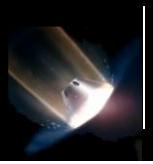


Response of Ablative Thermal Protection Materials to Degradation in Low Earth Orbit – Characterization of Specimens from MISSE-13

Peter Marshall[1]

Greg Gonzales[1], Matt Gasch[2], Kyle Hendrickson[1], Don Ellerby[2]

1: Analytical Mechanics Associates

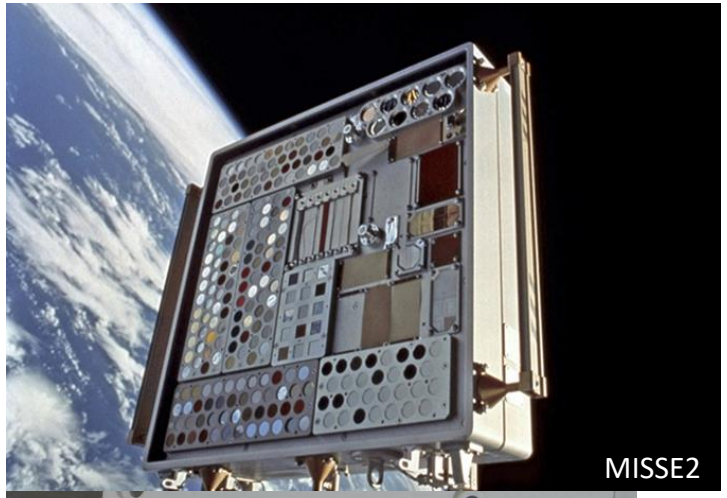
2: NASA

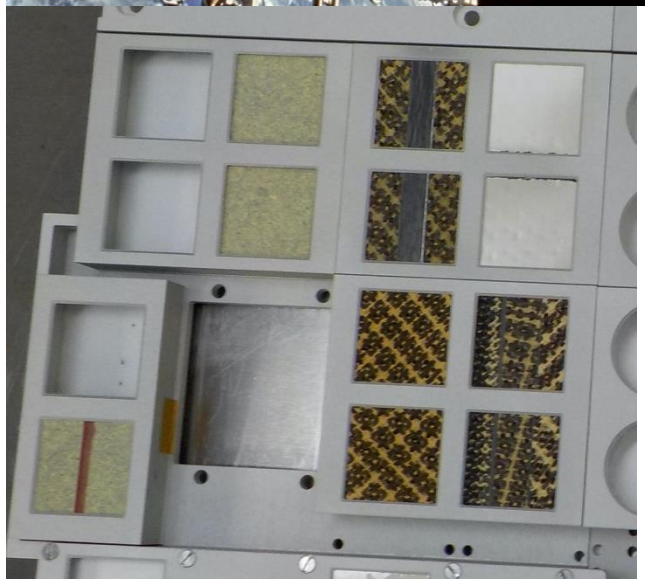
Outline

- MISSE-13 and Low Earth Orbit (LEO) Environment
- Ablative Thermal Protection System (TPS) Materials
- Relative Erosion
  - PICA vs HEEET, phenolic vs carbon fiber
- RTV Seam
- Silicone Coating
- Implications for Missions and Heatshield Design
- Conclusions & Questions

MISSE-13 and Low Earth Orbit (LEO) environment

- Materials International Space Station Experiment (MISSE) is a series exposing samples to the low Earth orbit (LEO) environment
  - Panels holding samples mounted on ram or wake side of the space station
- Specimens considered here spent 391 days on ram side during MISSE-13
  - Deployed between March 24, 2020 and April 19, 2021
- LEO Environment
  - Atomic oxygen (AO)
    - Highly reactive, surface oxidation, “line of sight”
    - Manifest as erosion if volatile oxide or passivating layer if stable
  - Vacuum & Ultraviolet (UV)
    - High energy UV-C: degradation of atomic bonds, crosslinking, point defects
    - Embrittlement and/or yellowing as typical for UV degraded polymers
    - Vacuum outgassing which can couple with above

