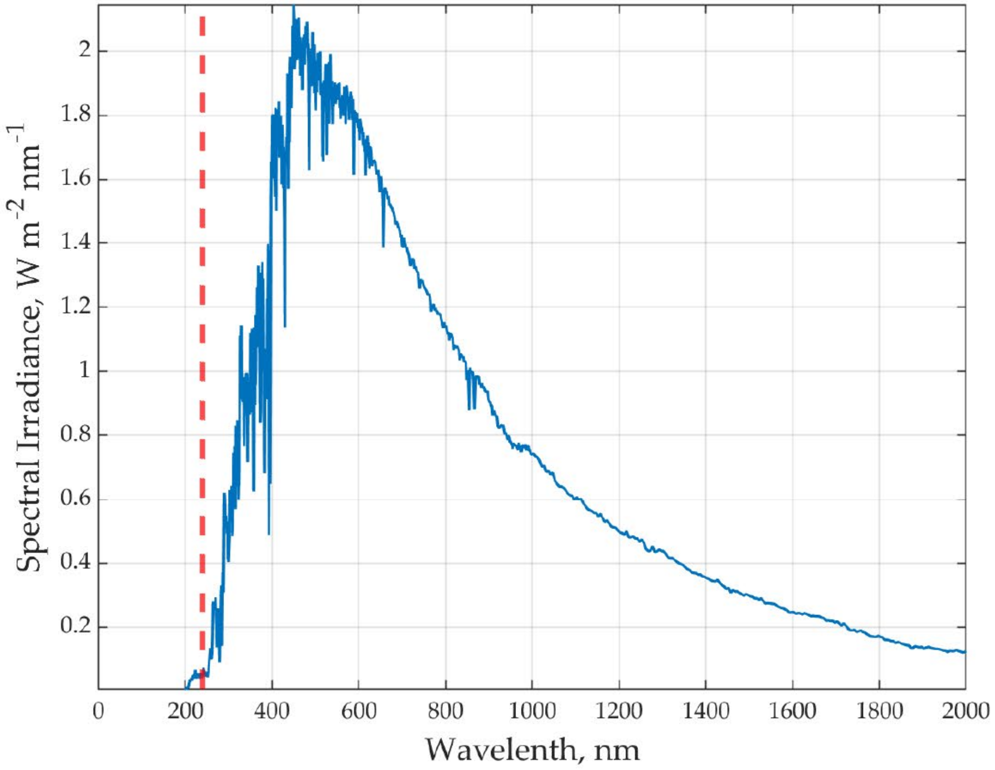
- Vacuum
- Neutral
- Plasma
- Radiation
- Micrometeoroid and Orbital Debris



International Space Station (ISS) with MISSE-6A and 6B Close-Up (de Groh and Banks, 2021)



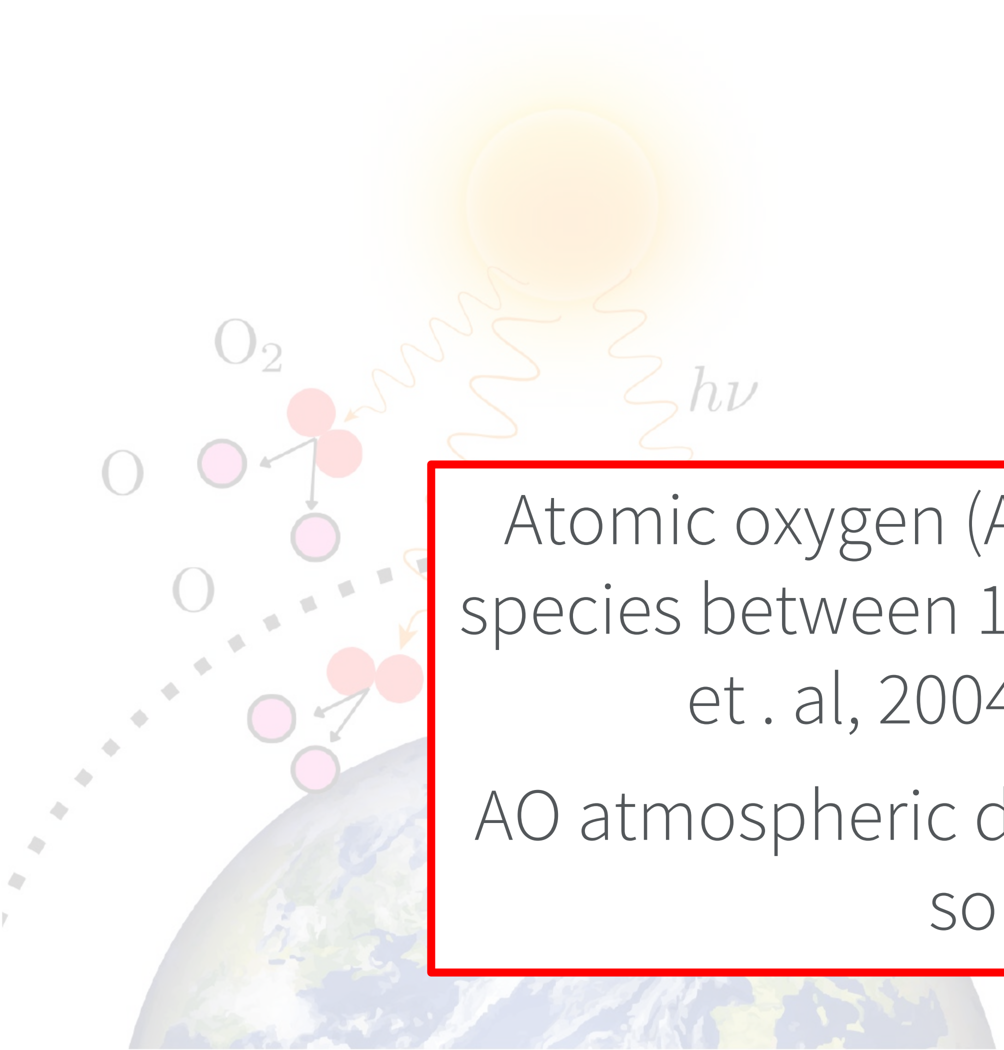
Atomic Oxygen Formation



Solar output spectrum with 241 nm highlighted

Atomic oxygen (AO) is the most abundant species between 180 km and 650 km (Banks, et . al, 2004; Silverman, 1995).

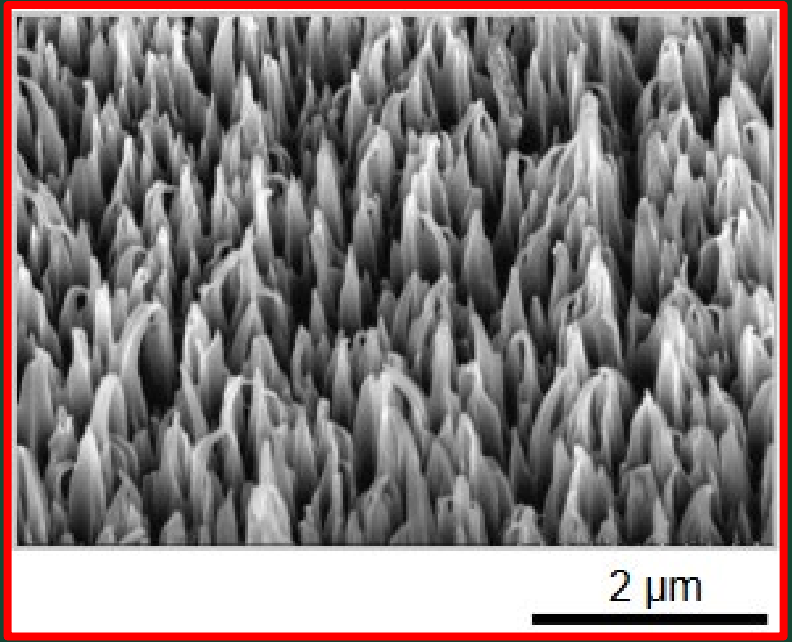
AO atmospheric density is dependent upon solar activity.



Atomic Oxygen Formation

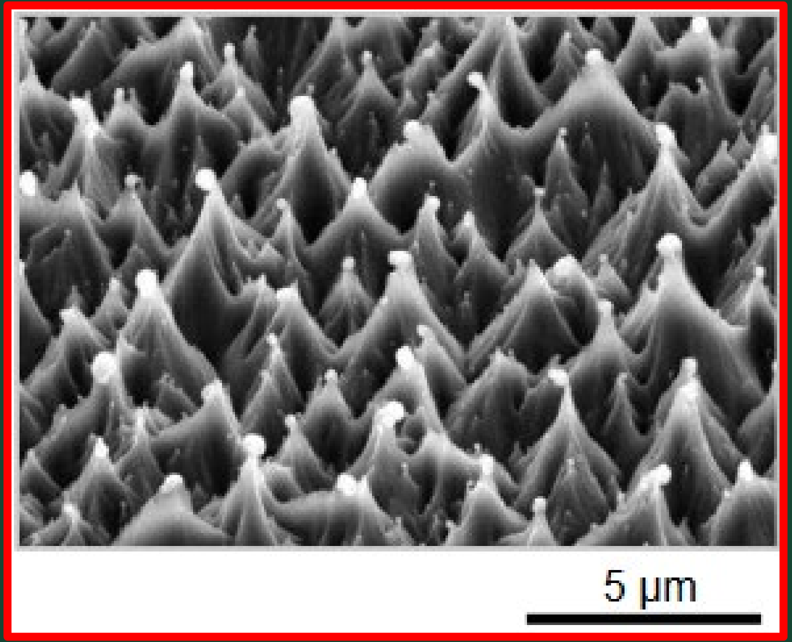
Solar output spectrum with 241 nm highlighted

Introduction and Background



Kapton H (EOIM III)

$F = 2.3 \times 10^{20}$ atoms/cm^2 (8 days)



Teflon FEP (LDEF mission)

$F = 8.43 \times 10^{21}$ atoms/cm^2 (5.7 years)

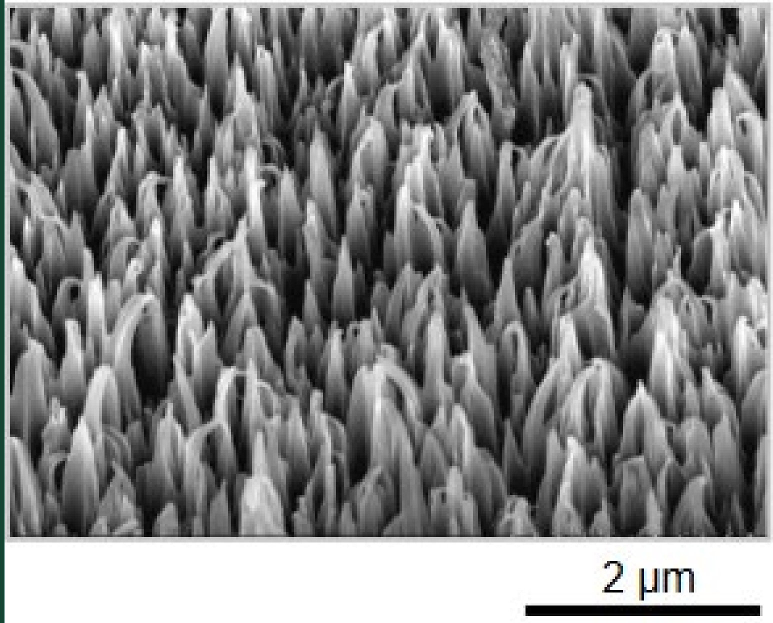
DC 93-500 (LDEF mission)

$F = 4.92 \times 10^{21}$ atoms/cm^2 (5.7 years)

Spacecraft Polymers Atomic Oxygen Durability Handbook, NASA, (2017)

Banks, et al. (1999)

Introduction and Background



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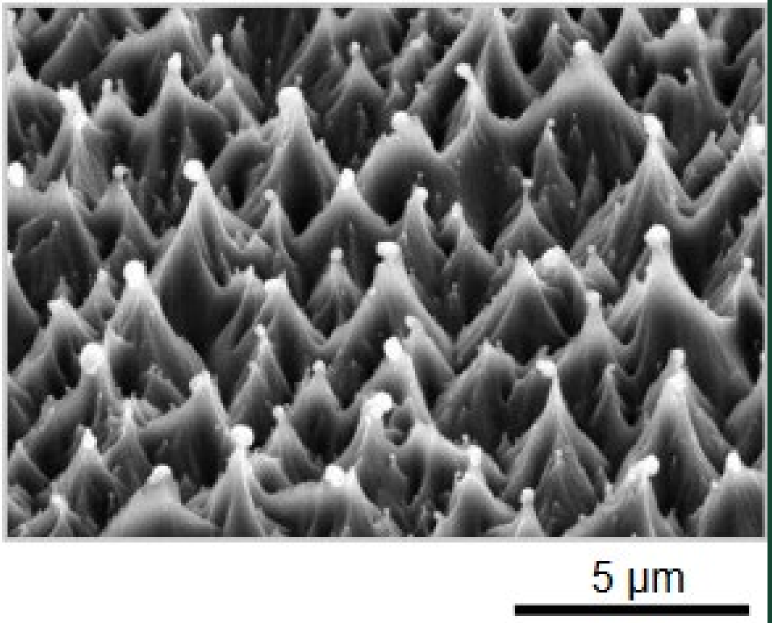

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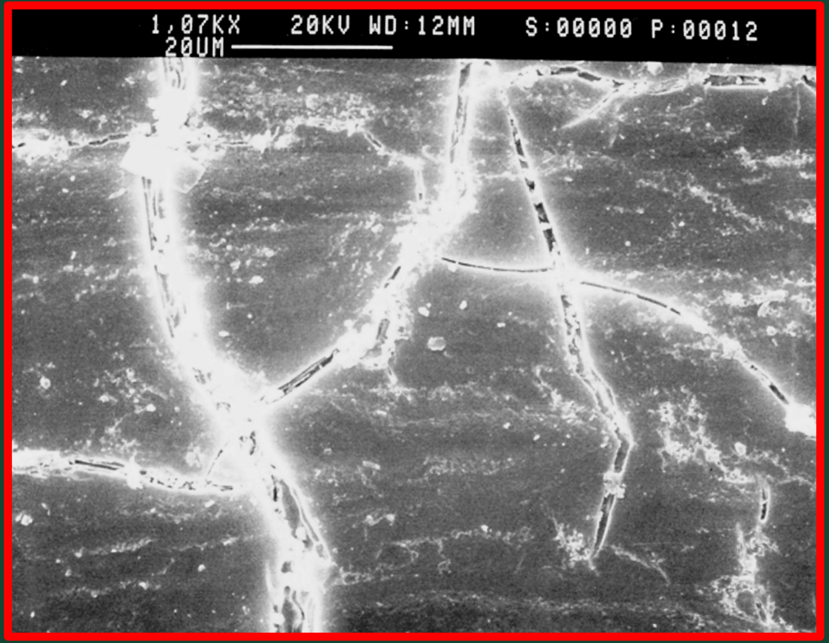

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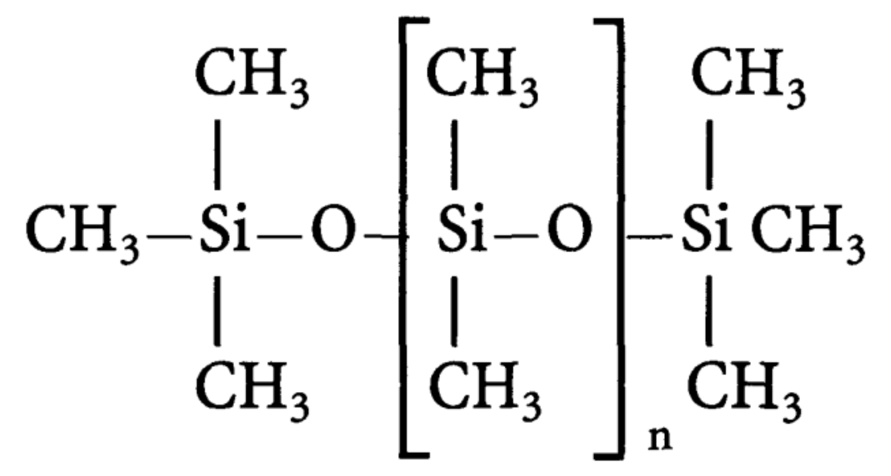
Introduction and Background

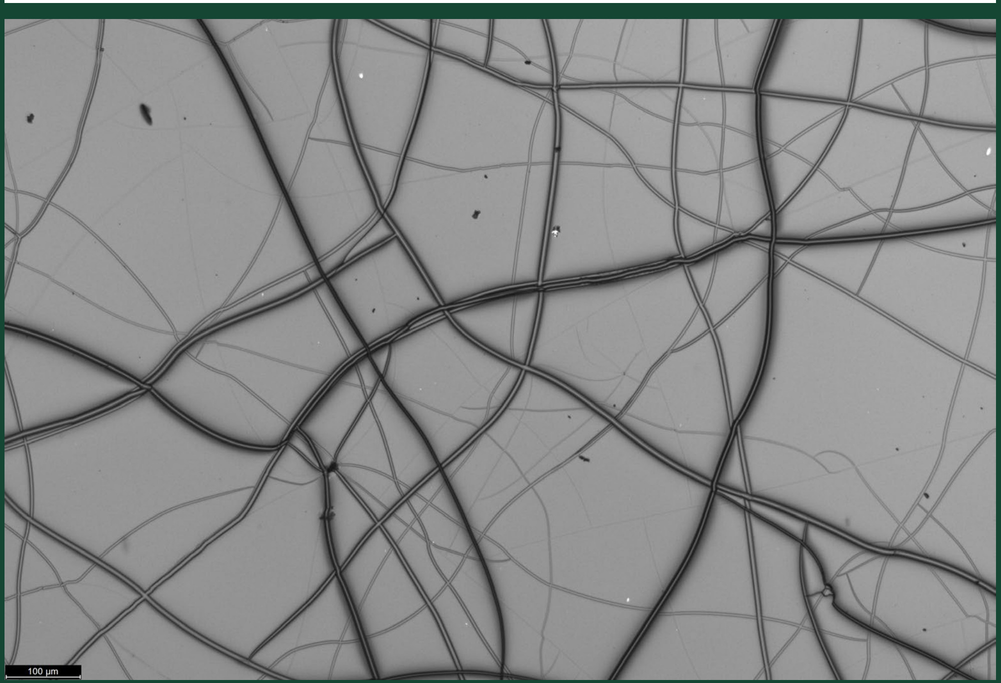
Silicones have been widely used on spacecraft over the years in:

- Potting compounds
- Adhesives
- Thermal transfer applications
- Seals and gaskets
- AO-resistant coatings (Banks, et al. 1999)

- Silicones do not erode in AO like other organic materials (Hung, Cantrell, 1994).
- Silicones lose methyl groups, but don't lose mass during AO-exposure; some gain mass (de Groh, et al., 2006).
- Tension between glassy surface and bulk underlying material results in cracking (Banks, et. al, 1999).



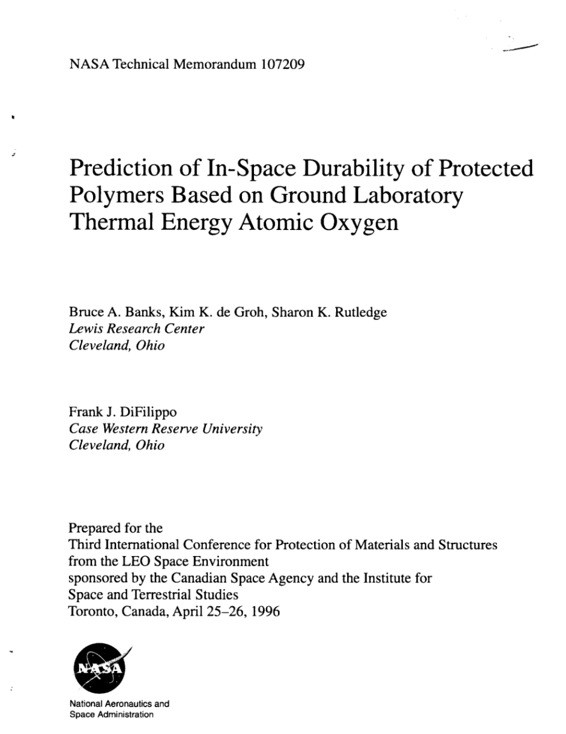
$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}\,CH_3$$



Top: Polydimethylsiloxane (PDMS) silicone
Bottom: DC 93-500 silicone exposed to 2 years ram AO (MISSE-6)

Introduction and Background

- Only two papers in literature that have studied surface morphology changes in space-grade silicones with AO as a predictor.
  1. Banks, de Groh, Rutlege (1996)
     - First to report how the glassy surface responded to indent force (AFM) with increasing AO fluence.
     - Two flight samples (EOIM-III)
  2. Hung and de Groh (2013)
     - First to quantify cracking structure through optical and SEM
     - AO fluence a significant predictor of area percent occupied by cracks
     - Eight flight samples (MISSE-2, 4)



NASA Technical Memorandum 107209

Prediction of In-Space Durability of Protected Polymers Based on Ground Laboratory Thermal Energy Atomic Oxygen

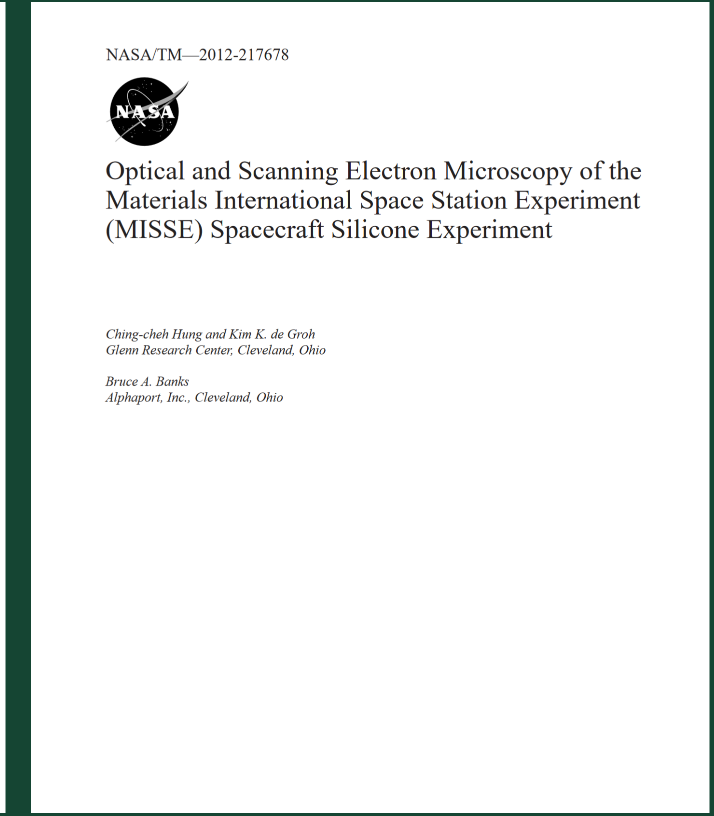
Bruce A. Banks, Kim K. de Groh, Sharon K. Rutledge
Lewis Research Center
Cleveland, Ohio

Frank J. DiFilippo
Case Western Reserve University
Cleveland, Ohio

Prepared for the
Third International Conference for Protection of Materials and Structures
from the LEO Space Environment
sponsored by the Canadian Space Agency and the Institute for
Space and Terrestrial Studies
Toronto, Canada, April 25–26, 1996

National Aeronautics and
Space Administration

Banks, de Groh, Rutledge (1996)



NASA/TM—2012-217678

Optical and Scanning Electron Microscopy of the Materials International Space Station Experiment (MISSE) Spacecraft Silicone Experiment

Ching-cheh Hung and Kim K. de Groh
Glenn Research Center, Cleveland, Ohio

Bruce A. Banks
Alphaport, Inc., Cleveland, Ohio

Hung and de Groh (2013)

Introduction and Background

Who cares about this?

- Missions utilizing silicones exposed to space environment
- LEO orbits
- HEO orbits
- Lunar* and Martian** missions
- Scientific missions concerned about contamination (i.e., SAGE-III)

*Lunar missions are considering AO effects on base materials during transit. (Razeto, et al., 2024)

**Besides transit to Mars, the predominant gas species in 200km – 400 km Mars orbit. (Miller and Banks, 2021)

Thesis Aim and Scope

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Silicone surface glassification in LEO by AO is known and well-documented…

… but there are no studies that utilize flight and ground data, with statistical predictions, to estimate the time it takes on orbit before silicate layer formation fully develops.