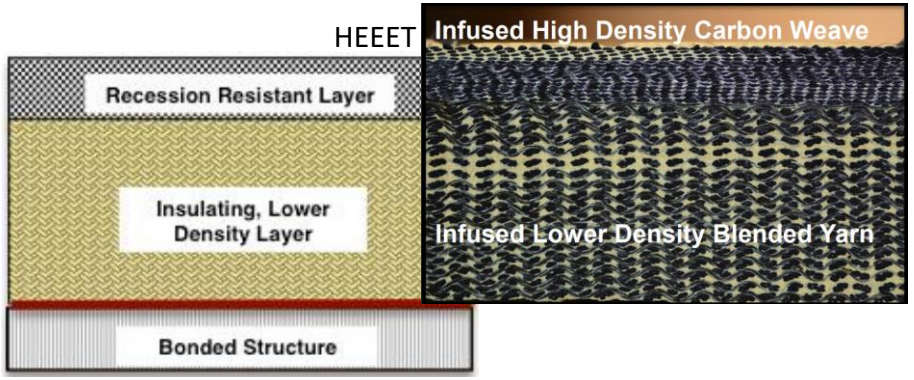

MISSE2


MISSE13

Ablative TPS Materials on MISSE-13

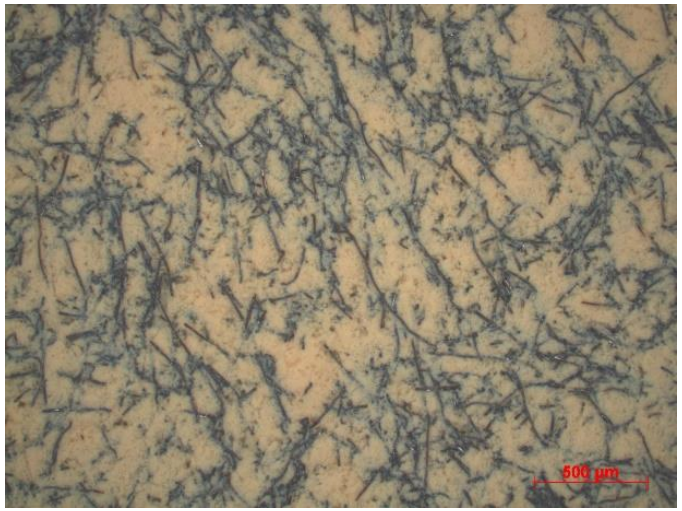
- TPS acreage materials
  - PICA-D: Phenolic Impregnated Carbon Ablator, Domestic raw materials
    - Very low density carbon foam infiltrated with low density/high surface area phenolic resin
    - Used on Stardust, Mars Science Laboratory, Mars2020, and others
  - HEEET: Heatshield for Extreme Entry Environment Technology
    - Mid-density material with woven carbon/phenolic fibers
    - Infiltrated with similar phenolic resin
    - Two layers: insulating layer (**IL**) and higher density, higher carbon layer for recession (**RL**)
- Seam – PICA-RTV sandwich
  - RTV560: silicone used in many tiled TPS joints and bonds
  - Flight heritage as seam in MSL and Mars2020
- Coatings – NuSil on HEEET IL
  - NuSil 1144-0: commercial low-volatility silicone coating for surface protection