Goal	Evaluation Method	Validation
Predict time on orbit before layer formation occurs	Statistical models and optical image processing	Statistical analysis, comparison to flight mission results
Quantify surface cracking and thickness	Optical microscopy and scanning electron microscopy	Statistical analysis, comparison with returned ISS flight samples
Study changes in chemical and optical properties	FTIR, diffuse reflectance spectroscopy	Comparison with returned ISS flight samples and literature

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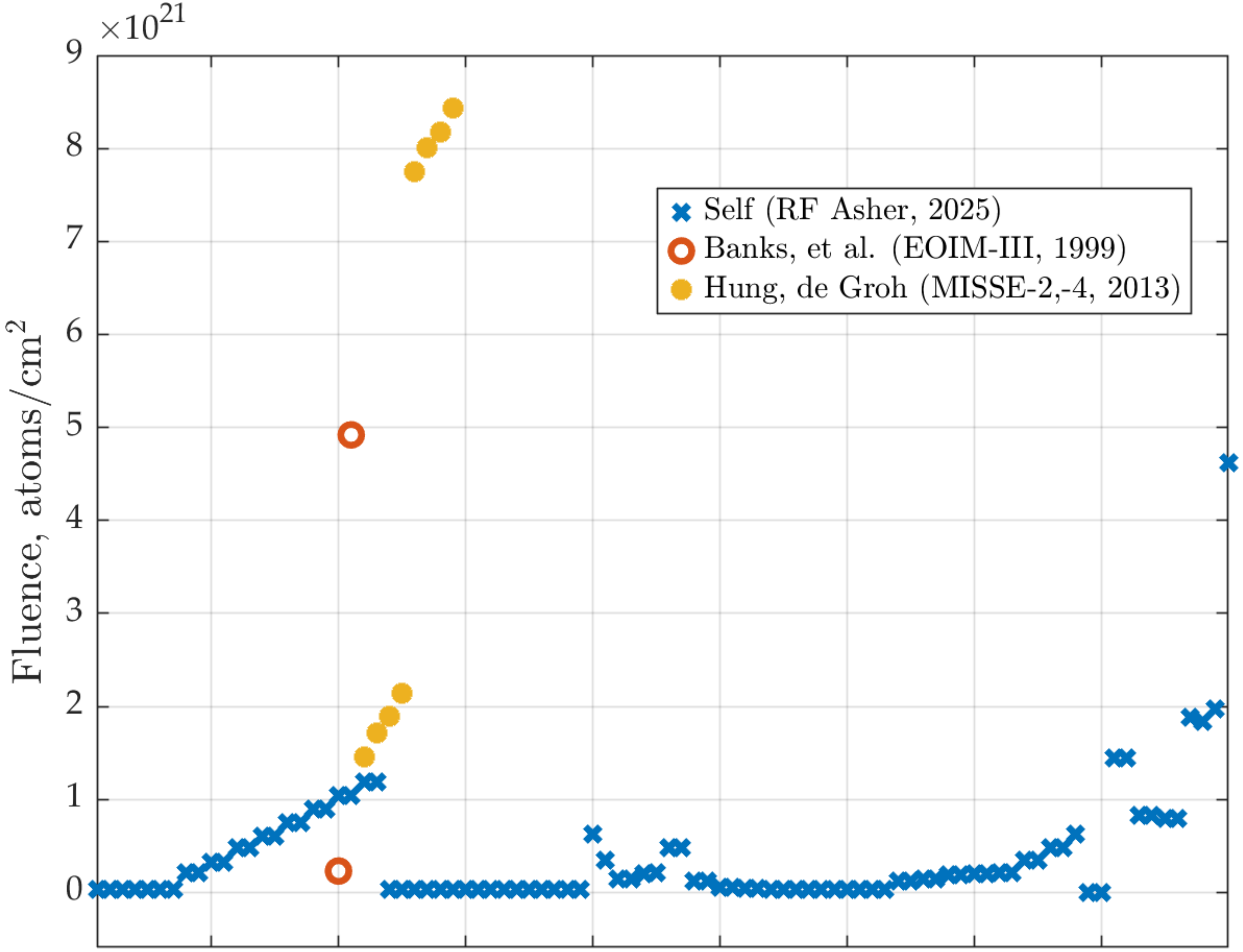
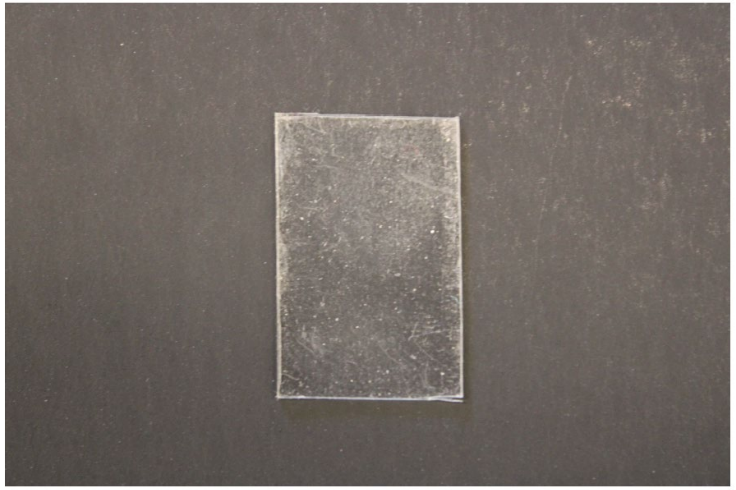

×10^21
9
8
7
6
5
4
3
2
1
0
Fluence, atoms/cm^2
Self (RF Asher, 2025)
Banks, et al. (EOIM-III, 1999)
Hung, de Groh (MISSE-2,-4, 2013)

Experimental Methods Summary

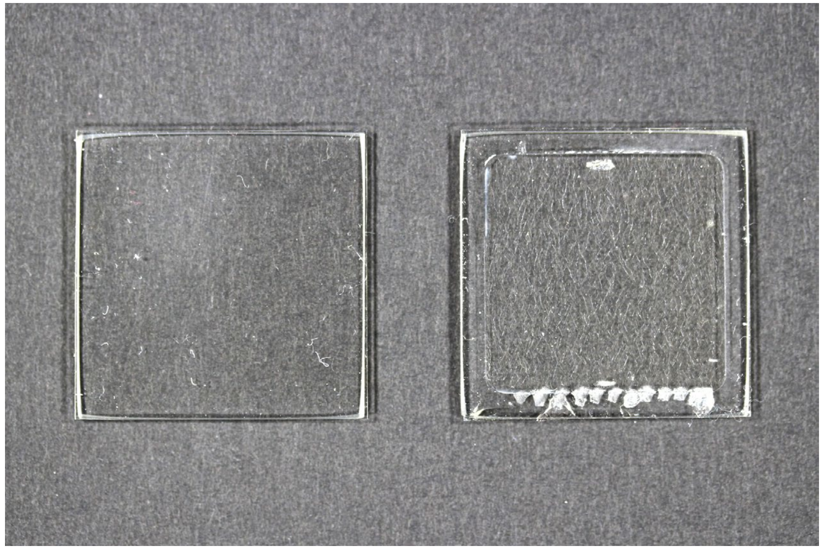
Experimental Test Articles

NuSil CV-2960

Wacker RTV-S691



Dow Corning (DC) 93-500



Dow Corning (DC) 93-500

Flight samples from MISSE-6 and -8

(Kim de Groh at NASA Glenn)

Experimental Methods: Testing Scheme

Prepare → Dehydrate (48h) → Measure → AO Exposure → Evaluate → Analyze

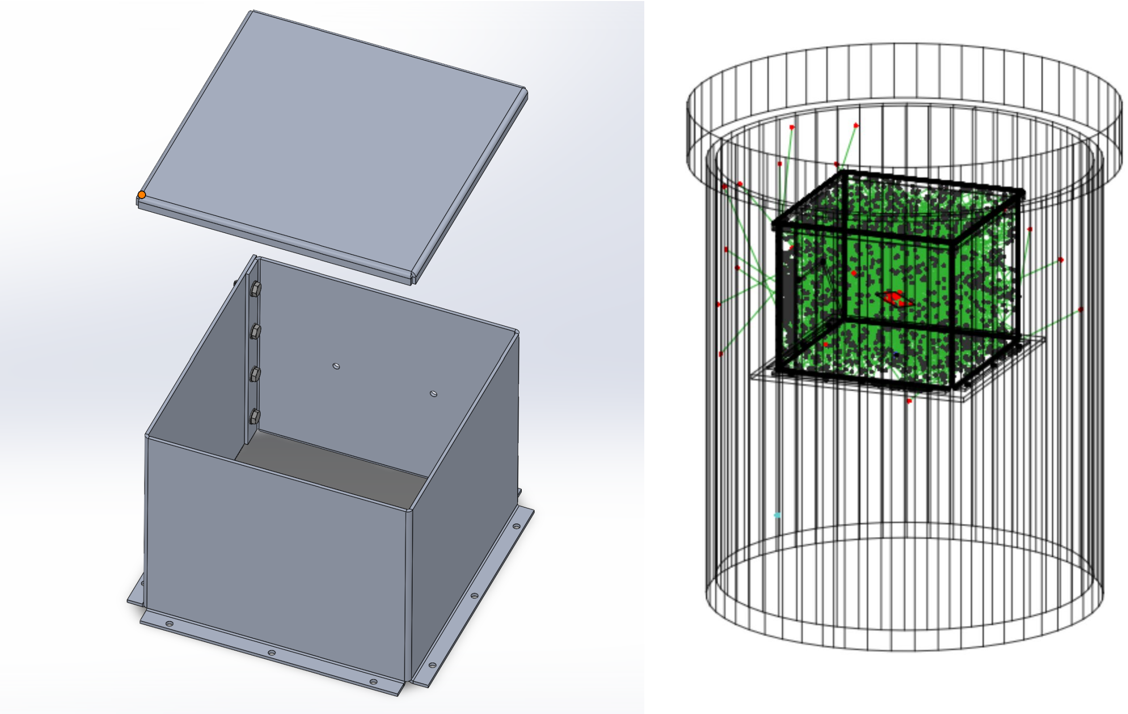
Results and Validation

Results and Validation

1. Silicone contamination
2. Percent of sample surface area occupied by cracks
3. Layer formation predictions
4. Approximate layer thickness (in backup slides)
5. Chemical changes
6. Reflectance spectroscopy
7. ISS Flight Samples vs. Ground Testing

Silicone Contamination

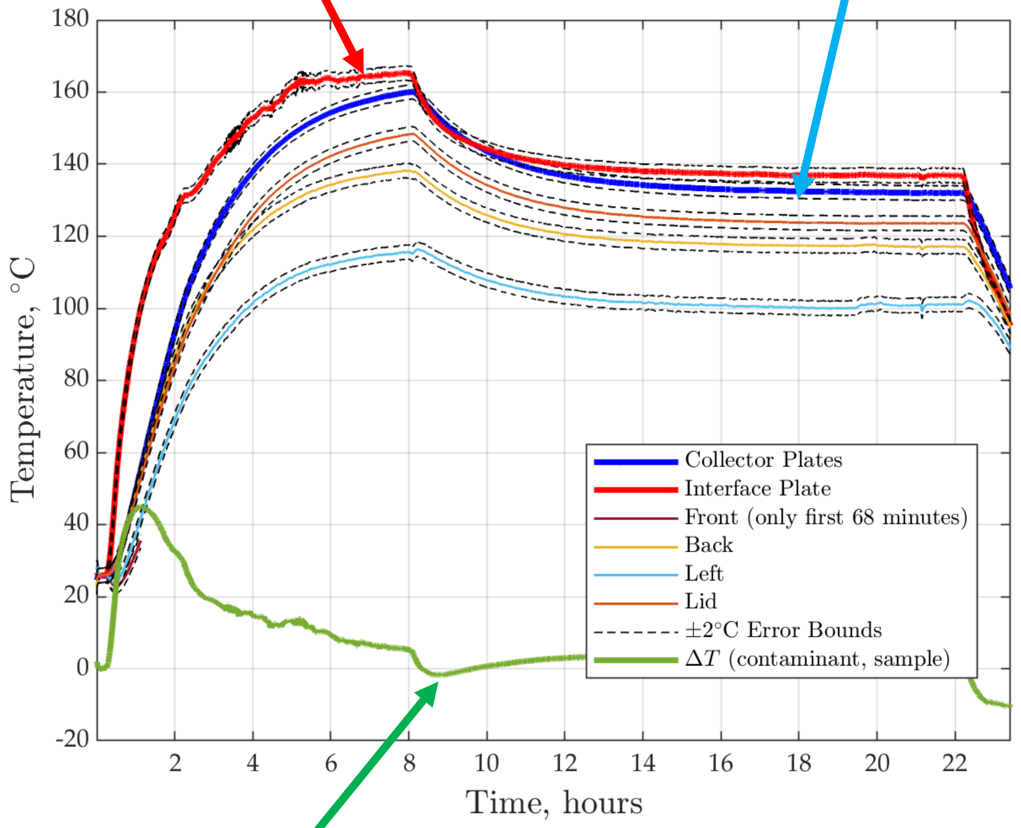
Results: Silicone Contamination



Effusion Cell CAD and Monte Carlo Ray Tracing Simulation

Hot contaminant

Cold collector plate

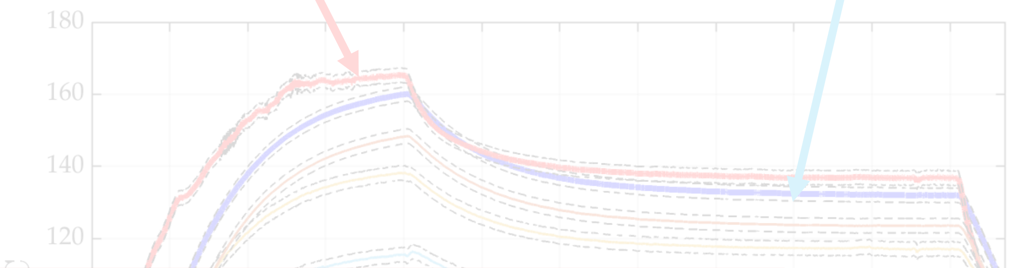


Hot – Cold = ΔT

The larger the better!

Results: Silicone Contamination

Effusion Cell CAD and Monte Carlo Ray Tracing Simulation



Hot contaminant

Cold collector plate

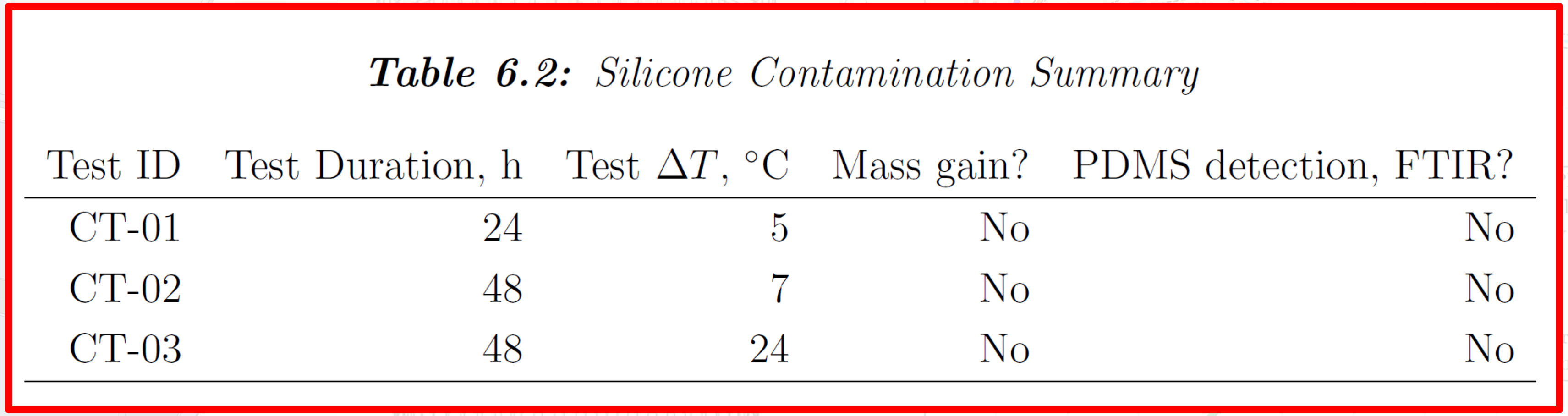


Table 6.2: Silicone Contamination Summary

Test ID	Test Duration, h	Test ΔT, °C	Mass gain?	PDMS detection, FTIR?
CT-01	24	5	No	No
CT-02	48	7	No	No
CT-03	48	24	No	No

Hot – Cold = ΔT

The larger the better!

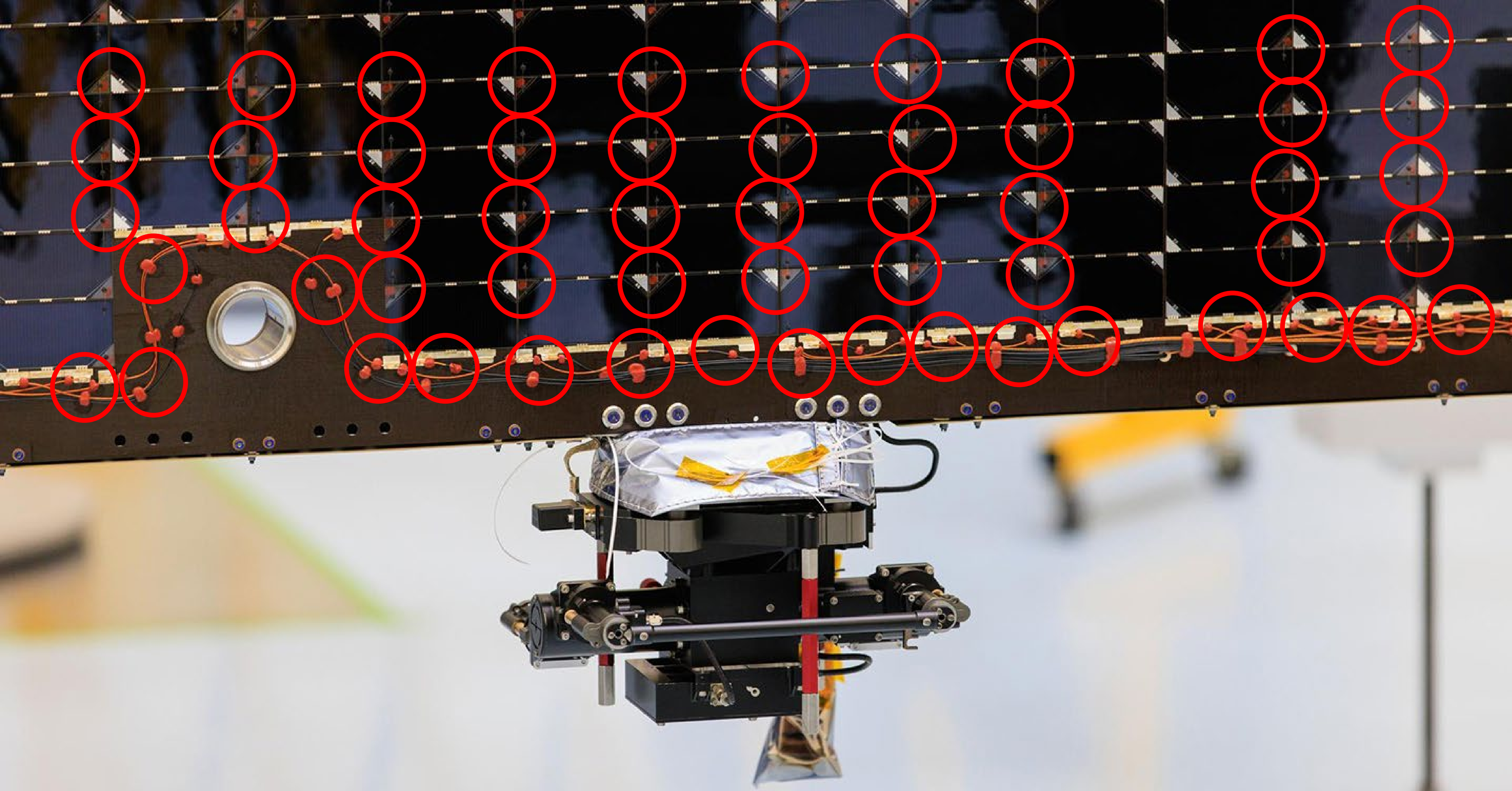
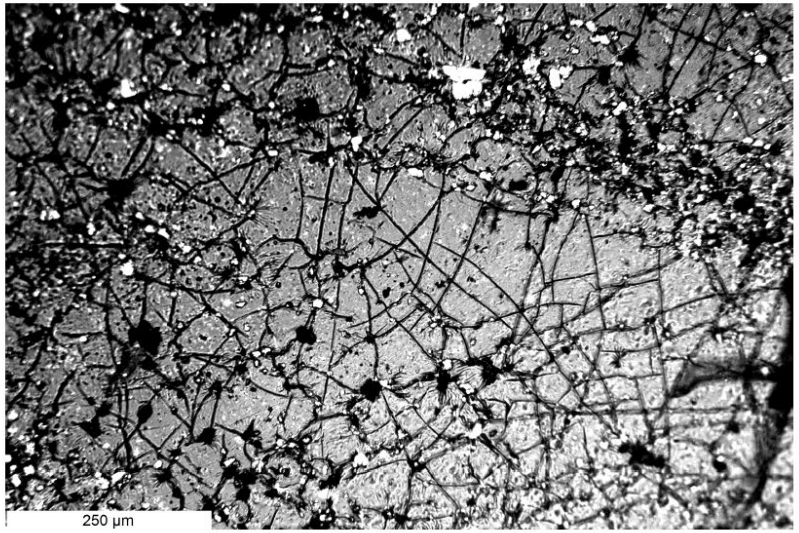


Image credit: Johns Hopkins Applied Physics Laboratory

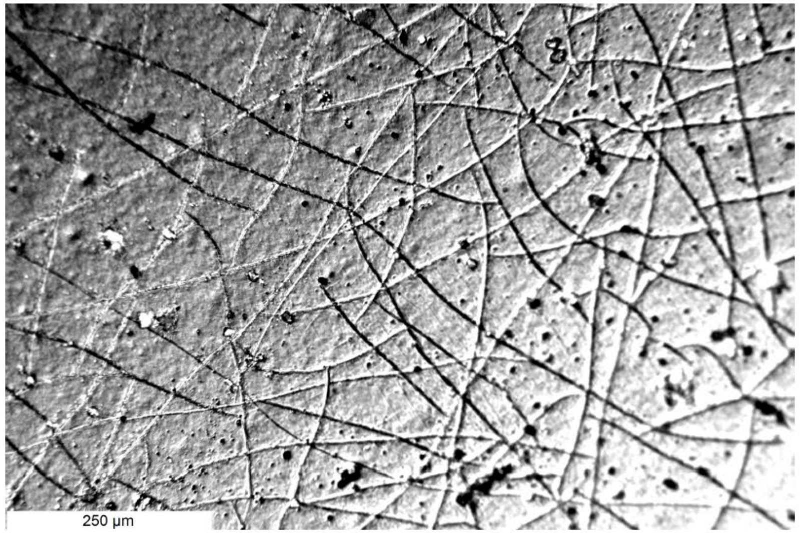
Percent of Sample Surface Area Occupied by Cracks

Results: Percent of Sample Surface Area Occupied by Cracks, $A_{s,ca}$

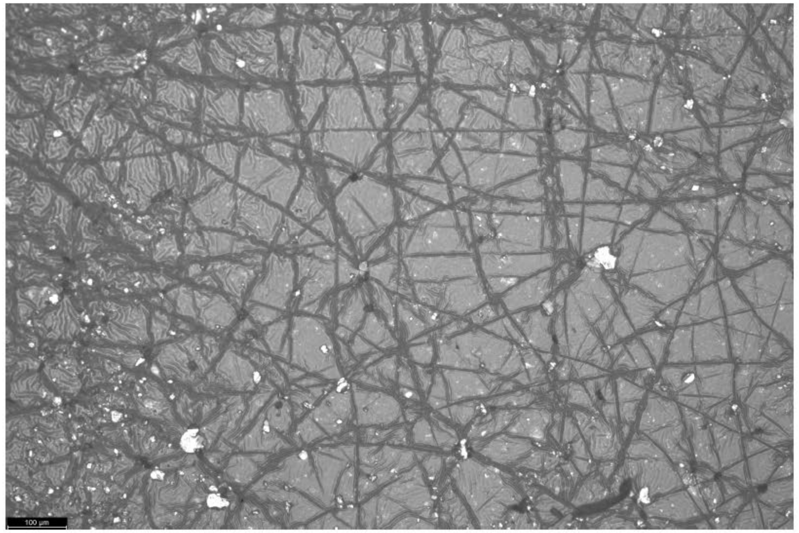
- 88 total samples were evaluated using optical microscopy for $\boldsymbol{A_{s,ca}}$
- One-way analysis of variance (ANOVA) was conducted to compare the effect of AO fluence on $\boldsymbol{A_{s,ca}}$
- AO fluence was a significant predictor of $\boldsymbol{A_{s,ca}}$ for both silicones tested ($p < .0001$)
- Percent sample surface area ranged from 0% to 52.8% over a fluence range of $\mathbf{2.83 \pm 0.214 \times 10^{19}}$ to $\mathbf{1.88 \pm 0.0520 \times 10^{21}\ atoms/cm^2}$



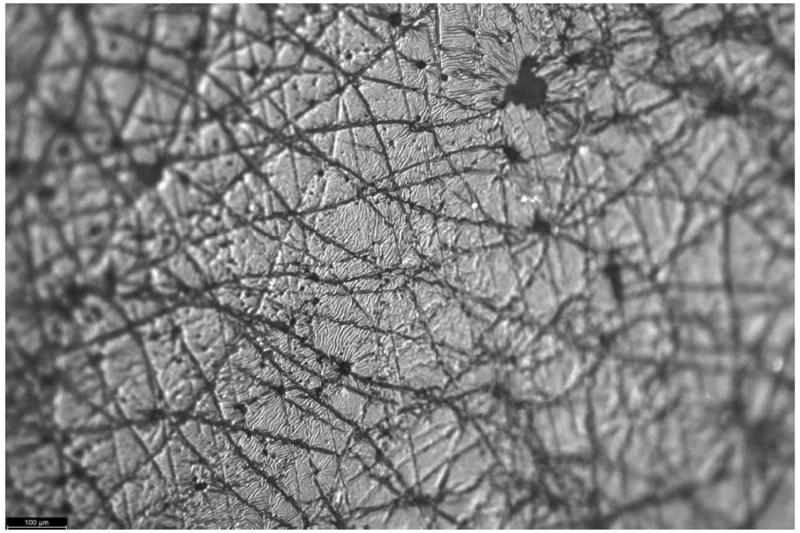
(a) *1h: CV-2960*, $A_{s,ca} = 16.663\%$



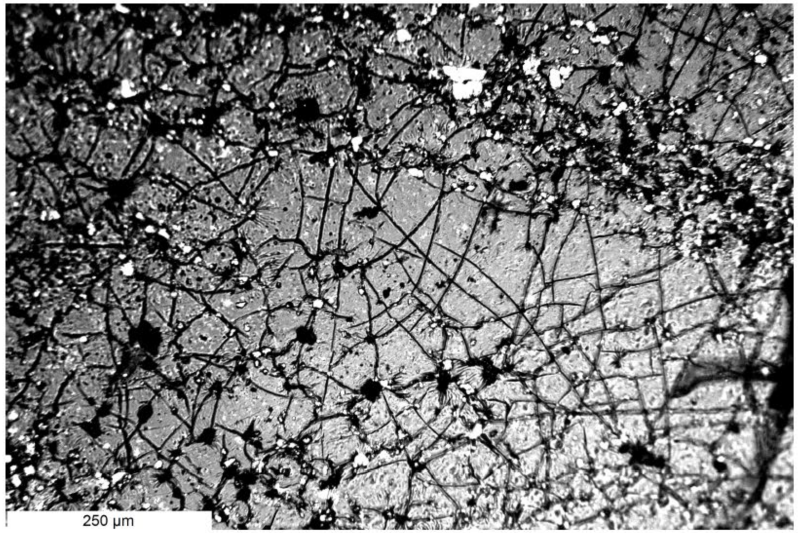
(b) *1h: RTV-S691*, $A_{s,ca} = 9.485\%$



(c) *3h: CV-2960*, $A_{s,ca} = 44.216\%$



(d) *3h: RTV-S691*, $A_{s,ca} = 30.063\%$



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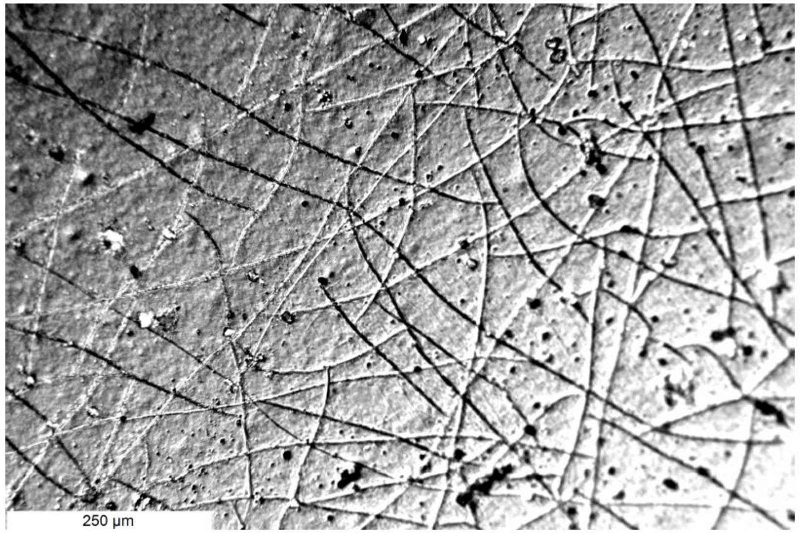

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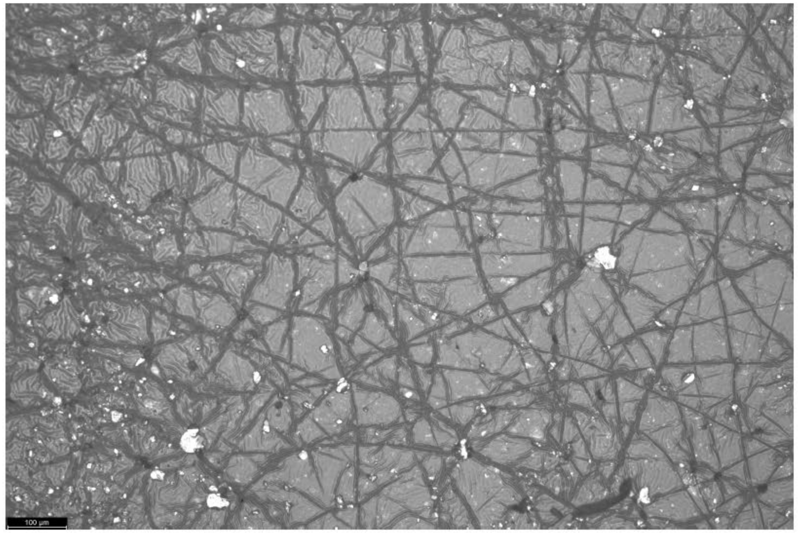

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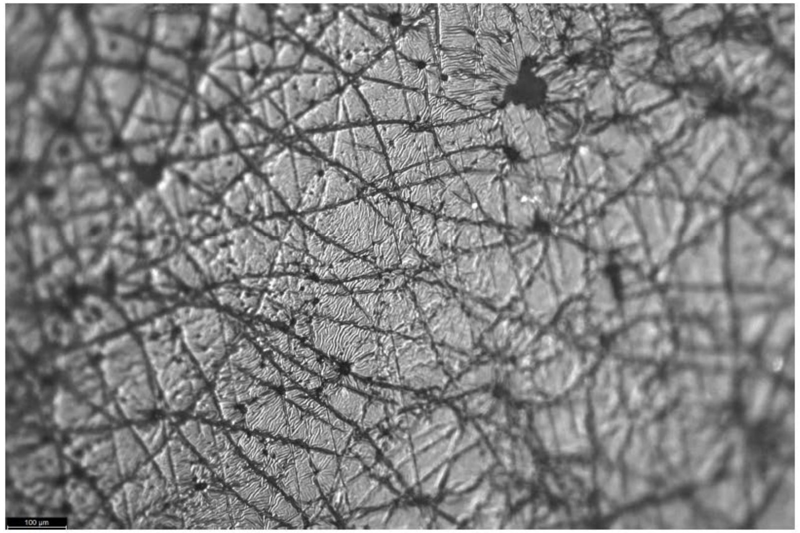

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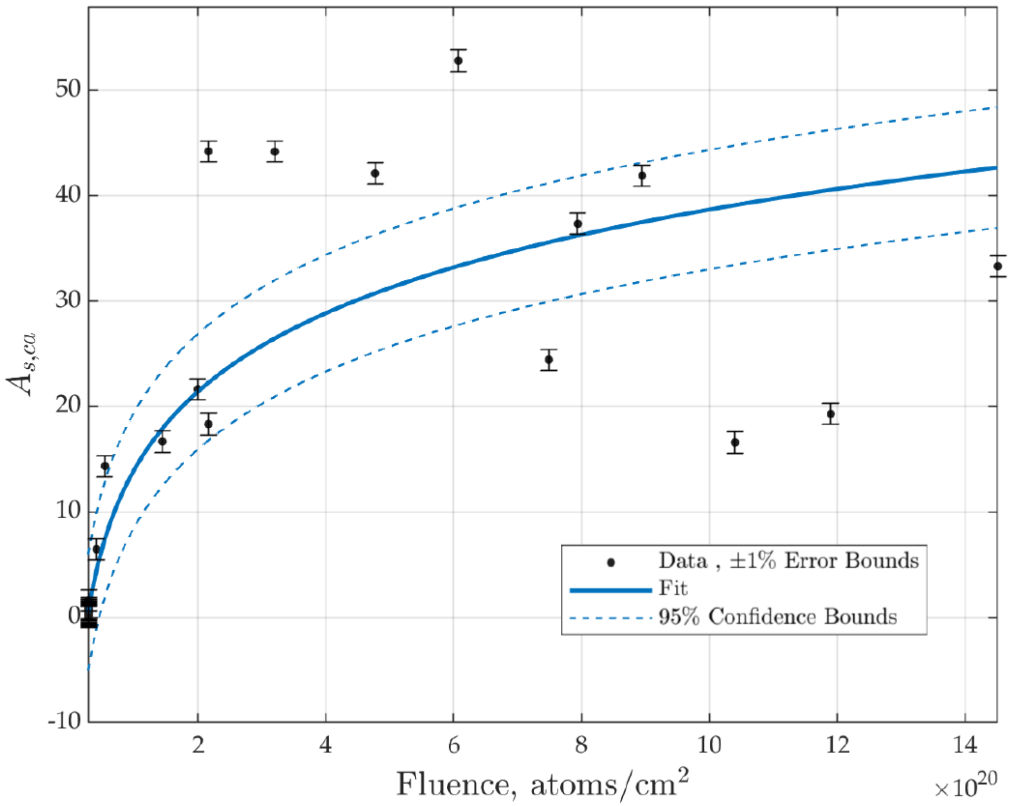
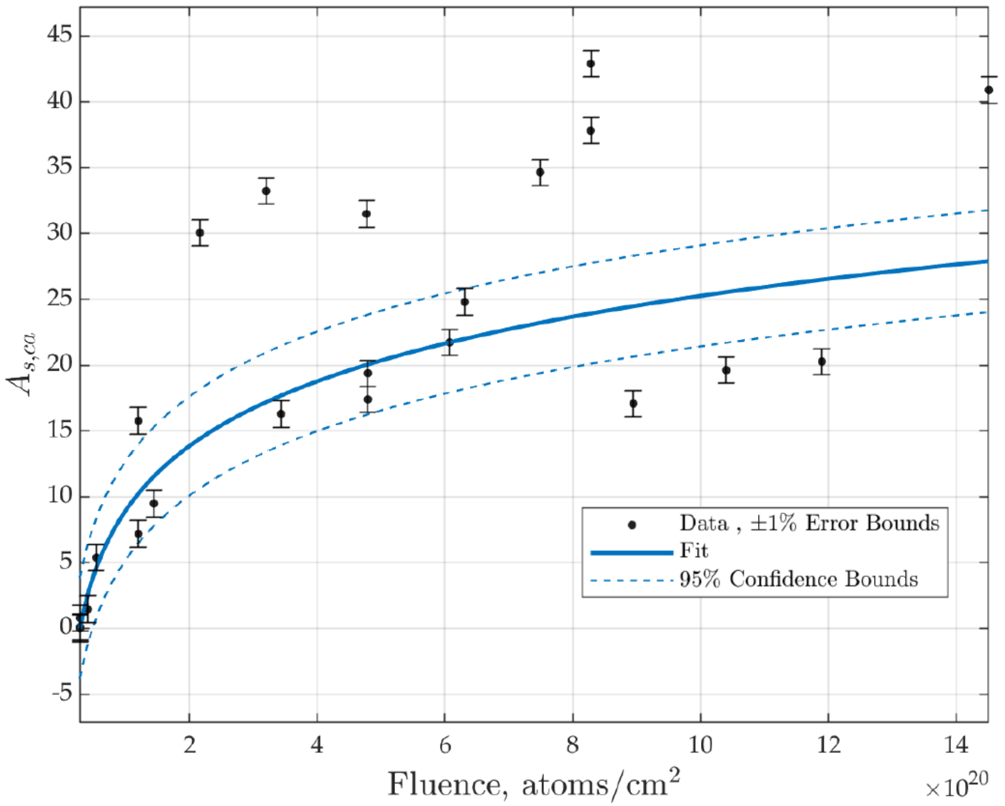
Results: Percent of Sample Surface Area Occupied by Cracks



CV-2960 Model Fit



RTV-S691 Model Fit

Results: Percent of Sample Surface Area Occupied by Cracks

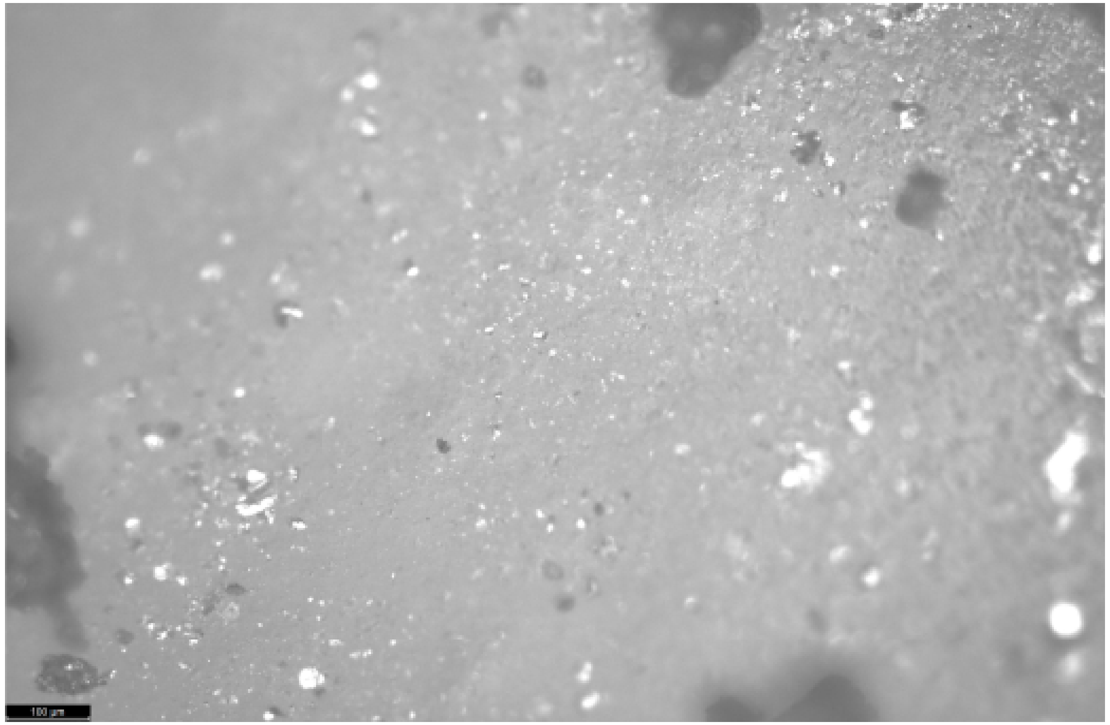
$$A_{s,ca} = \alpha \ln(F_E) + \beta$$

Table 6.9: *Sample Surface Occupied by Cracks, $A_{s,ca}$, Model Fit Summary with Lower and Upper Confidence Interval Bounds*

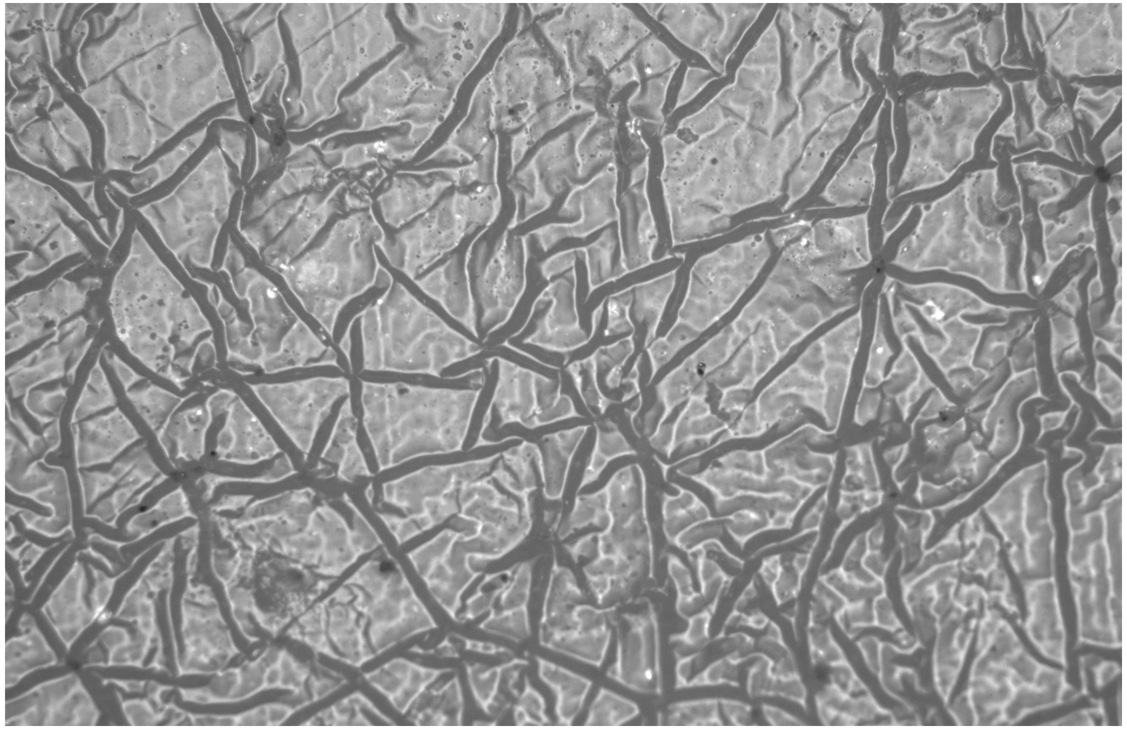
Sample	α (L_{CI}, U_{CI})	β (L_{CI}, U_{CI})	Model R^2
CV-2960	10.73 (10.1, 11.36)	-480 (-509, -451)	0.974
RTV-S691	7.085 (6.674, 7.496)	-317.3 (-336.4, -298.2)	0.981

Layer Formation Predictions

Results: Probability of Layer Formation on Orbit



Pristine CV-2960

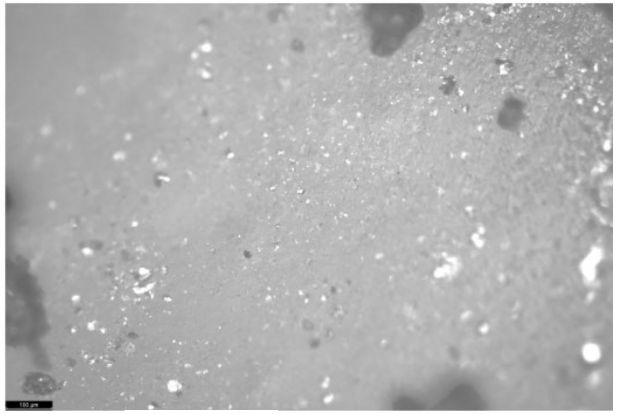


Exposed 24 hours

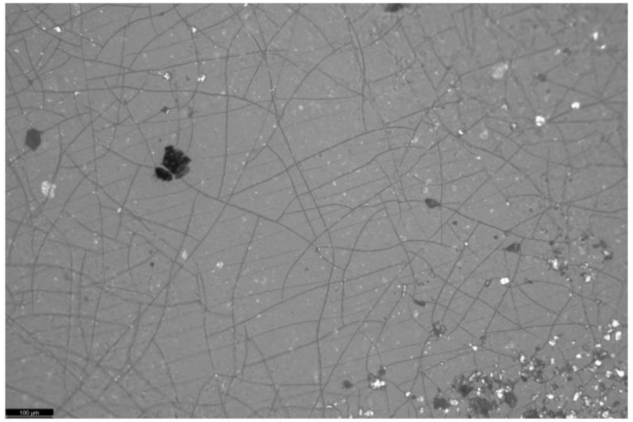
$$F = 1.44 \pm 0.046 \times 10^{21} atoms/cm^2$$

About 6 months on orbit

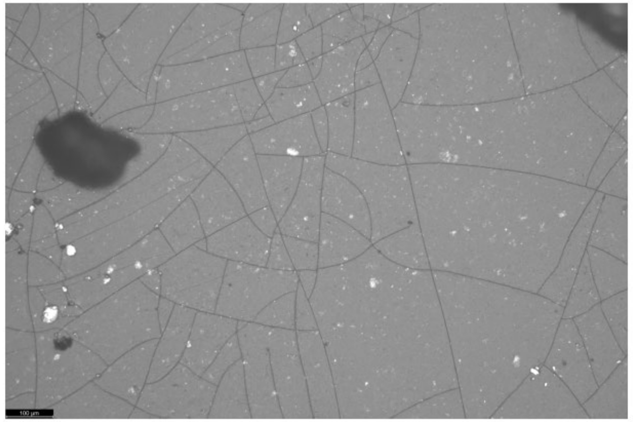
Results: Probability of Layer Formation on Orbit