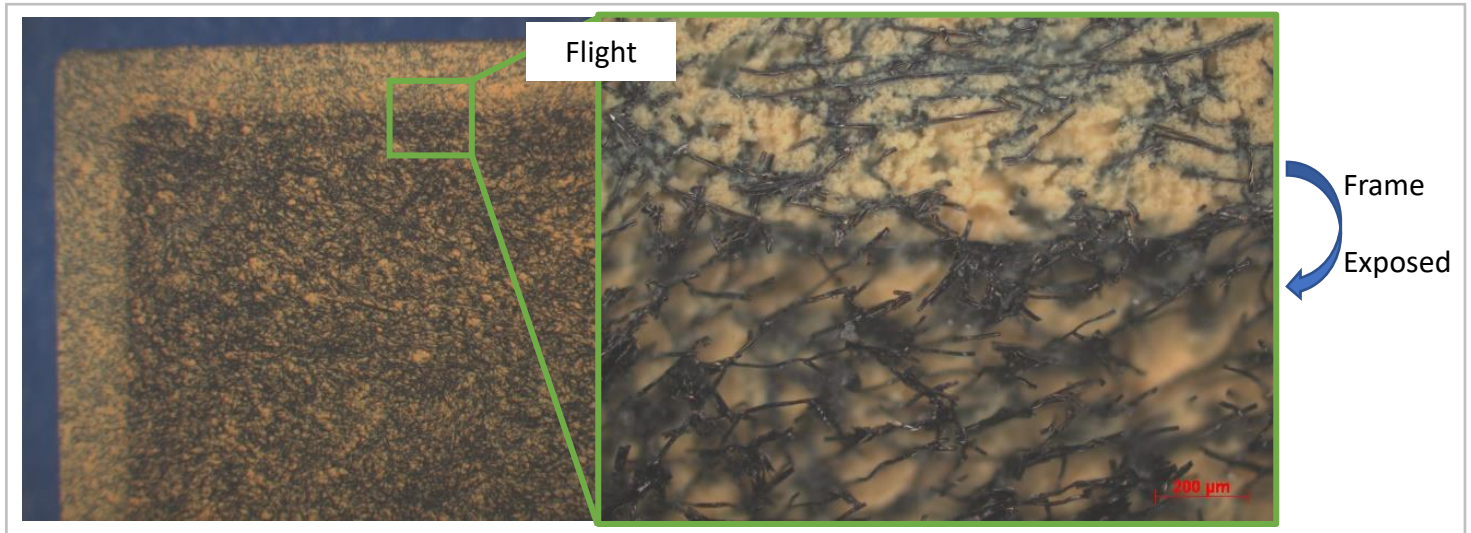
Mars2020 Heatshield - PICA



Acreage Erosion – PICA-D

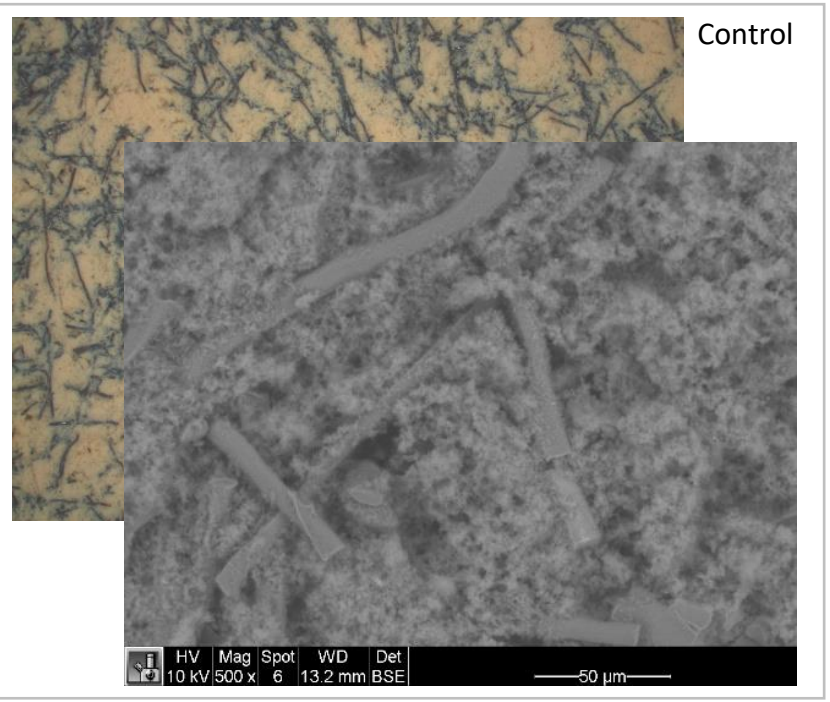
- Carbon and phenolic (like many other organics) are eroded by AO
  - Oxidation to CO, CO_2, and H_2O
- Manifest as material loss from surface with clear difference between exposed and neighboring region beneath mounting frame (lighter colored edge region in middle image below)
- Density has large impact on depth of erosion
  - Low density phenolic has much larger depth of erosion than carbon fibers
  - Pitting damage on surface of carbon fibers themselves