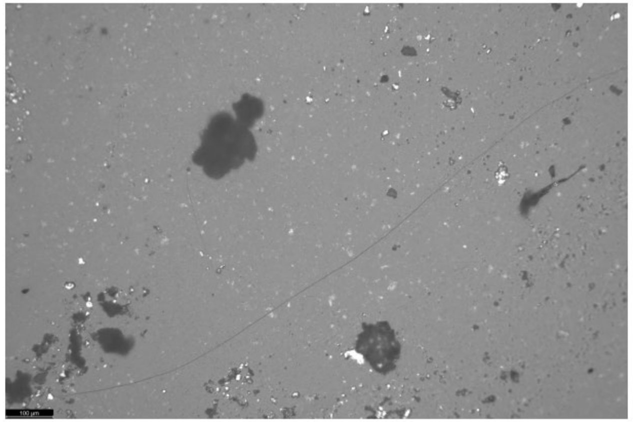
Pristine CV-2960



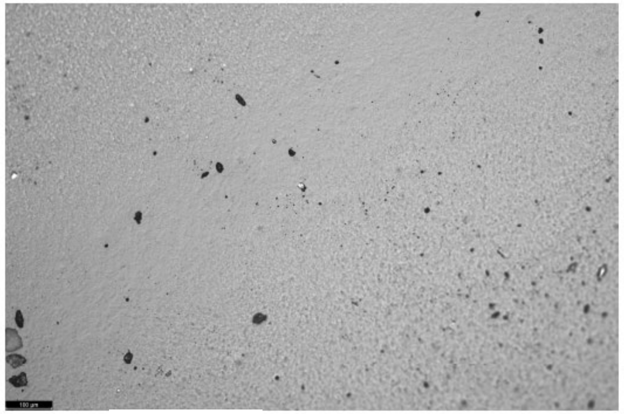
CV-2960, 5 min



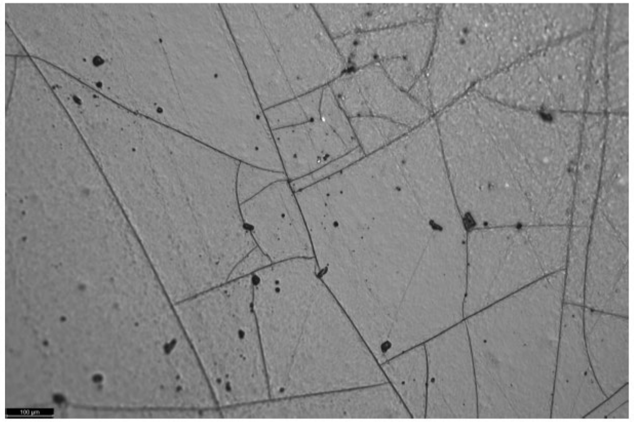
CV-2960, 2.5 min



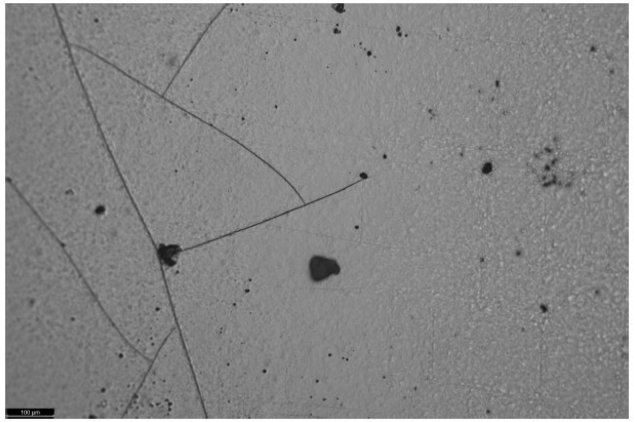
CV-2960, 1 min



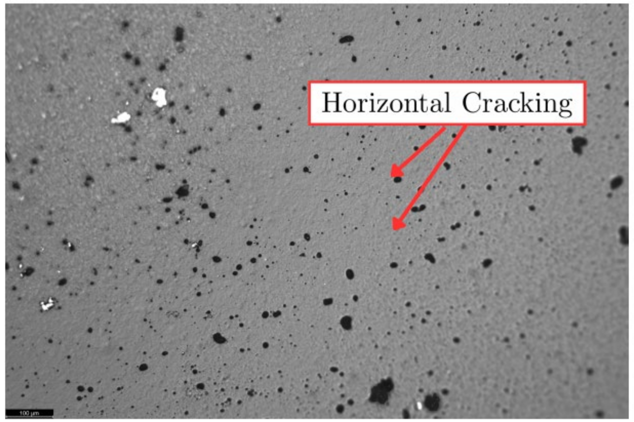
Pristine RTV-S691



RTV-S691, 5 min

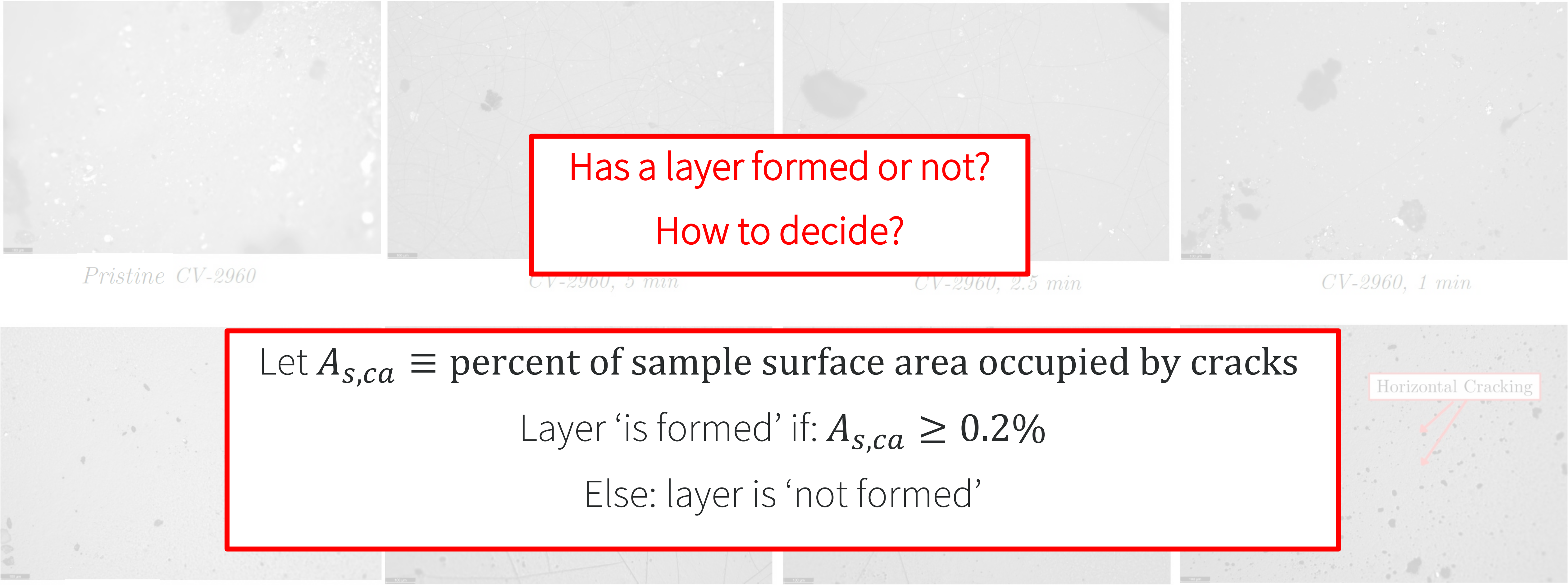


RTV-S691, 2.5 min



RTV-S691, 1 min

Results: Probability of Layer Formation on Orbit



Pristine CV-2960 *CV-2960, 5 min* *CV-2960, 2.5 min* *CV-2960, 1 min*

Pristine RTV-S691 *RTV-S691, 5 min* *RTV-S691, 2.5 min* *RTV-S691, 1 min*

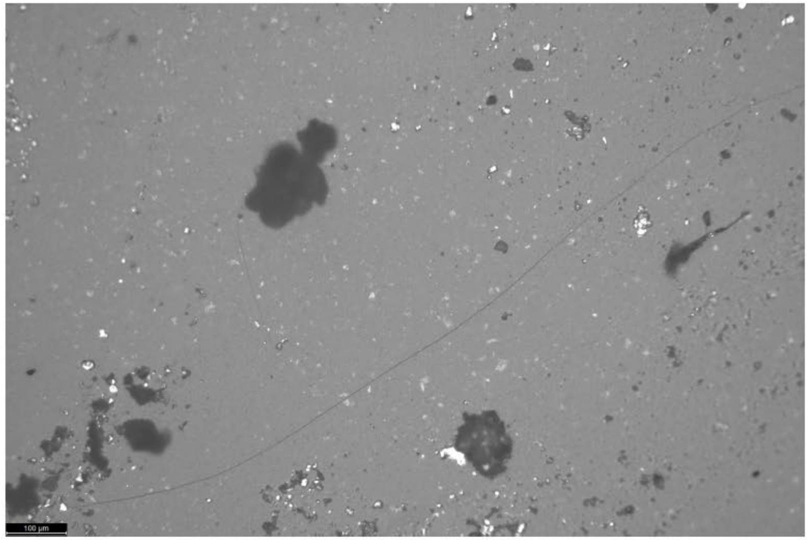
Has a layer formed or not?

How to decide?

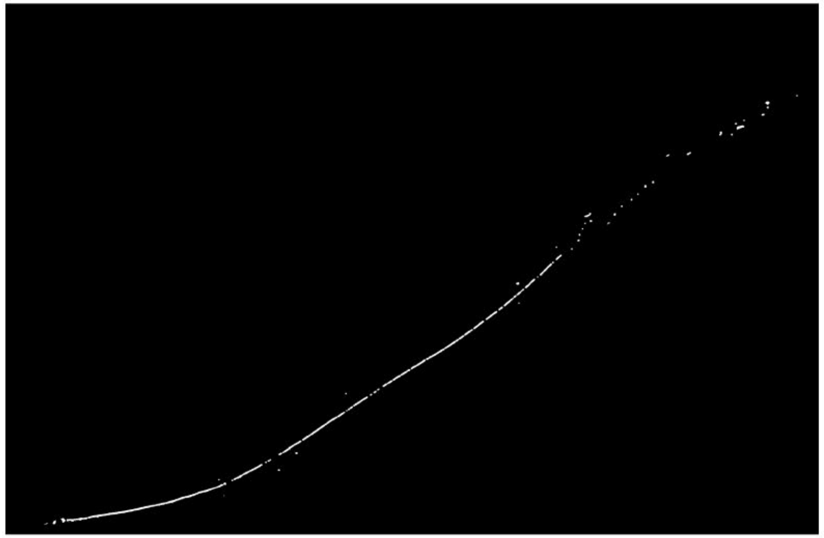
Let $A_{s,ca} \equiv \text{percent of sample surface area occupied by cracks}$

Layer ‘is formed’ if: $A_{s,ca} \geq 0.2\%$

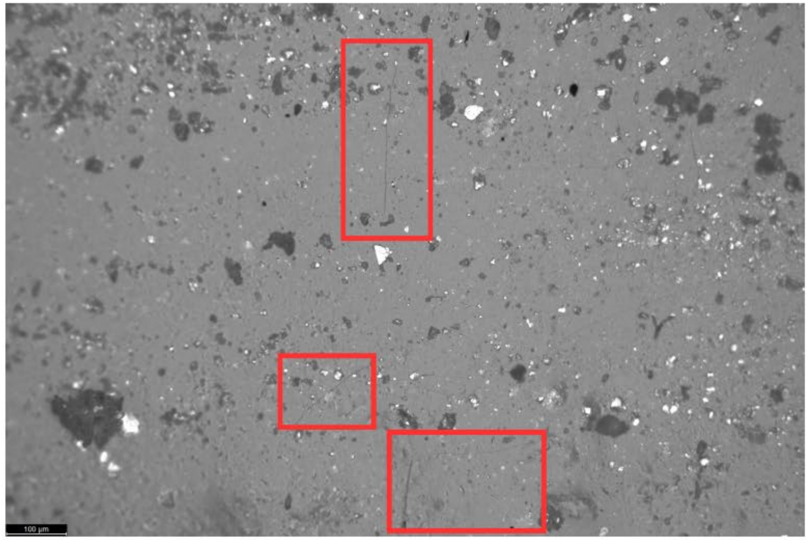
Else: layer is ‘not formed’



Optical



$A_{s,ca} = 0.253$ *(Layer)*



Optical

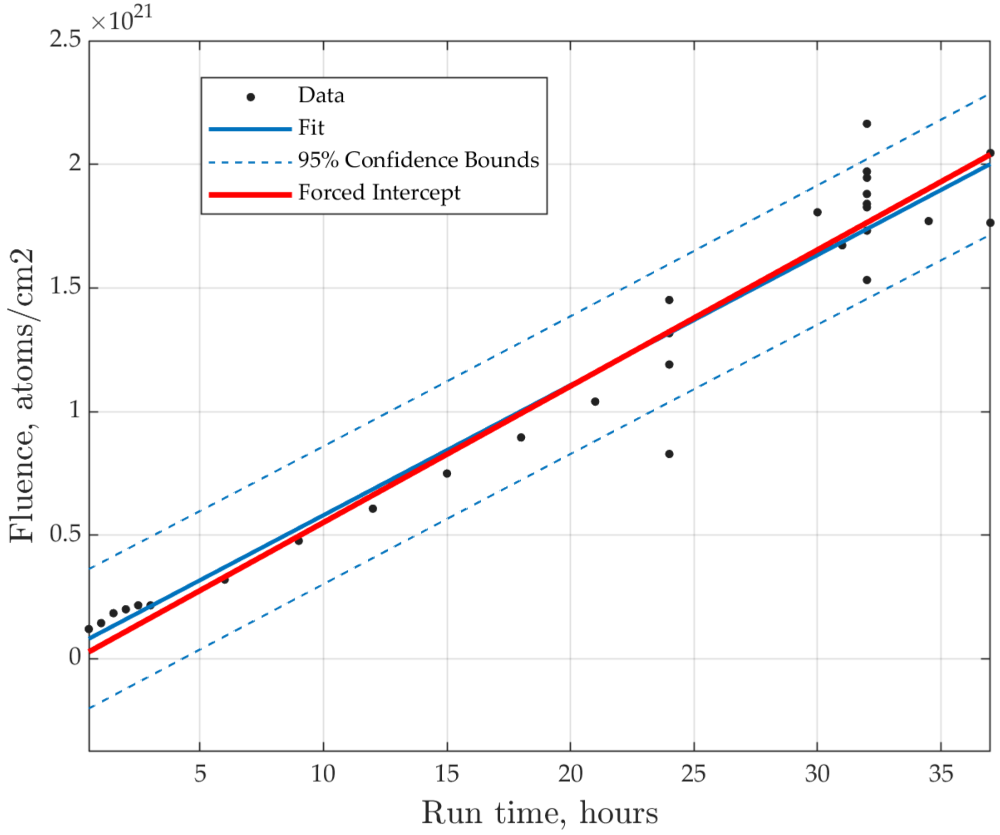
$A_{s,ca} = 0.073$ *(No Layer)*

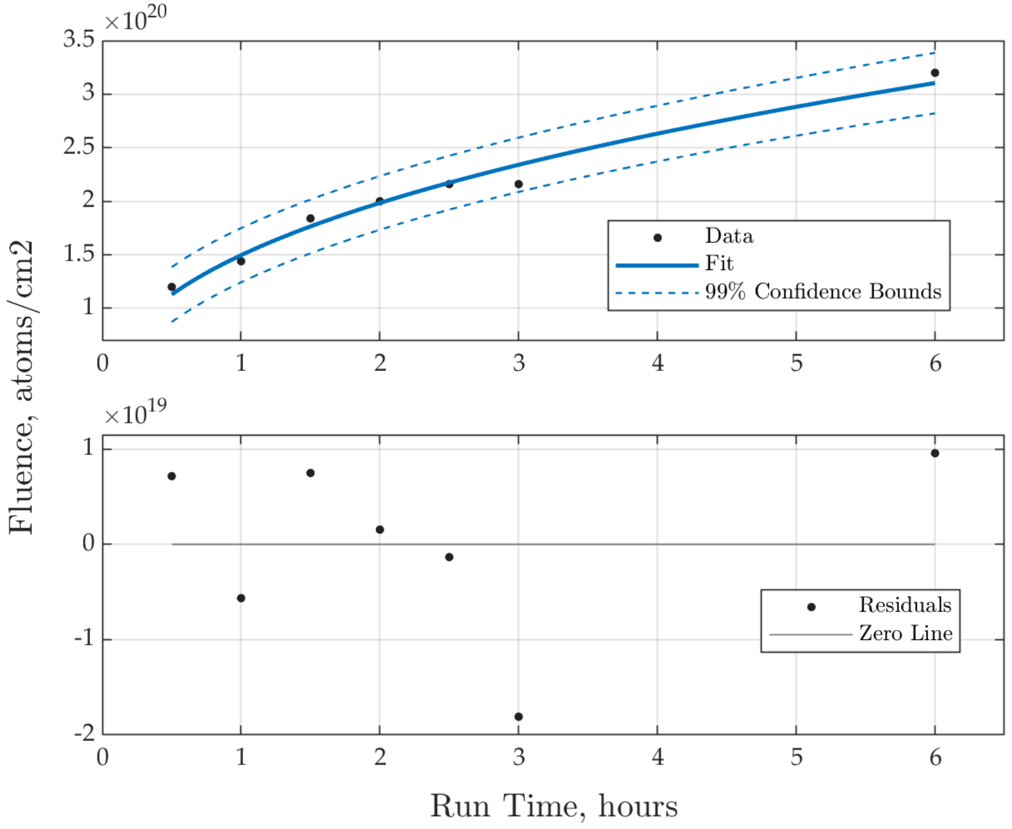
Results: Probability of Layer Formation on Orbit

$$F_E = \frac{\cancel{\Delta M_K}}{A_K \rho_K E_K}$$

But what if you cannot measure the Kapton mass loss?

Results: Fluence Approximation for Short-Duration Tests





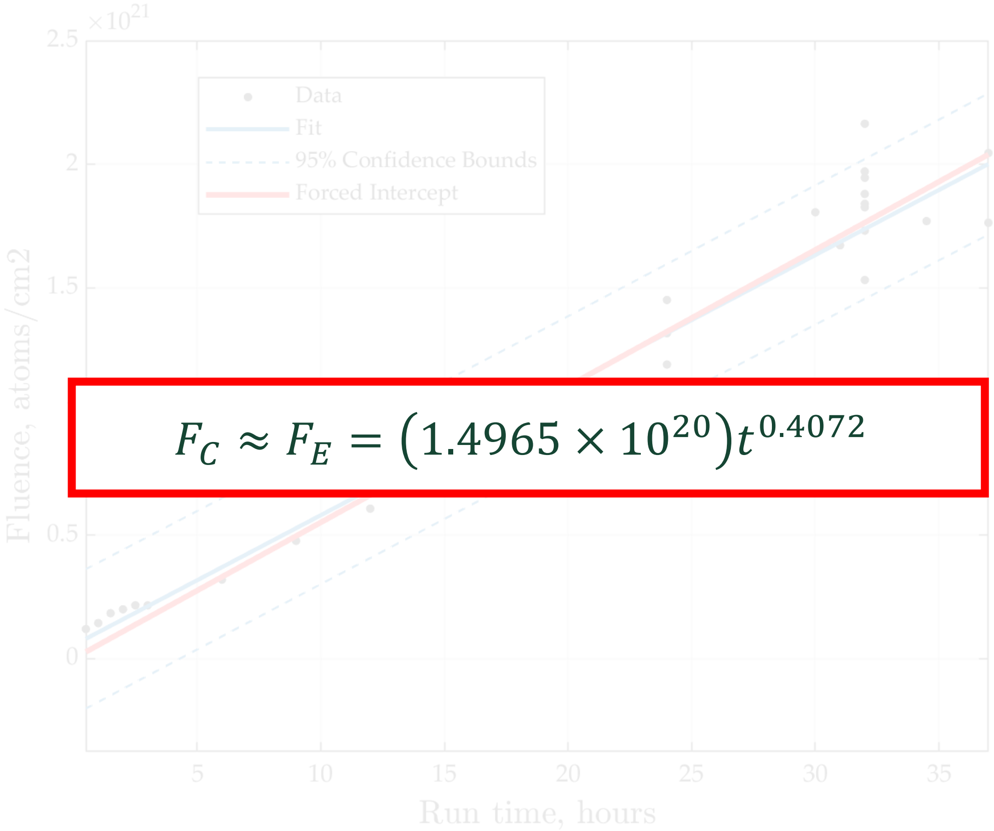
Old model: linear fit

Good for long run times and general trend at 95% confidence, not so good for short run times

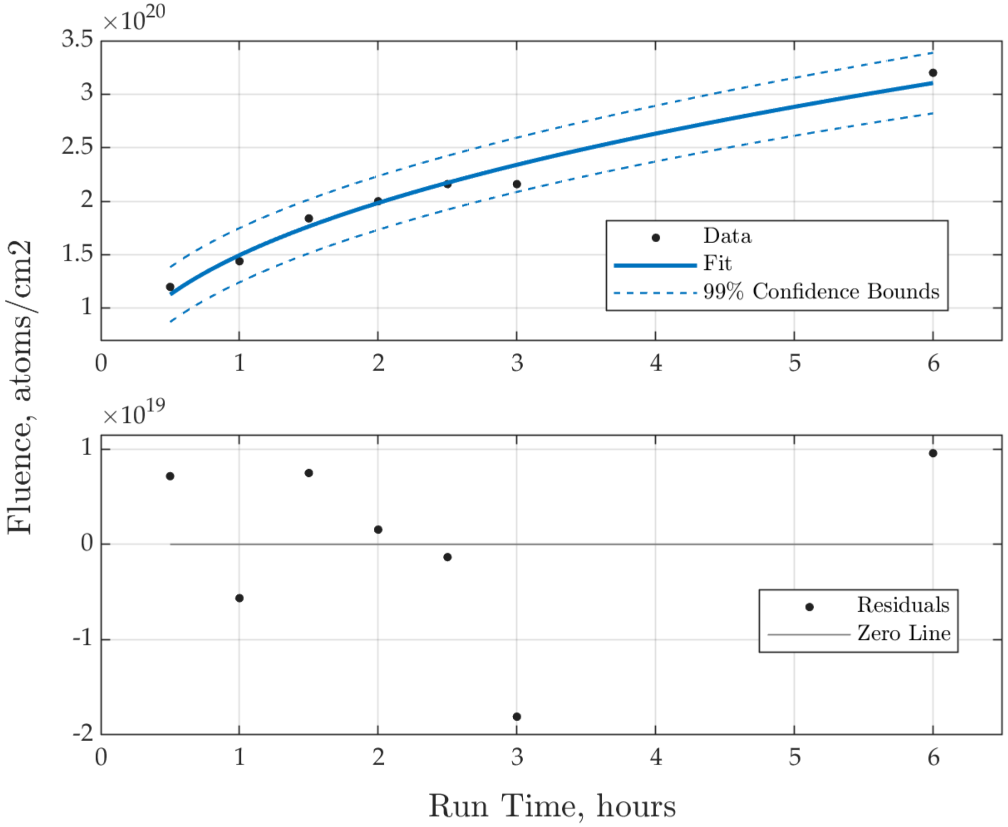
New model: power fit

Fits lab data well ($R^2 = 0.96$) at 99% confidence bounds for short run times

Results: Fluence Approximation for Short-Duration Tests



$$F_C \approx F_E = \left(1.4965 \times 10^{20}\right) t^{0.4072}$$



Old model: linear fit

Good for long run times and general trend at 95% confidence, not so good for short run times

New model: power fit

Fits lab data well ($R^2 = 0.96$) at 99% confidence bounds for short run times

Results: Probability of Layer Formation on Orbit

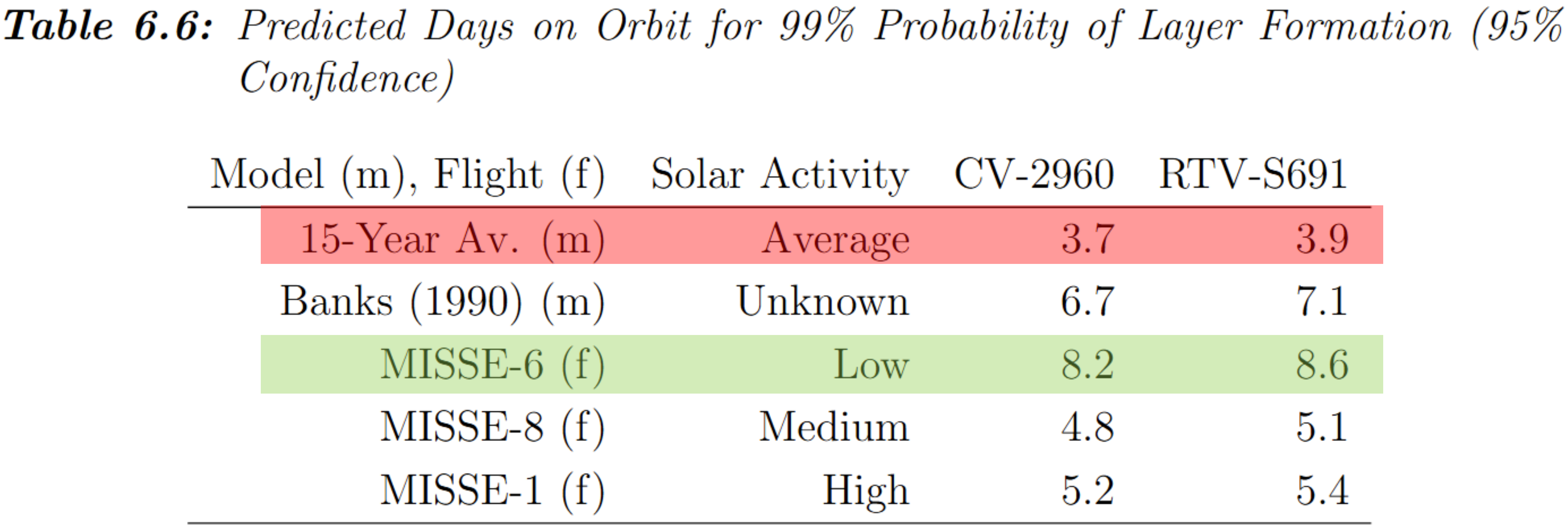


Table 6.6: *Predicted Days on Orbit for 99% Probability of Layer Formation (95% Confidence)*

Model (m), Flight (f)	Solar Activity	CV-2960	RTV-S691
15-Year Av. (m)	Average	3.7	3.9
Banks (1990) (m)	Unknown	6.7	7.1
MISSE-6 (f)	Low	8.2	8.6
MISSE-8 (f)	Medium	4.8	5.1
MISSE-1 (f)	High	5.2	5.4

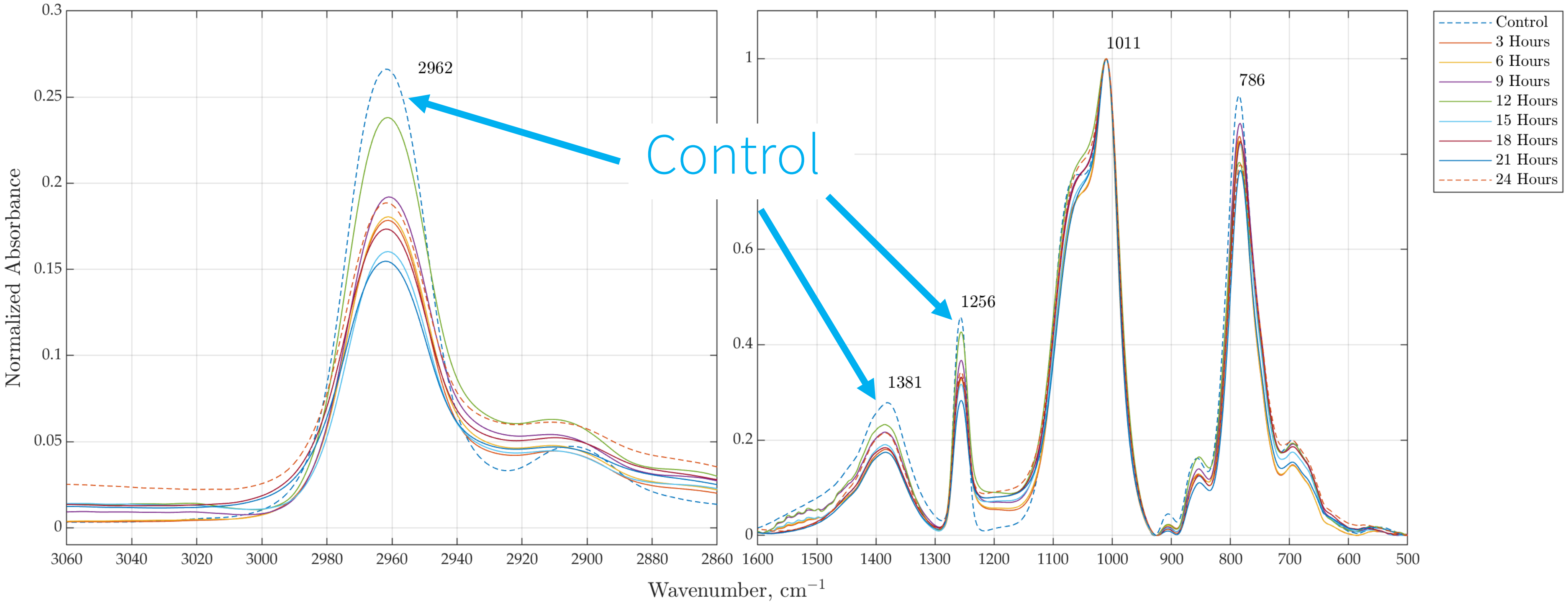
This study finds that, with 95% confidence, CV-2960 and RTV-S691 silicones are predicted to form a fully-developed surface layer between 4-9 days

Chemical Changes

Table 6.11: *Polydimethylsiloxane Group Wavenumbers (IR)*

Wavenumber, cm^{-1}	Intensity	Functional Group
2970	Medium	Asymmetric CH_3 stretch
2910	Strong	Symmetric CH_3 stretch
1380	Medium	Asymmetric CH_3 deformation
1260	Very strong	Symmetric CH_3 deformation
1130 - 1000	Very strong	Asymmetric Si–O–Si stretch
1060	Shoulder	Si-O
870 - 750	Very strong	CH_3 rock, Si–C stretch
695	Medium	Si-Phenyl

CV-2960

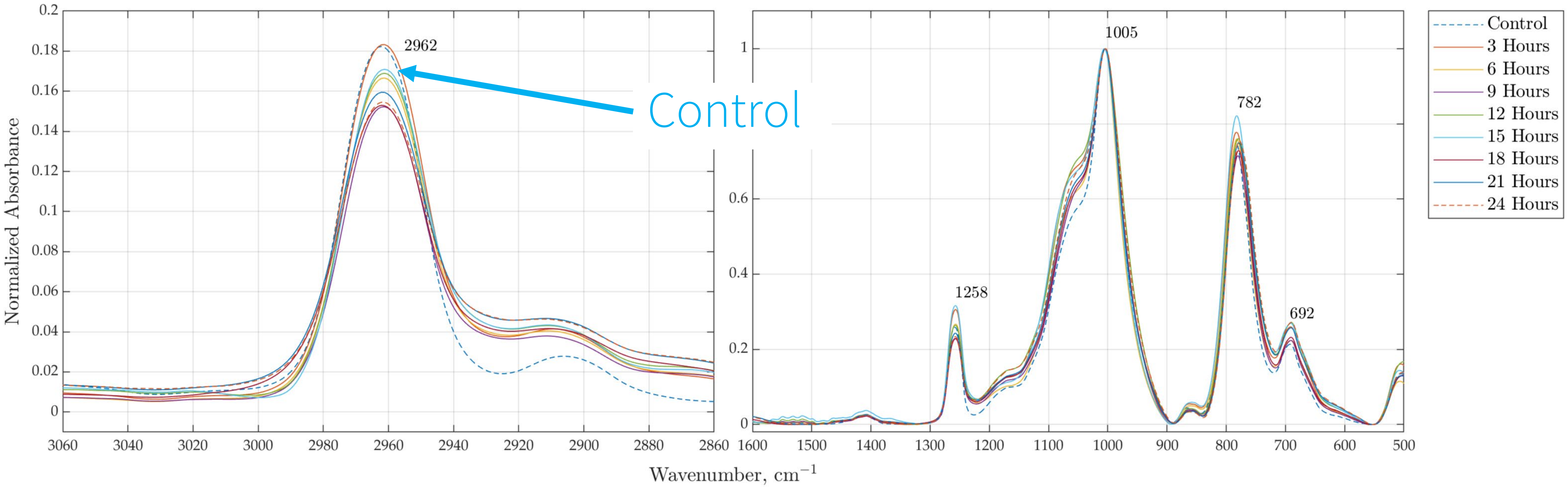


Control

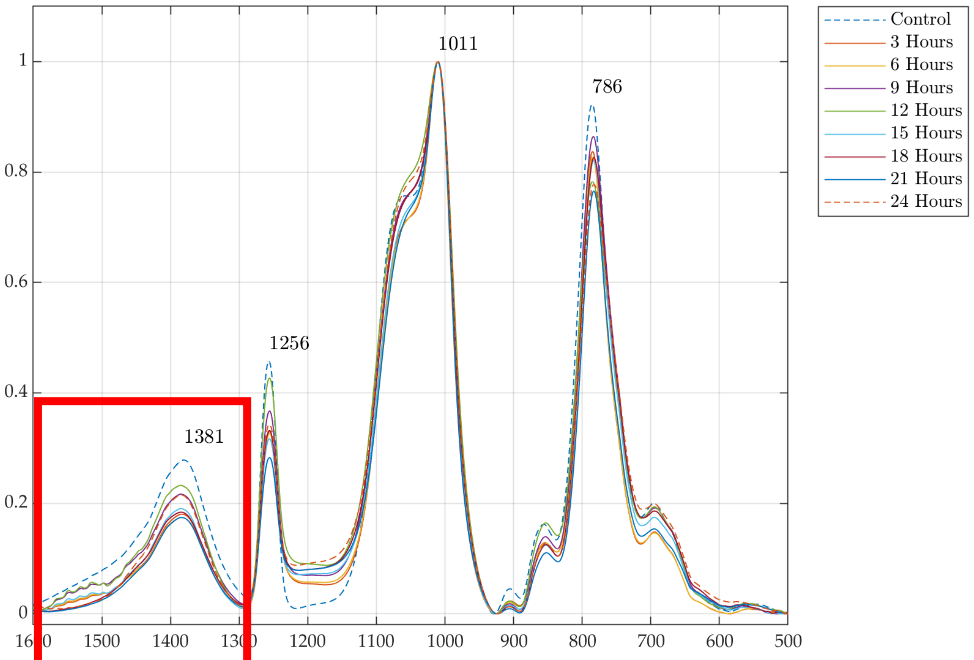
Table 6.11: *Polydimethylsiloxane Group Wavenumbers (IR)*

Wavenumber, cm^{-1}	Intensity	Functional Group
2970	Medium	Asymmetric CH_3 stretch
2910	Strong	Symmetric CH_3 stretch
1380	Medium	Asymmetric CH_3 deformation
1260	Very strong	Symmetric CH_3 deformation
1130 - 1000	Very strong	Asymmetric Si–O–Si stretch
1060	Shoulder	Si-O
870 - 750	Very strong	CH_3 rock, Si–C stretch
695	Medium	Si-Phenyl

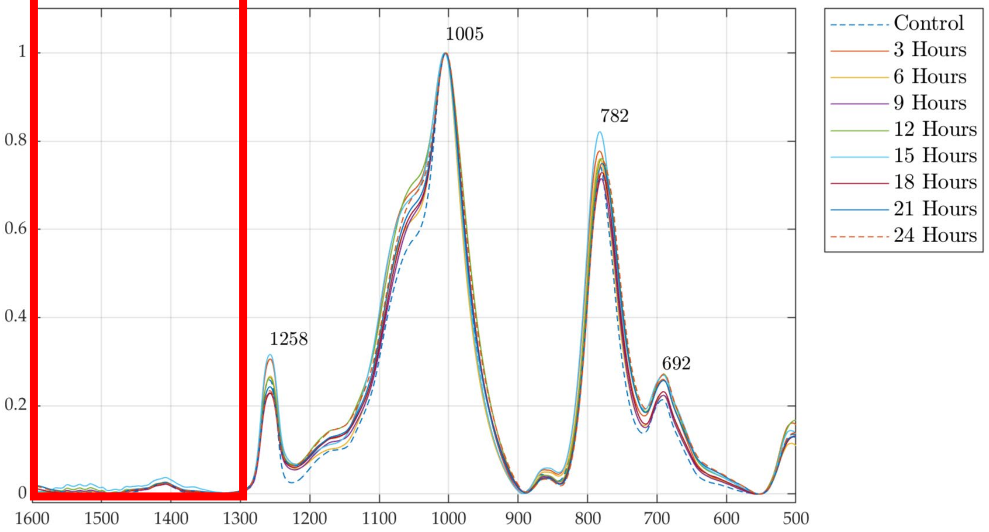
RTV-S691



CV-2960



RTV-S691



RTV-S691 is a PVMQ, which means that methyl groups are replaced with phenyl groups.

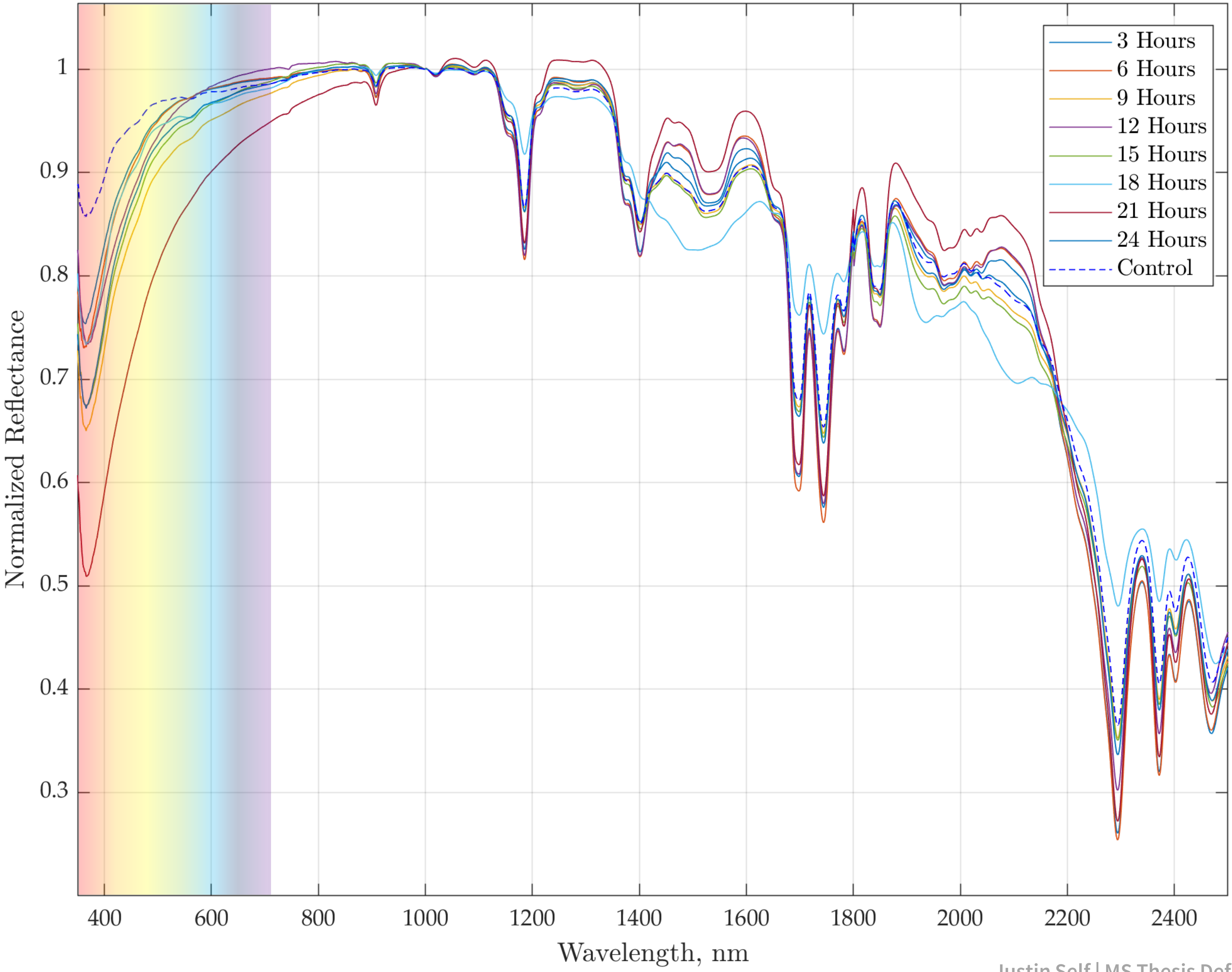
Phenyl groups in silicones slow down the process by which AO converts the surface to a glassy silicate layer.

Reflectance Spectroscopy

RTV-S691 **CV-2960**

Back: Control

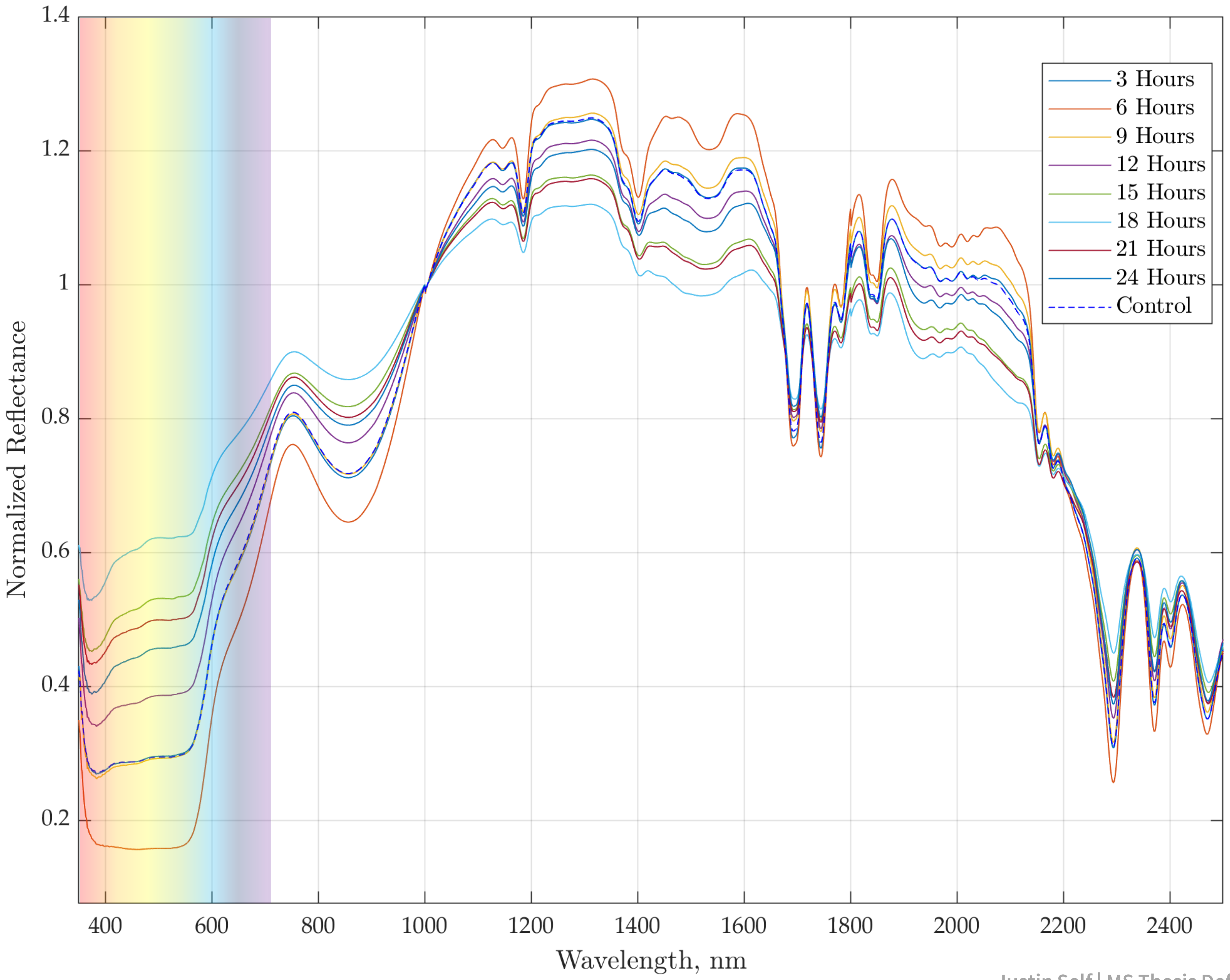
Front: Exposed



RTV-S691 CV-2960

Back: Control

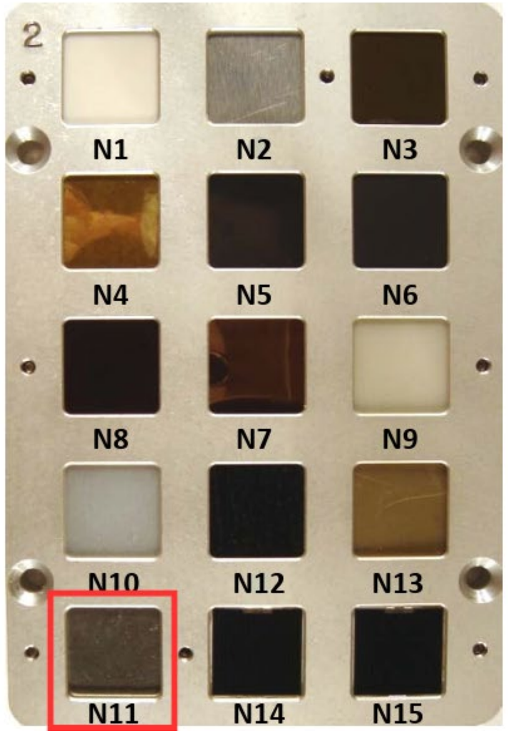
Front: Exposed



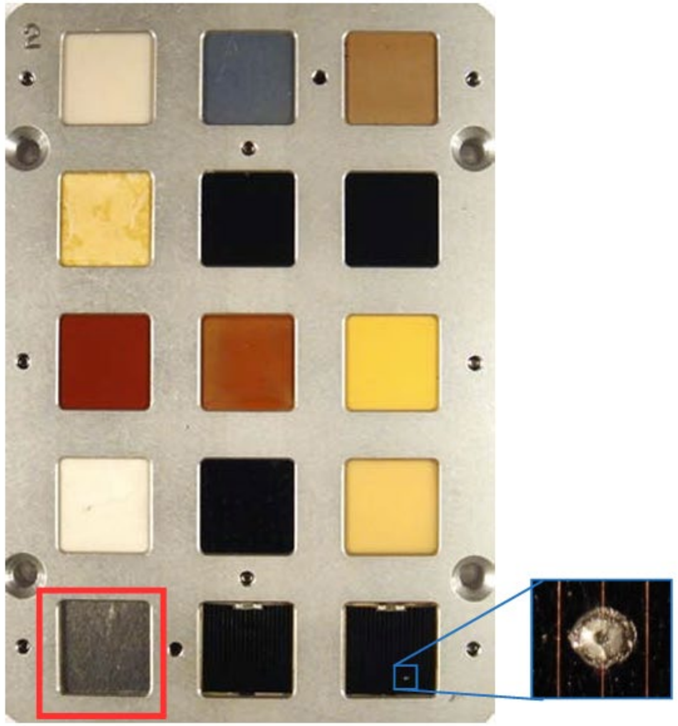
LEARN BY DOING CAL POLY

ISS Flight Samples vs. Ground Testing

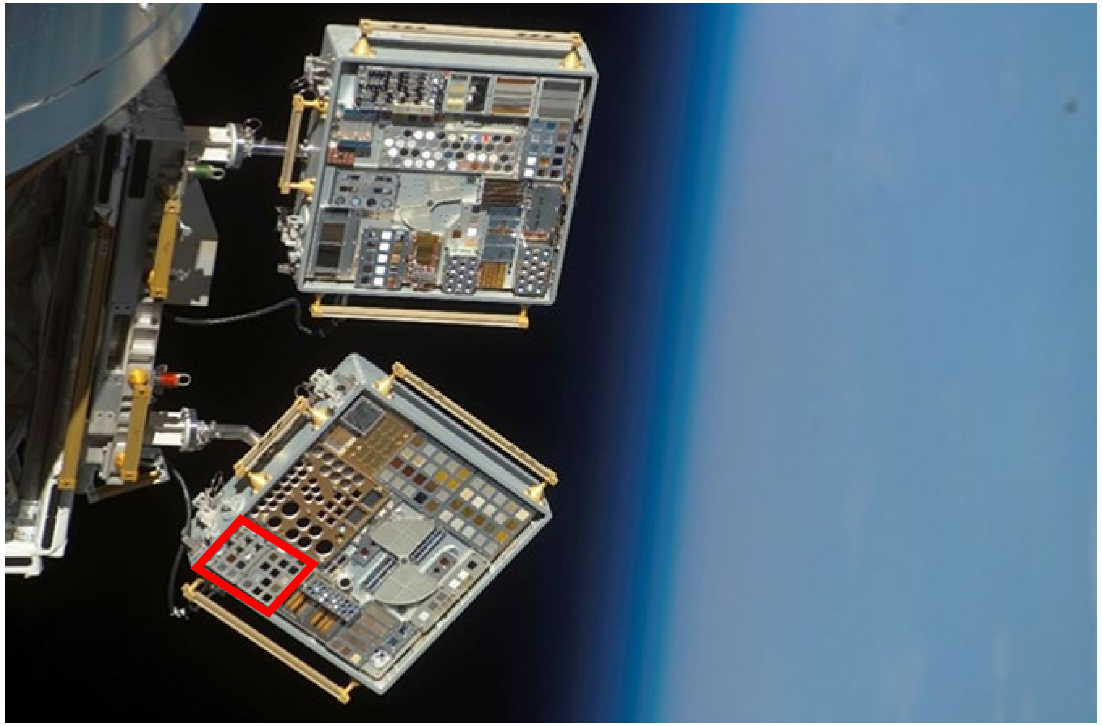
Results: DC 93-500 Reflectance



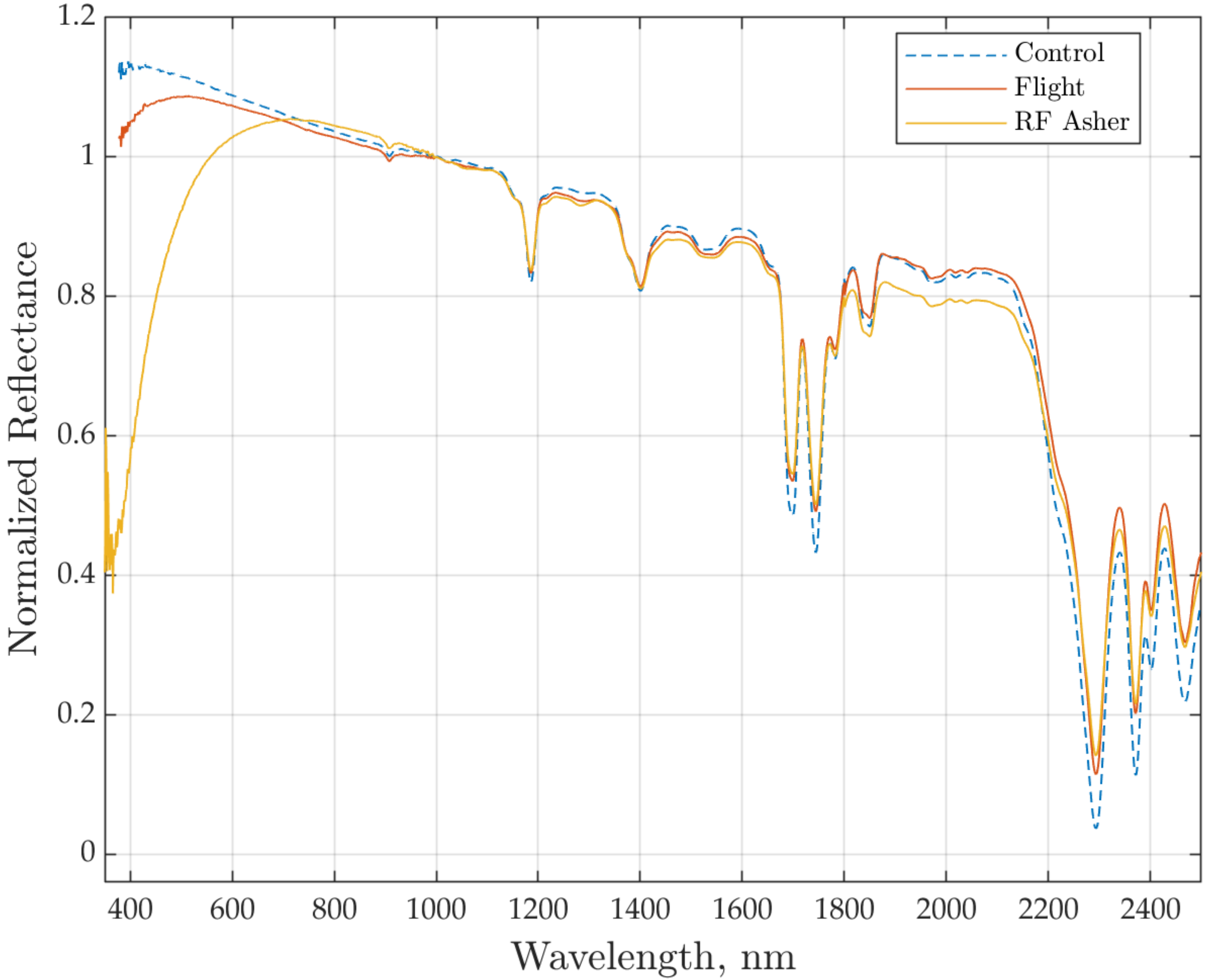
Pre-flight



Post-flight



MISSE-6: 1.45 years ram AO on the ISS
(March 2008 – Sept. 2009)

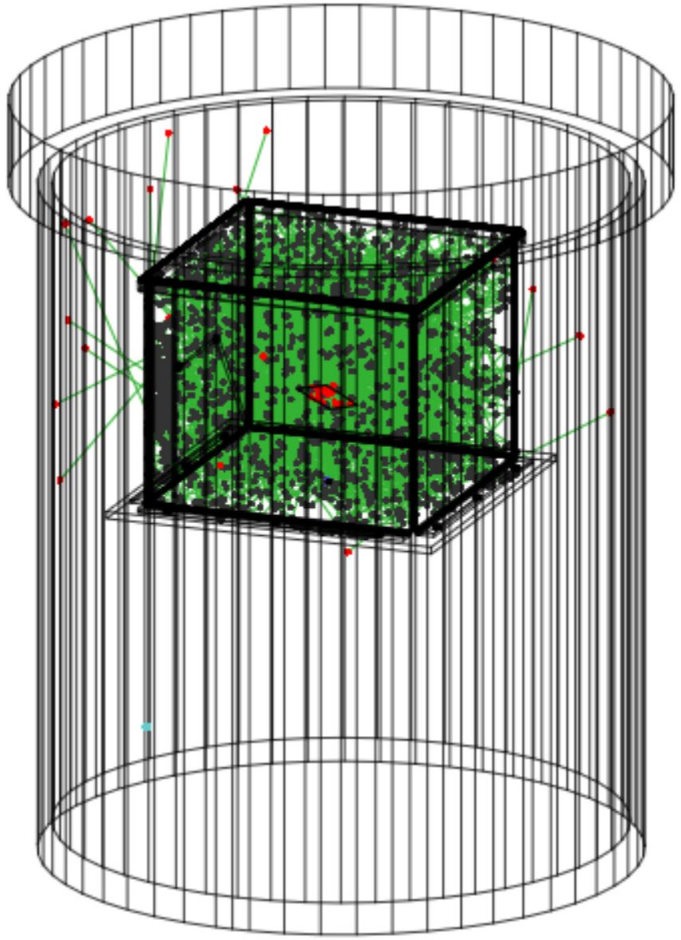


1.2
1
0.8
0.6
0.4
0.2
0
Normalized Reflectance
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength, nm
Control
Flight
RF Asher

Conclusions and Future Work

Conclusions

- Silicone vacuum contamination mechanism
  - Ultimately did not result in measurable deposition
  - Results drove research focus shift
  - Useful output: vacuum effusion cell (x3) for the Cal Poly SEL



Conclusions

Layer formation probability studies

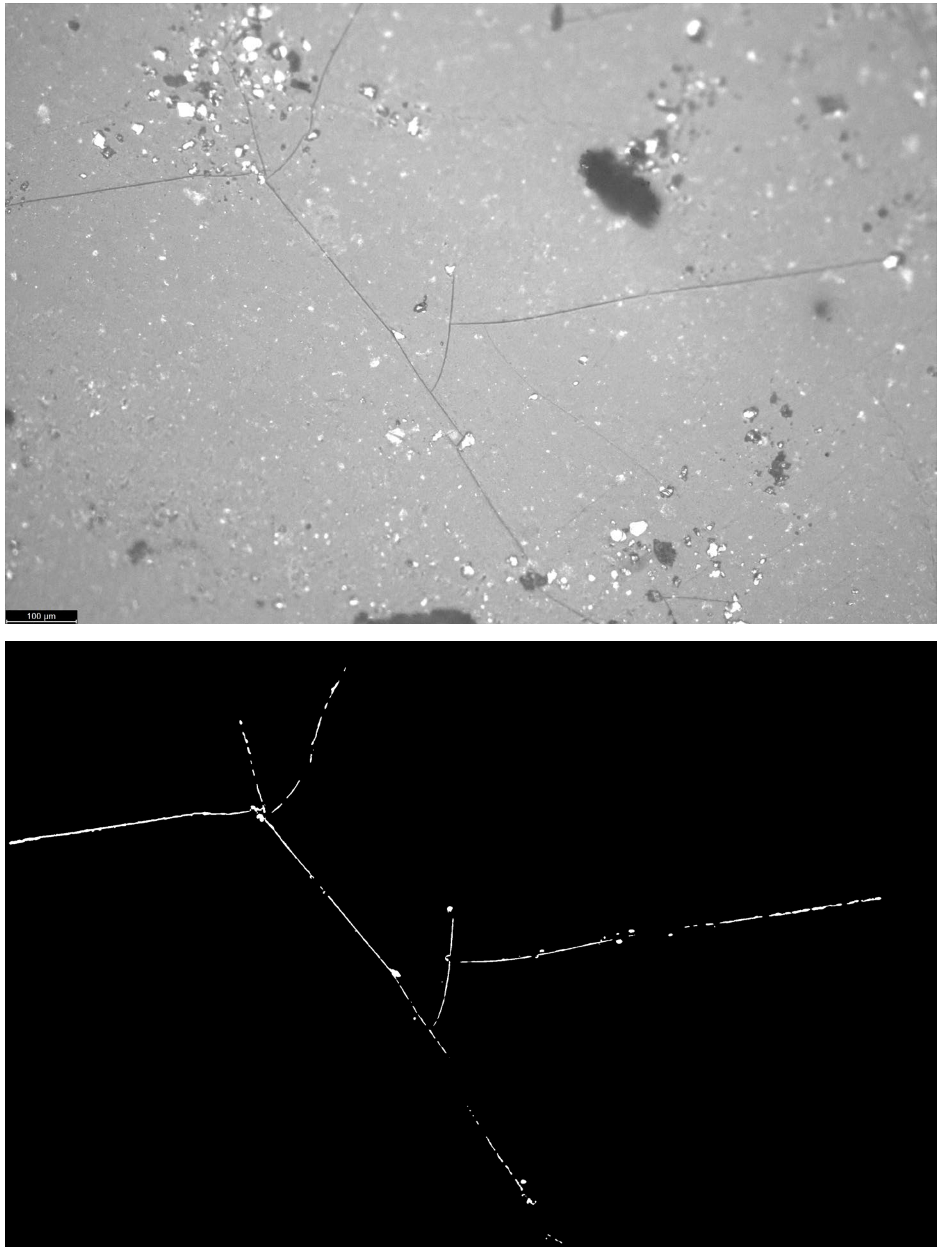
- With 95% confidence, CV-2960 and RTV-S691 are predicted to form a silicate layer on orbit after 4-9 days of ram AO
- Much faster than most literature suggests; validated by SAGE-III data

Model (m), Flight (f)	Solar Activity	CV-2960	RTV-S691
15-Year Av. (m)	Average	3.7	3.9
Banks (1990) (m)	Unknown	6.7	7.1
MISSE-6 (f)	Low	8.2	8.6
MISSE-8 (f)	Medium	4.8	5.1
MISSE-1 (f)	High	5.2	5.4

Conclusions

Percent of sample surface area occupied by cracks

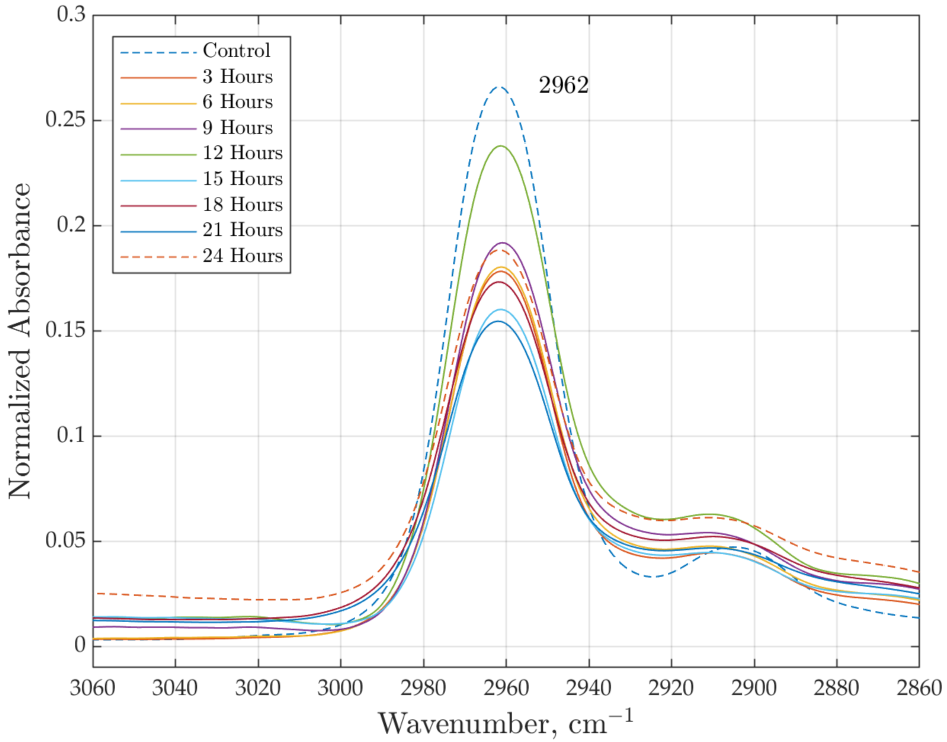
- Exposure times: 60 sec to 24 hours
- Logarithmic model ($R^2 = 0.97$ to 0.98)
- Significantly linked to AO exposure ($p < .0001$)
- Percent cracks ranged from 0% to 52.8%
- CV-2960 forms cracks more quickly than RTV-S691, thought to be due to phenyl groups present in the RTV-S691



Conclusions

Chemical Changes

- Both CV-2960 and RTV-S691 exhibited methyl group loss after AO exposure
- CV-2960 consistently exhibited quicker and more substantial methyl group loss than the RTV-S691
- Phenyl-containing silicones may be more resistant to silicate layer formation

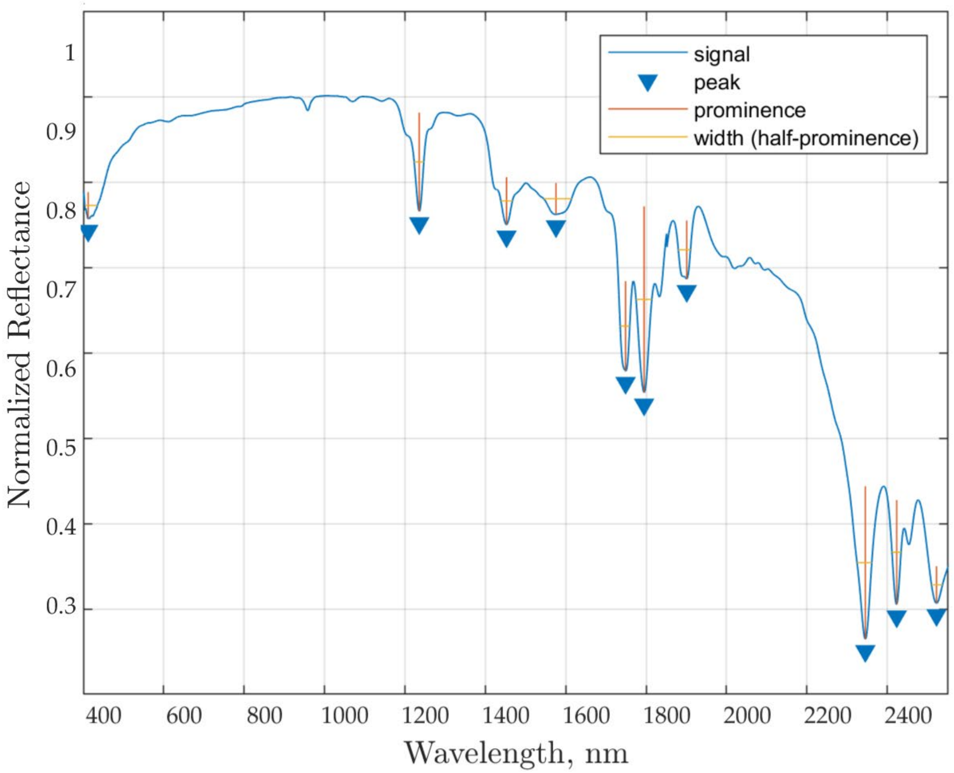


FTIR spectra of CV-2960 at $2962\ cm^{-1}$

Conclusions

Reflectance Changes

- CV-2960 showed immediate discoloration; RTV-S691 did not
- On average, CV-2960 FWHM values decreased after exposure, RTV-S691 increased, in general—thought to be due to the presence of phenyl groups in the RTV-S691



Reflectance spectra with FWHM peaks identified (CV-2960)

Future Work

- Characterize thermal response to AO in each silicone tested
  - **Could measure thermal emittance and quantify changes in α**
- Study synergistic effects of AO + vacuum ultraviolet radiation concurrently, start with validation of MISSE-6 or -8 samples
  - **Upgrade or replace VUV lamp in the SEL**
- Perform PDMS contamination studies using the CVCM chamber in the SEL
  - **Study contamination as analog for CRS vehicle arrivals**
- Study silicate layer thickness
- Study chemical changes in MISSE-6 and -8 flight samples using FTIR
- Utilize more analysis capabilities: TEM, SEM-EDS, XPS, AFM

Investigation Into Silicone-Silicate Conversion Due to Atomic Oxygen in the Low Earth Orbit Environment

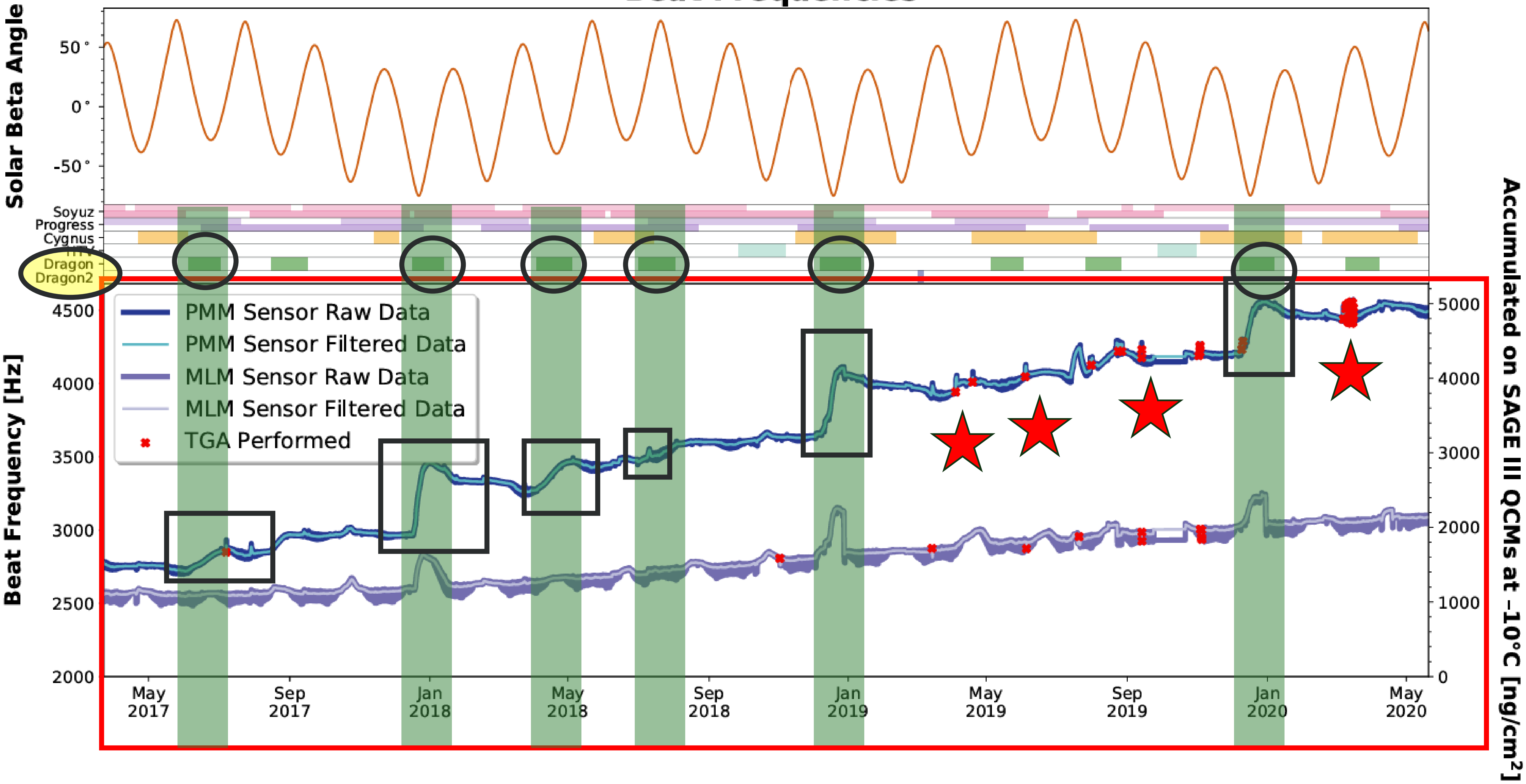
Backup

JUSTIN SELF | MS THESIS DEFENSE

ADVISOR: DR. KIRA ABERCROMBY

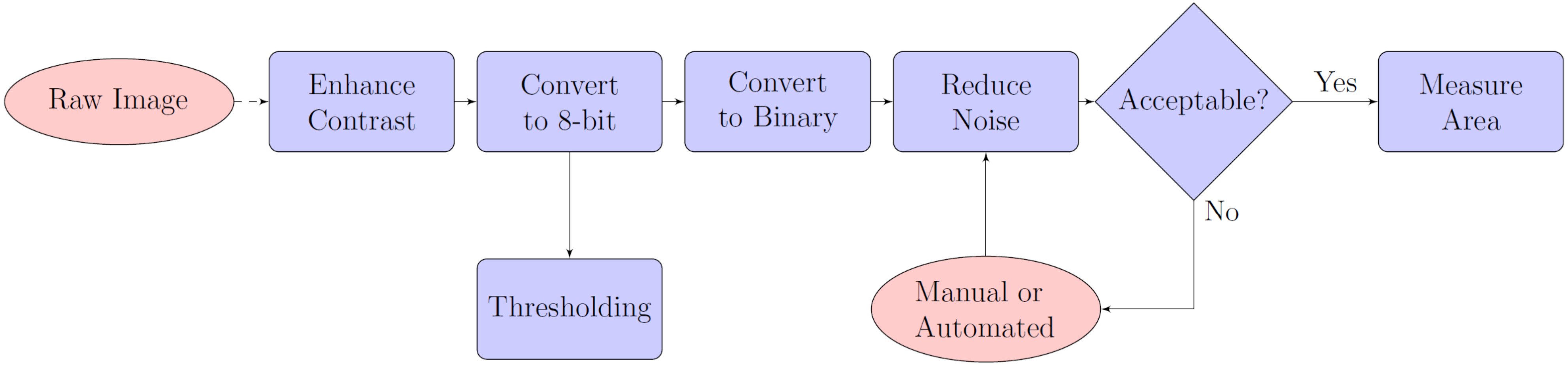
06 JUNE 2025

Solar Beta Angle and Contamination Monitoring Package Beat Frequencies

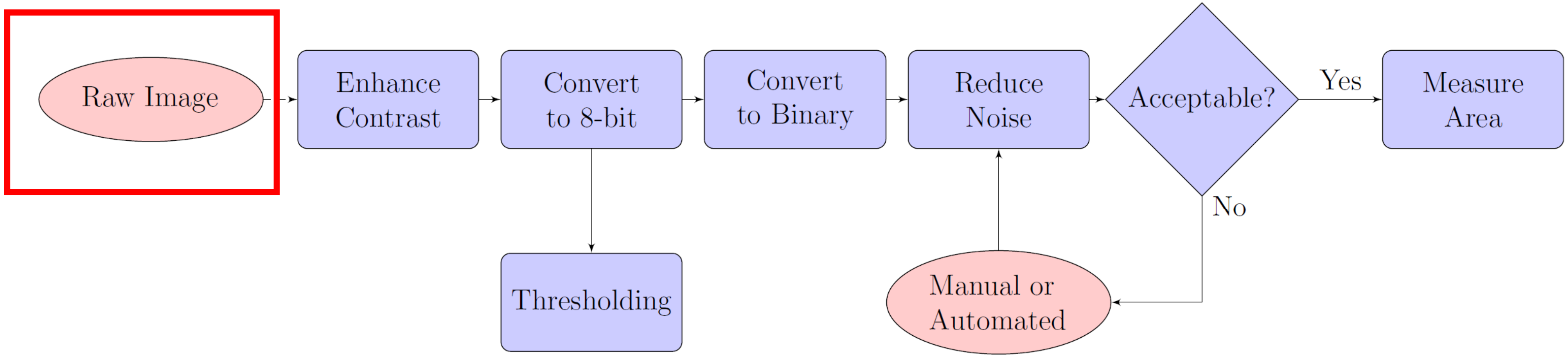


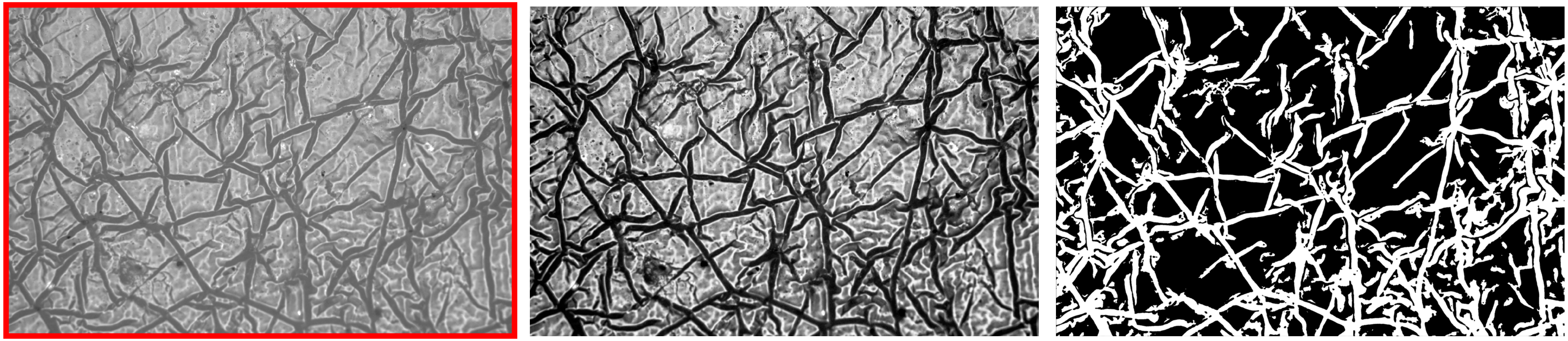
Roell, et al. (2023)

Analysis: Image Capture and Processing

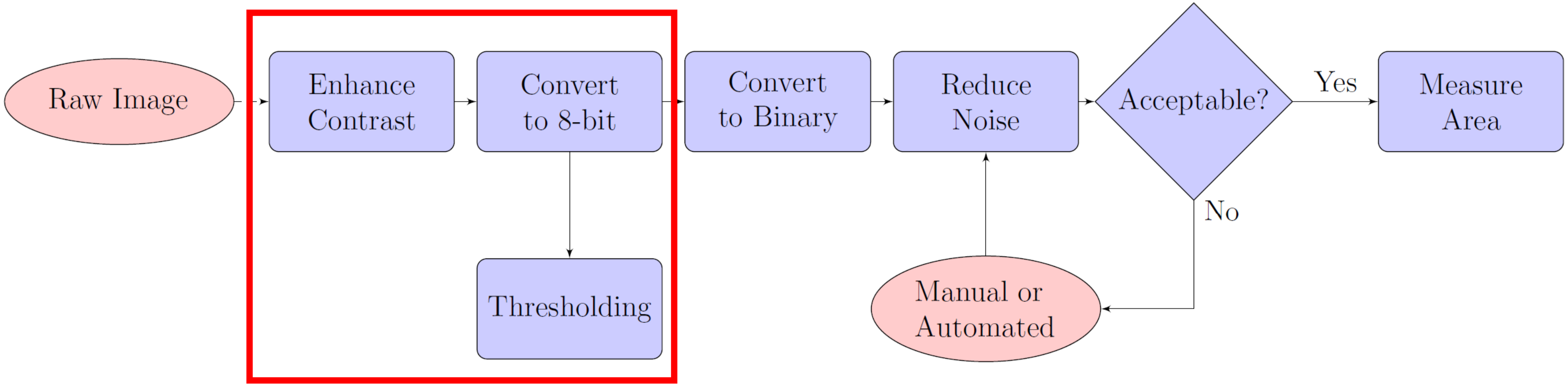


Analysis: Image Capture and Processing





Analysis: Image Capture and Processing



Raw Image

Enhance Contrast

Convert to 8-bit

Thresholding

Convert to Binary

Reduce Noise

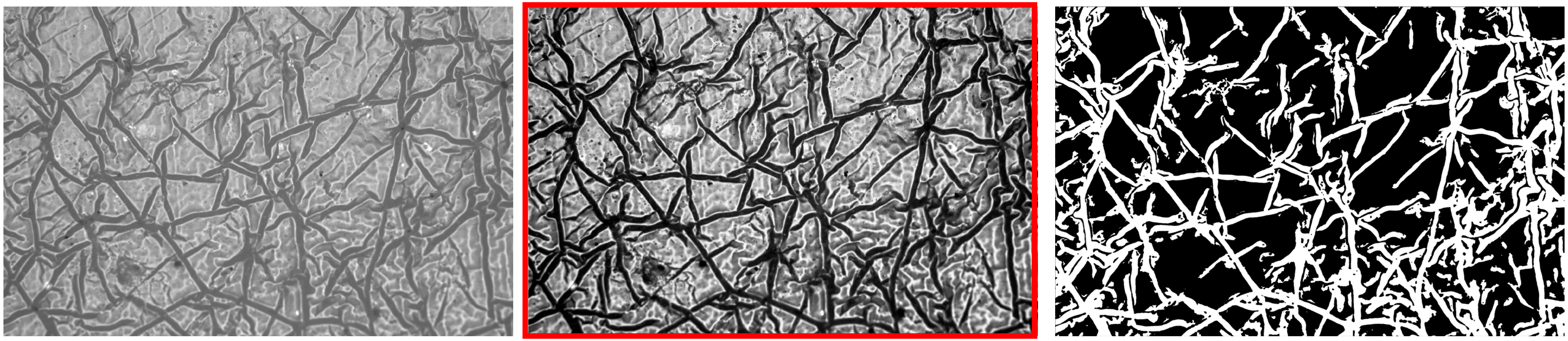
Acceptable?

Yes

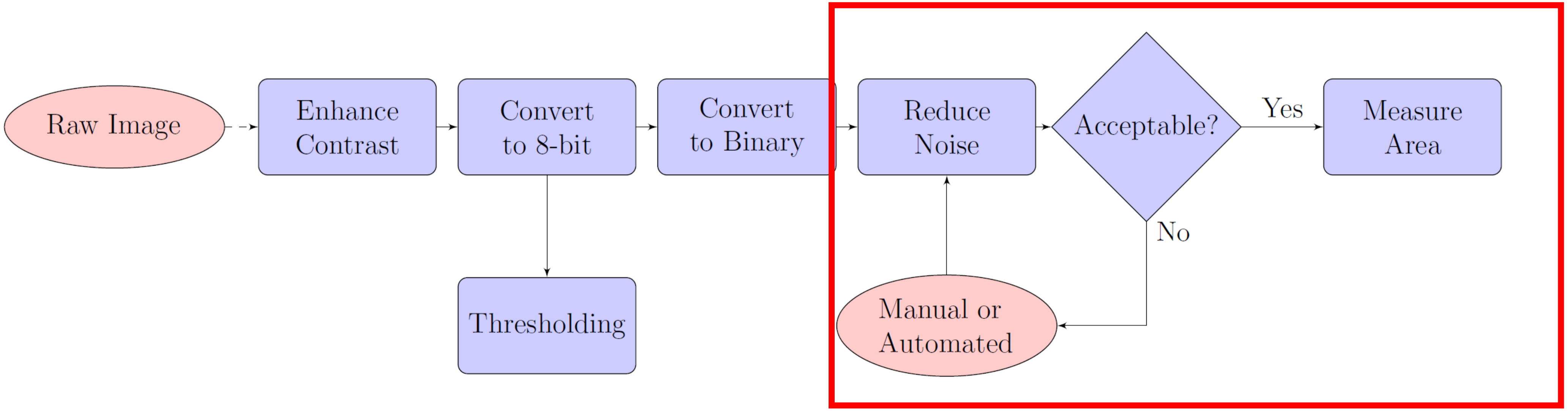
No

Manual or Automated

Measure Area



Analysis: Image Capture and Processing



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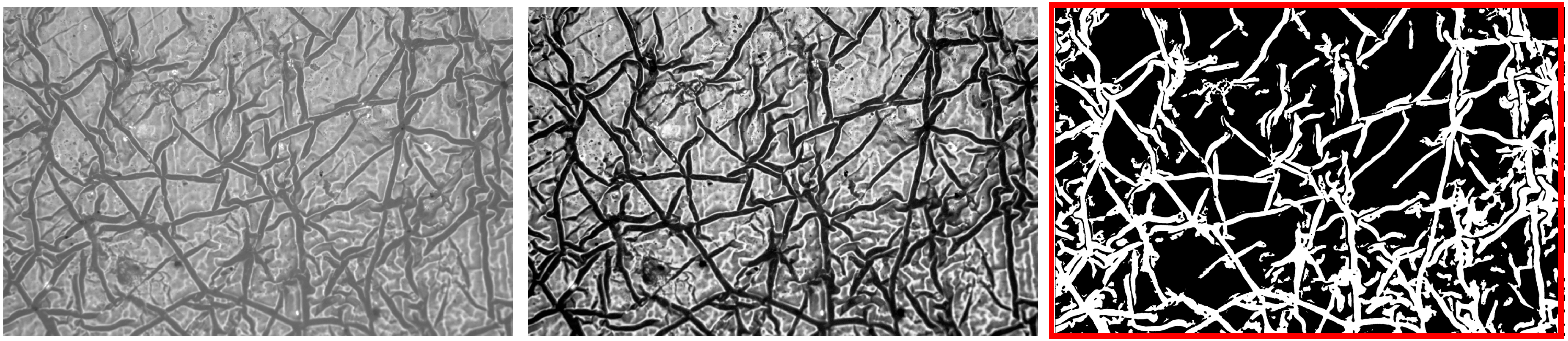
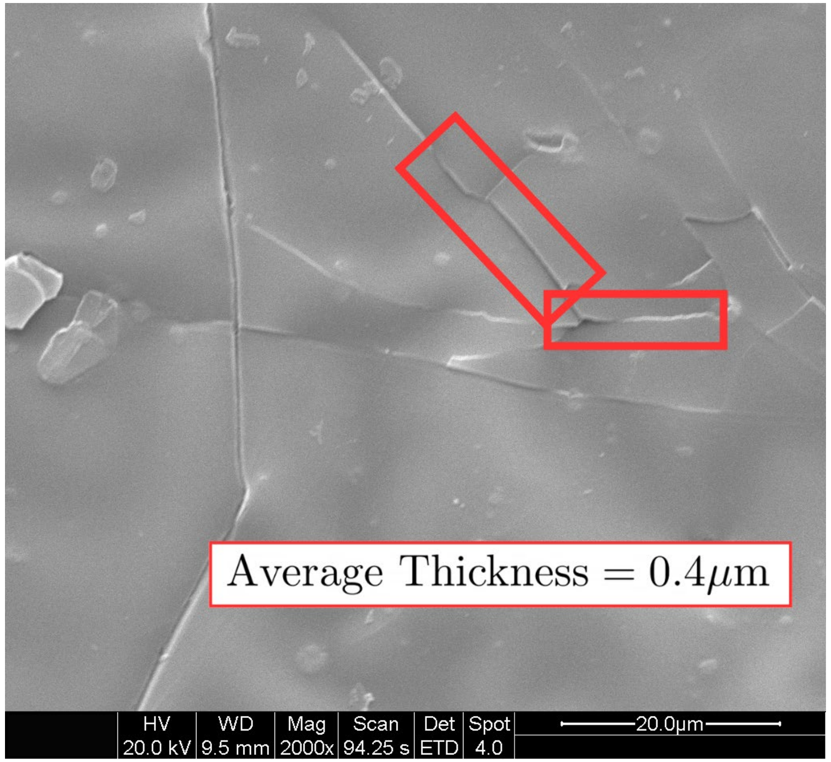
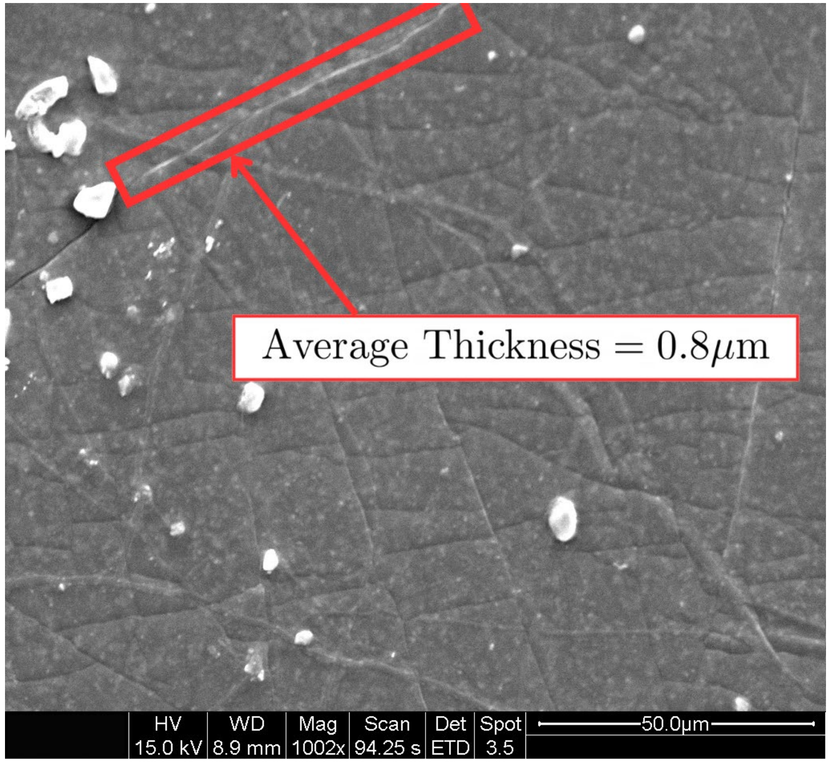


Conclusions





Silicate layer thicknesses after 24 hours exposure

- CV-2960: 0.4μm
- RTV-S691: 0.8μm

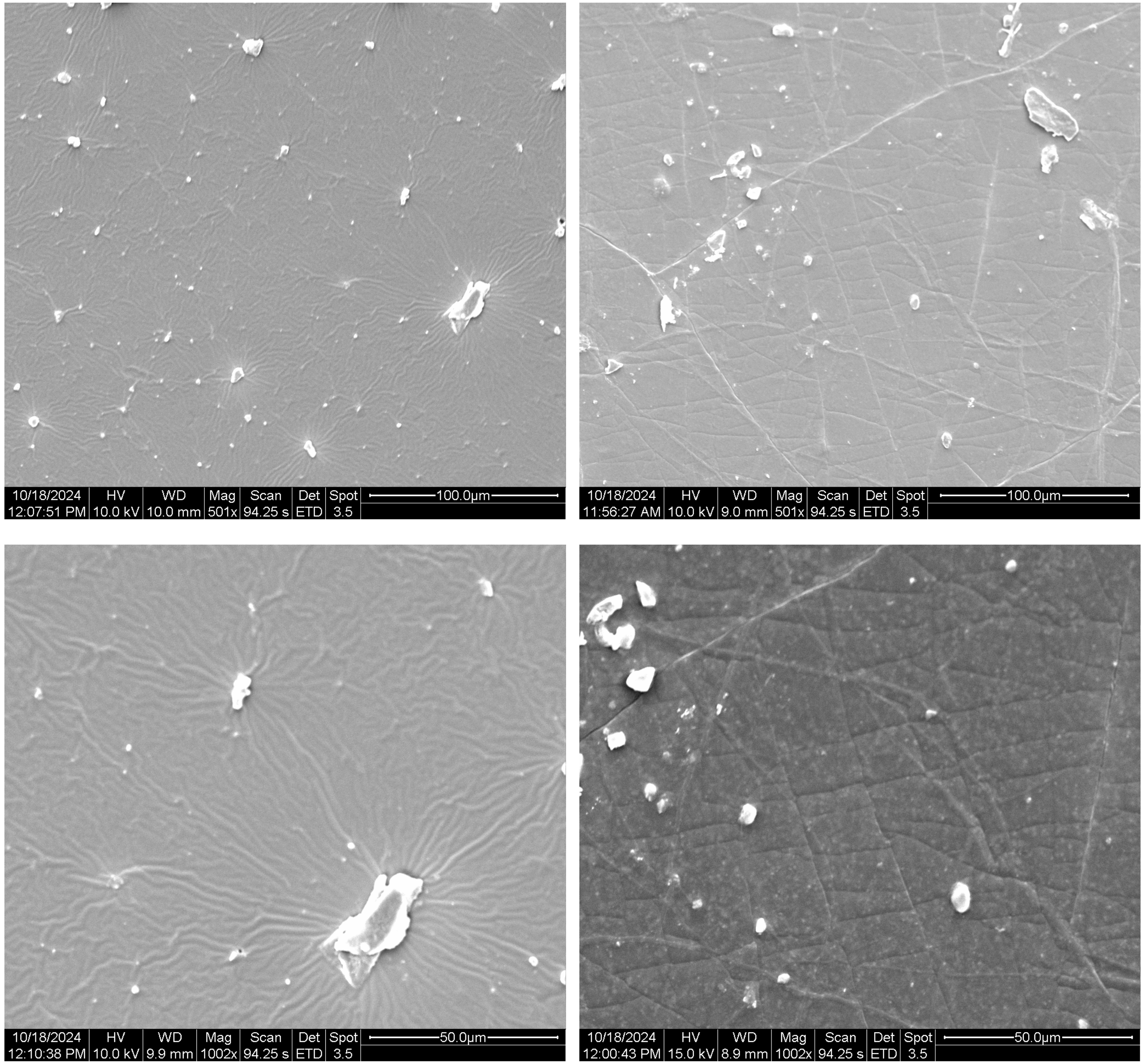
SEM Results: RTV-S691

Top left: Pristine, 500x

Top right: Exposed, 500x

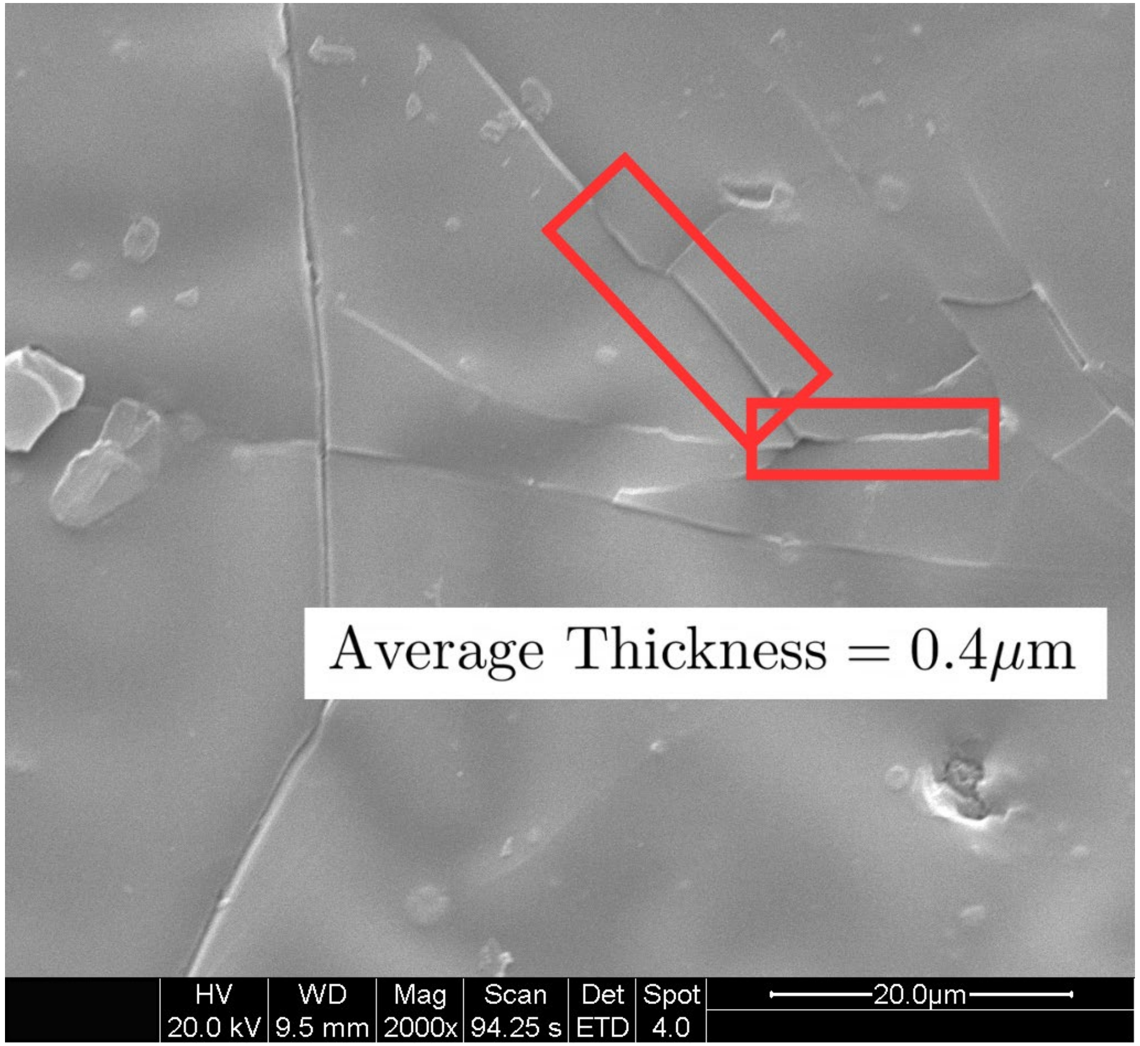
Bottom left: Pristine, 1000x

Bottom right: Exposed, 1000x

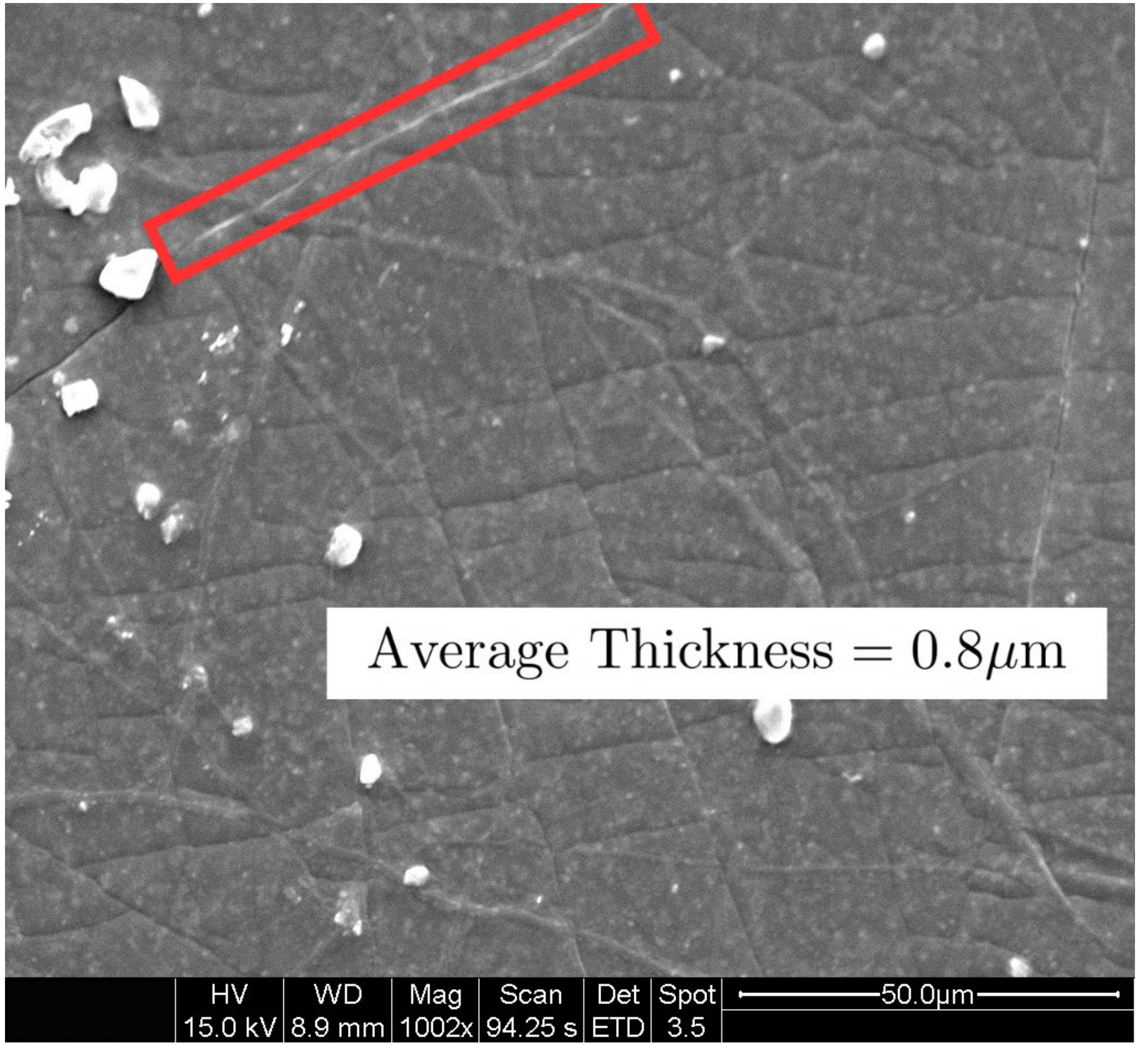


CAL POLY

Approximate Layer Thickness



CV-2960

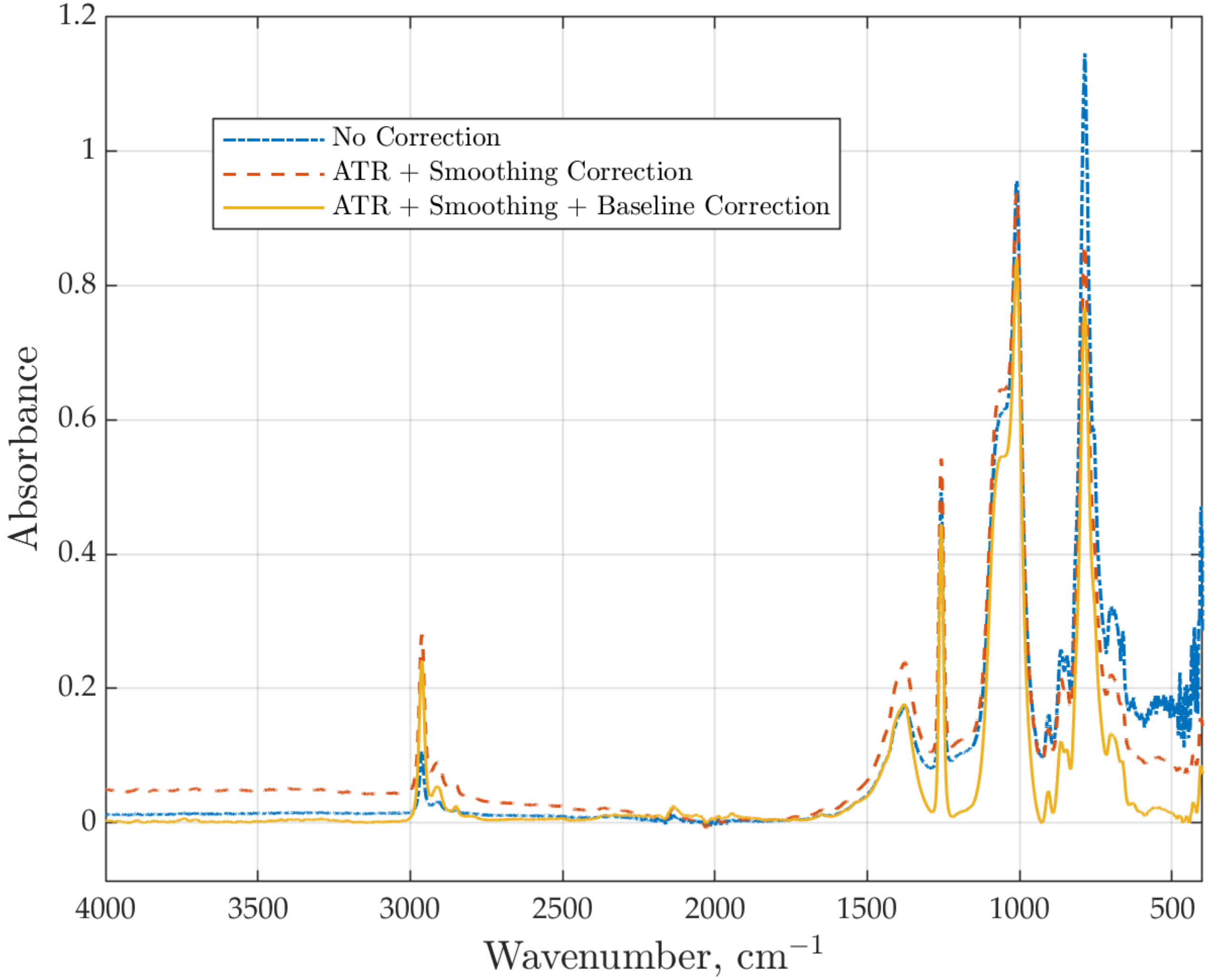


RTV-S691

Analysis Methods

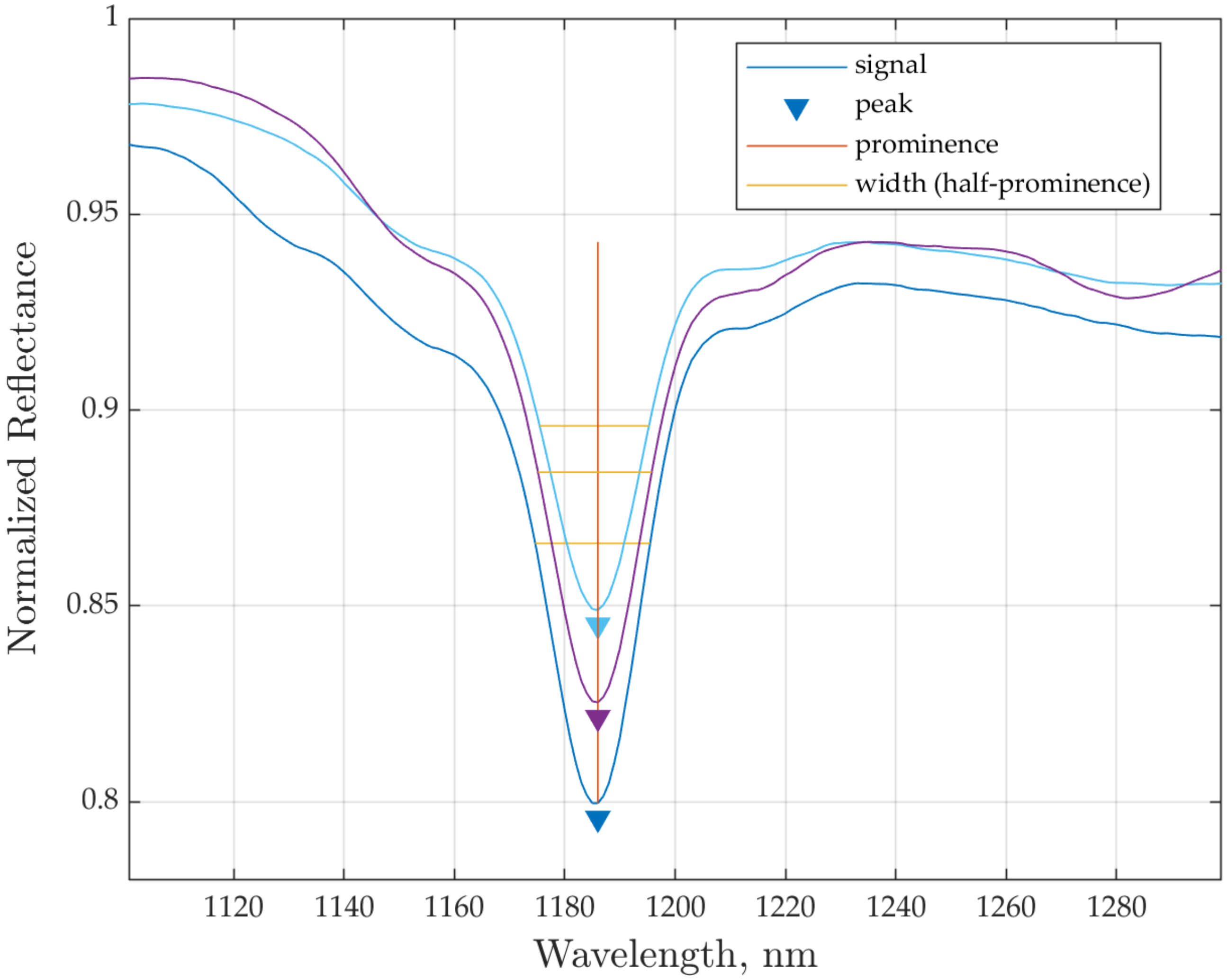
Analysis: Fourier-Transform Infrared Spectroscopy (FTIR)

- ATR-corrected
  - Helps correct for distortions due to effect of light penetration depth and wavenumber
- Baseline corrected
  - Drift, interference, etc.
- Smoothing applied
- Normalized at highest peak
  - Allows for more precise comparison between multiple samples



Analysis: Reflectance and FTIR Peaks: FWHM

- Full-width half-maximum values were computed from FTIR and reflectance spectroscopy peaks
- All analysis was performed using MATLAB and Spectragryph



Statistical Analysis

- JMP Pro 18 statistical software
- Initial analysis revealed quasi-complete separation in the data
- Bootstrap procedure (random resampling) helped
- Normality (Shapiro-Wilk) and unequal variance (Levene) tests explored before performing ANOVA

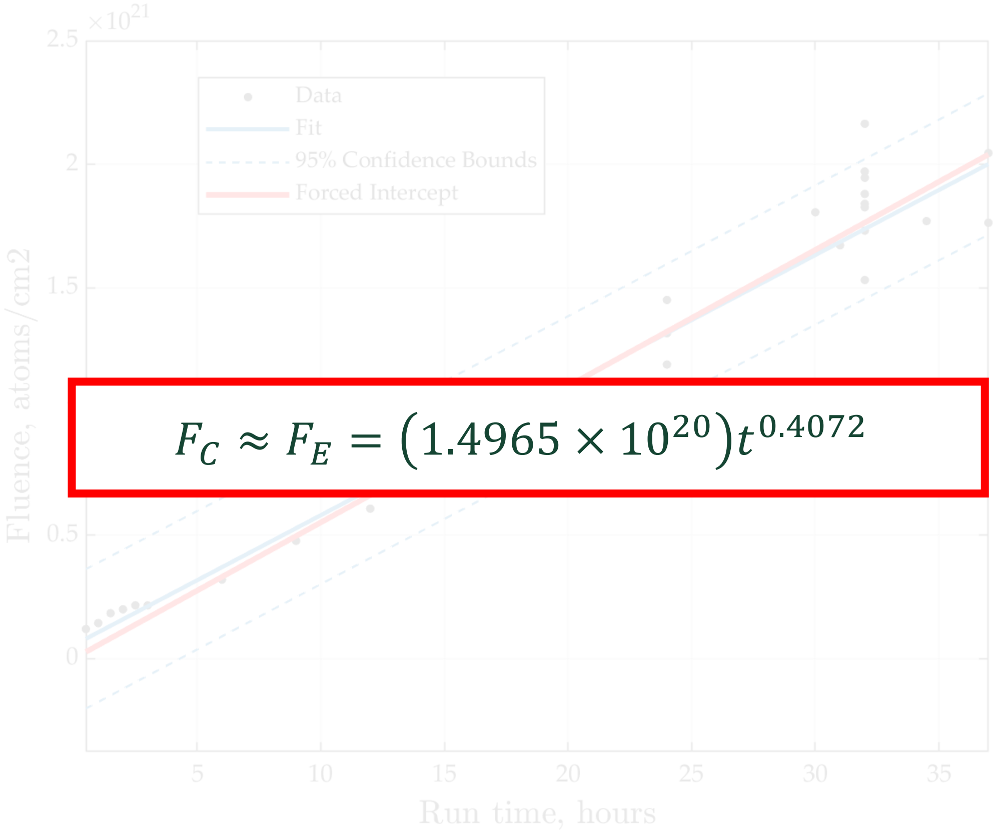
Results: Percent of Sample Surface Area Occupied by Cracks

$$A_{s,ca} = \alpha \ln(F_E) + \beta$$

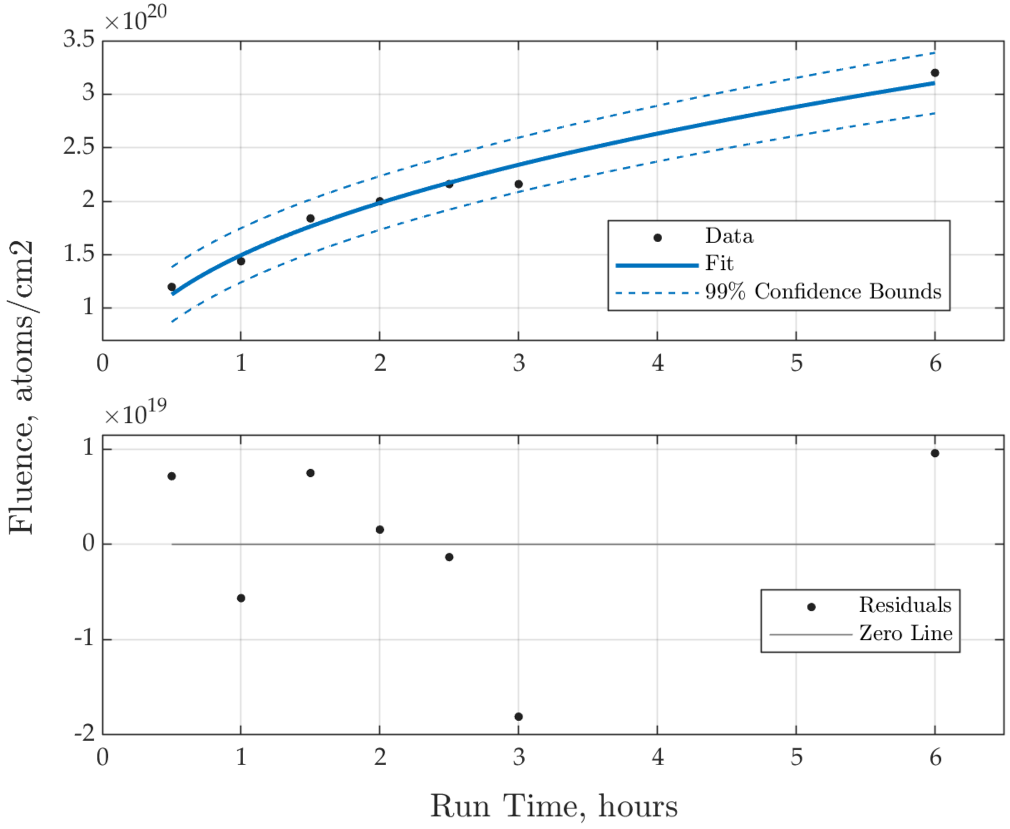
Table 6.9: *Sample Surface Occupied by Cracks, $A_{s,ca}$, Model Fit Summary with Lower and Upper Confidence Interval Bounds*

Sample	α (L_{CI}, U_{CI})	β (L_{CI}, U_{CI})	Model R^2
CV-2960	10.73 (10.1, 11.36)	-480 (-509, -451)	0.974
RTV-S691	7.085 (6.674, 7.496)	-317.3 (-336.4, -298.2)	0.981

Analysis: Fluence Approximation for Short-Duration Tests (backup)



$$F_C \approx F_E = \left(1.4965 \times 10^{20}\right) t^{0.4072}$$



Old model: linear fit

Good for long run times and general trend at 95% confidence, not so good for short run times

New model: power fit

Fits lab data well ($R^2 = 0.96$) at 99% confidence bounds for short run times

Results: Silicone Contamination (backup)

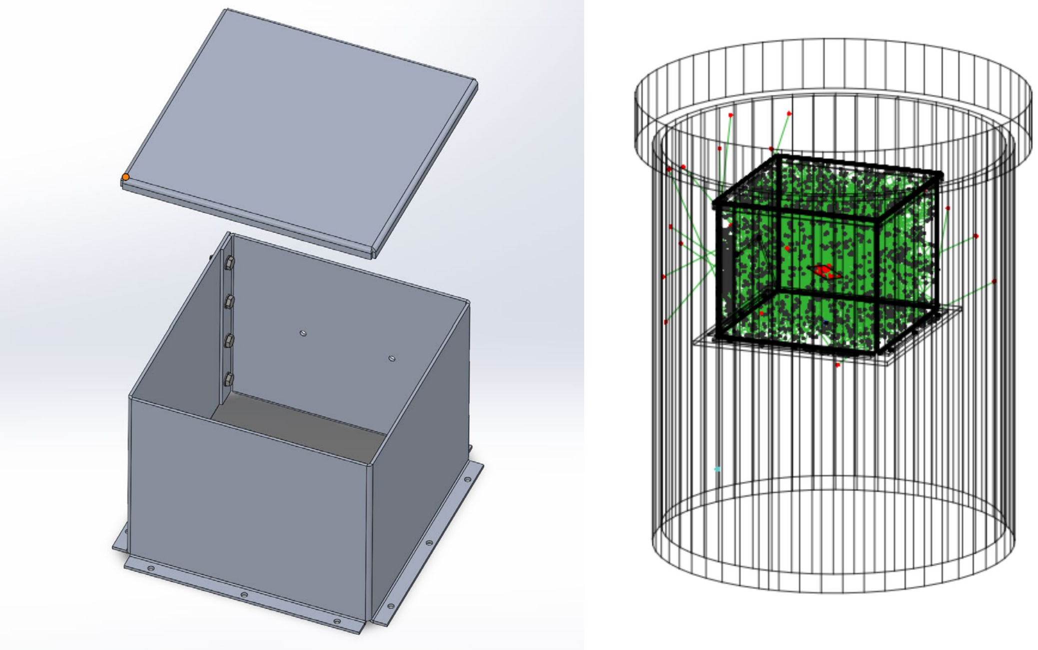
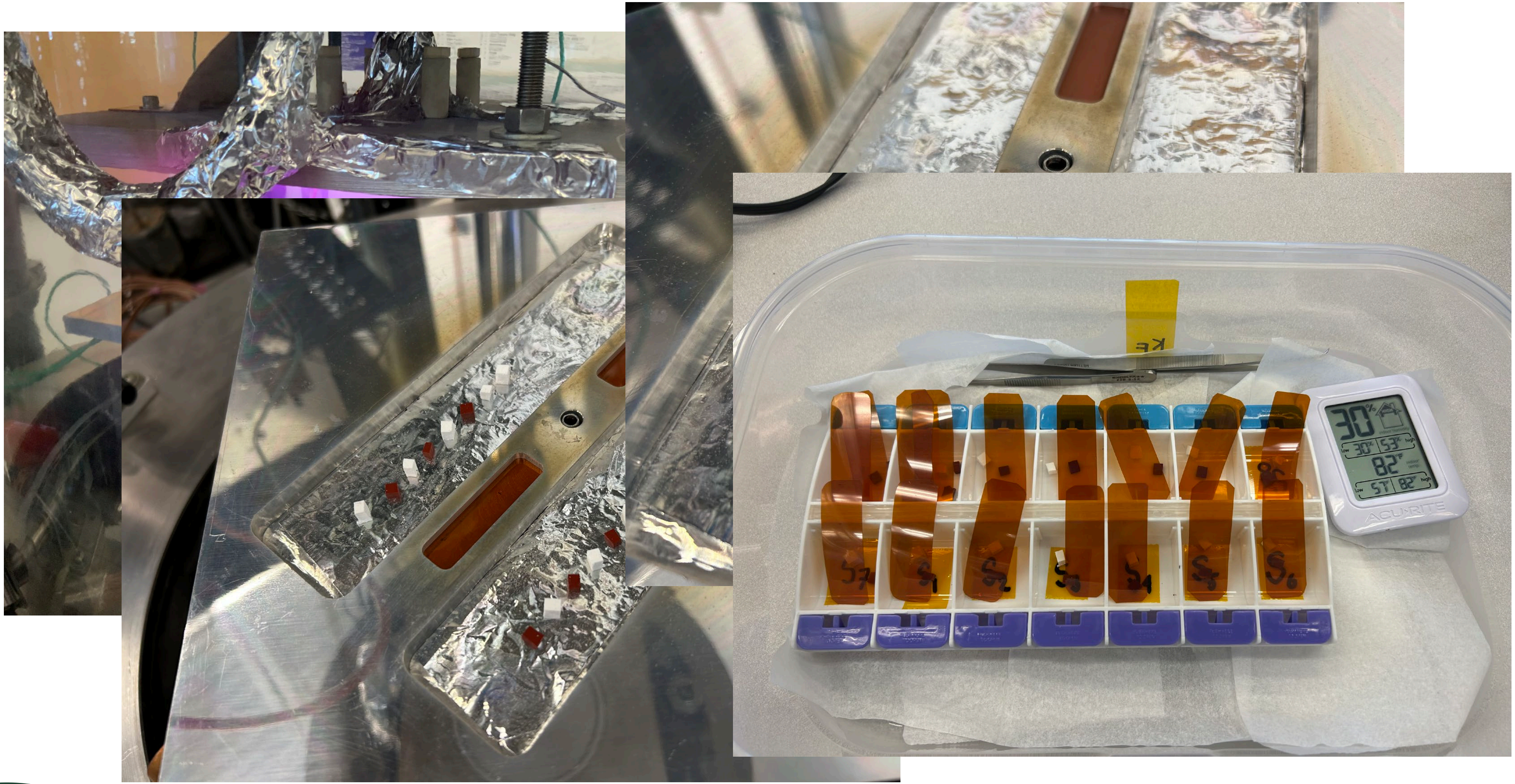


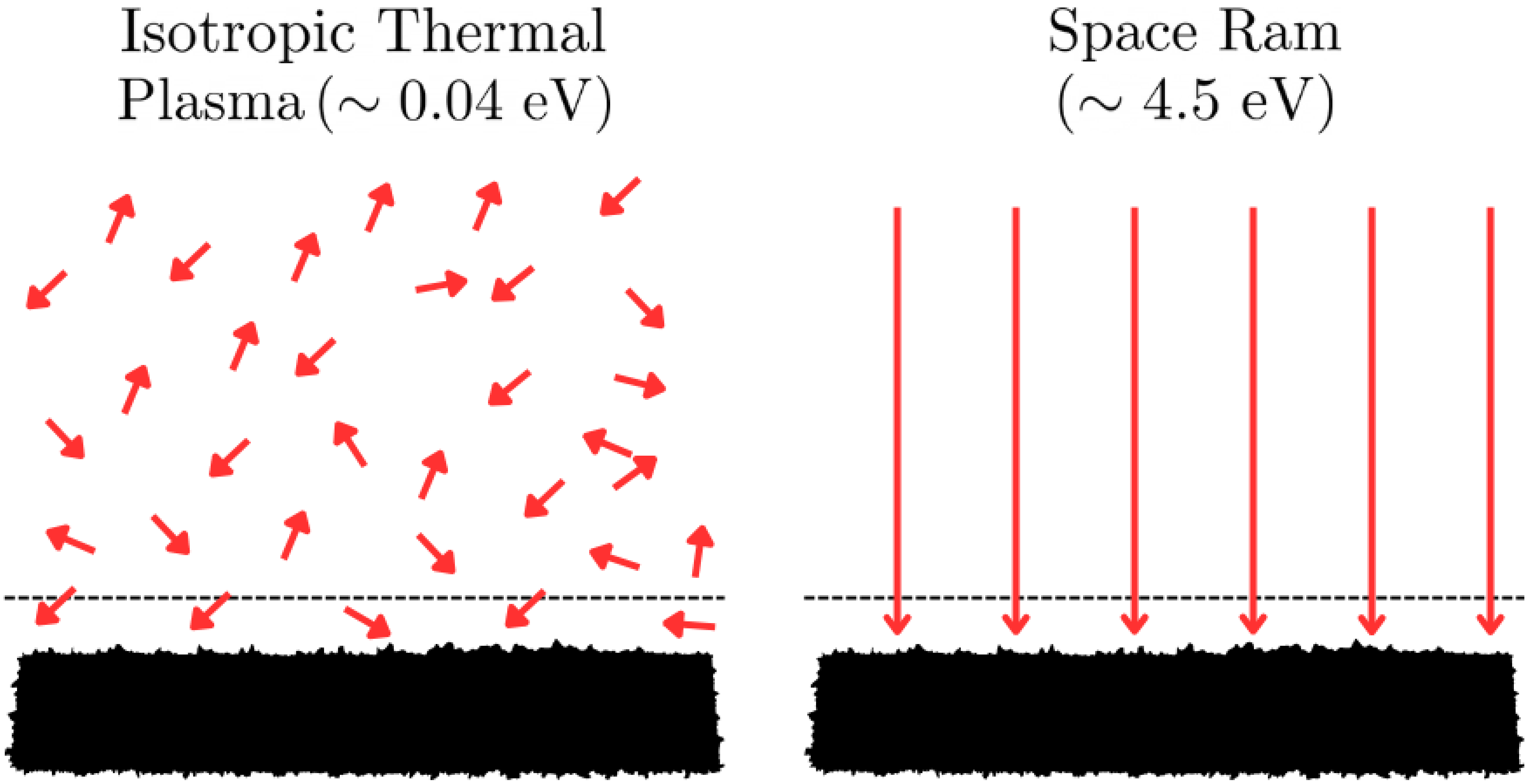
Figure 6.1: *Effusion Cell Design and Outgassing Simulation*

Table 6.1: *Transport Factor With and Without Effusion Cell*

	Without Cell	With Cell
Collector Plate surface area (cm^2)	6.45	6.45
Transport factor to chamber walls (%)	69.5	45.1
Transport factor to chamber lid (%)	25.0	9.76
Transport factor to collector plate, top (%)	0.00	19.5
Transport factor to collector plate, bottom(%)	5.47	25.6

Introduction and Background




Isotropic Thermal
Plasma (~ 0.04 eV)
Space Ram
(~ 4.5 eV)

Experimental Error Analysis

$$\delta q = \left(\left(\frac{\partial q}{\partial x} \delta x \right)^2 + \cdots + \left(\frac{\partial q}{\partial z} \delta z \right)^2 \right)^{1/2} \tag{5.4}$$

$$\begin{aligned}
\delta F_E &= \left(\left(\frac{\delta \Delta M_K}{A_K \rho_K E_K} \right)^2 + \left(-\frac{F_E \, \delta A_K}{A_K} \right)^2 + \left(-\frac{F_E \, \delta \rho_K}{\rho_K} \right)^2 + \left(-\frac{F_E \, \delta E_K}{E_K} \right)^2 \right)^{1/2} \\
&= \left(\frac{\delta \Delta M_K^2}{A_K^2 \rho_K^2 E_K^2} + \frac{F_E^2 \, \delta A_K^2}{A_K^2} + \frac{F_E^2 \, \delta \rho_K^2}{\rho_K^2} + \frac{F_E^2 \, \delta E_K^2}{E_K^2} \right)^{1/2}
\end{aligned} \tag{5.5}$$