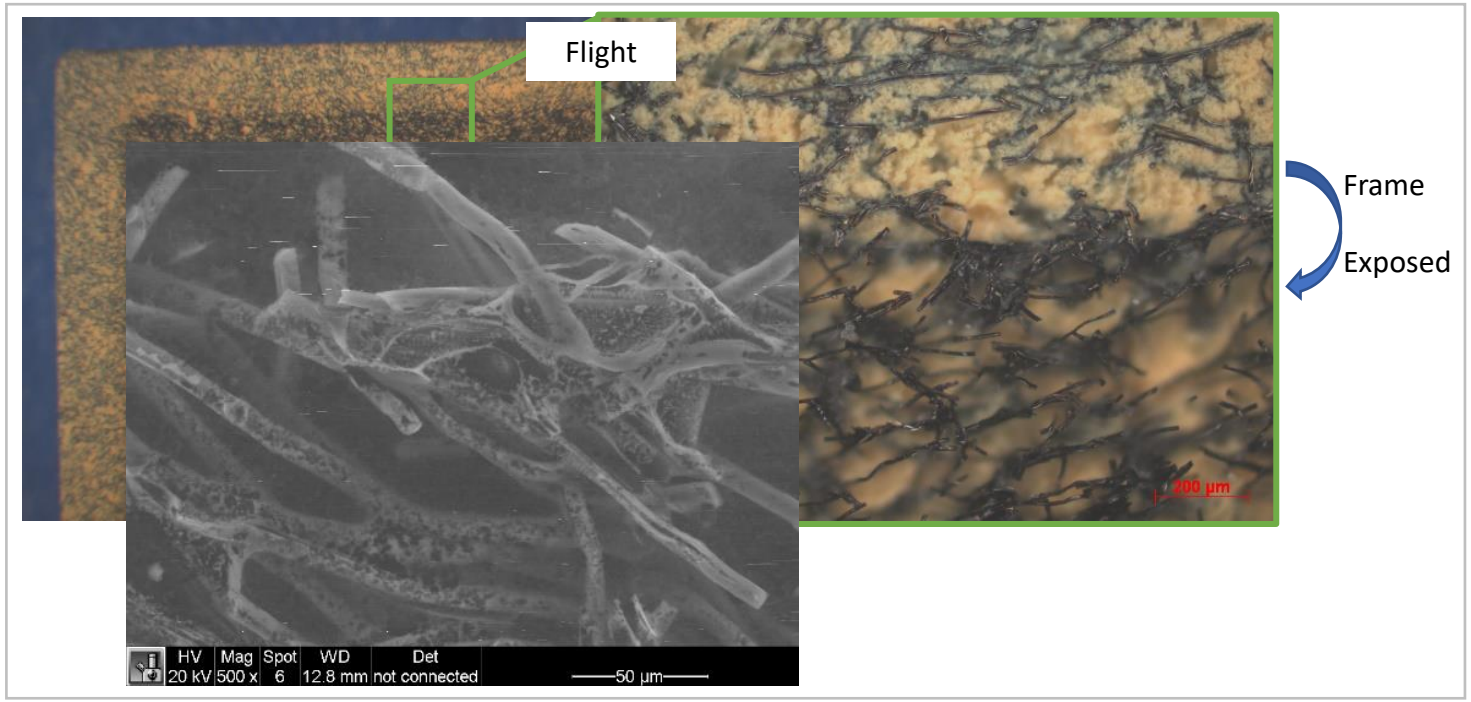




Acreage Erosion – PICA-D

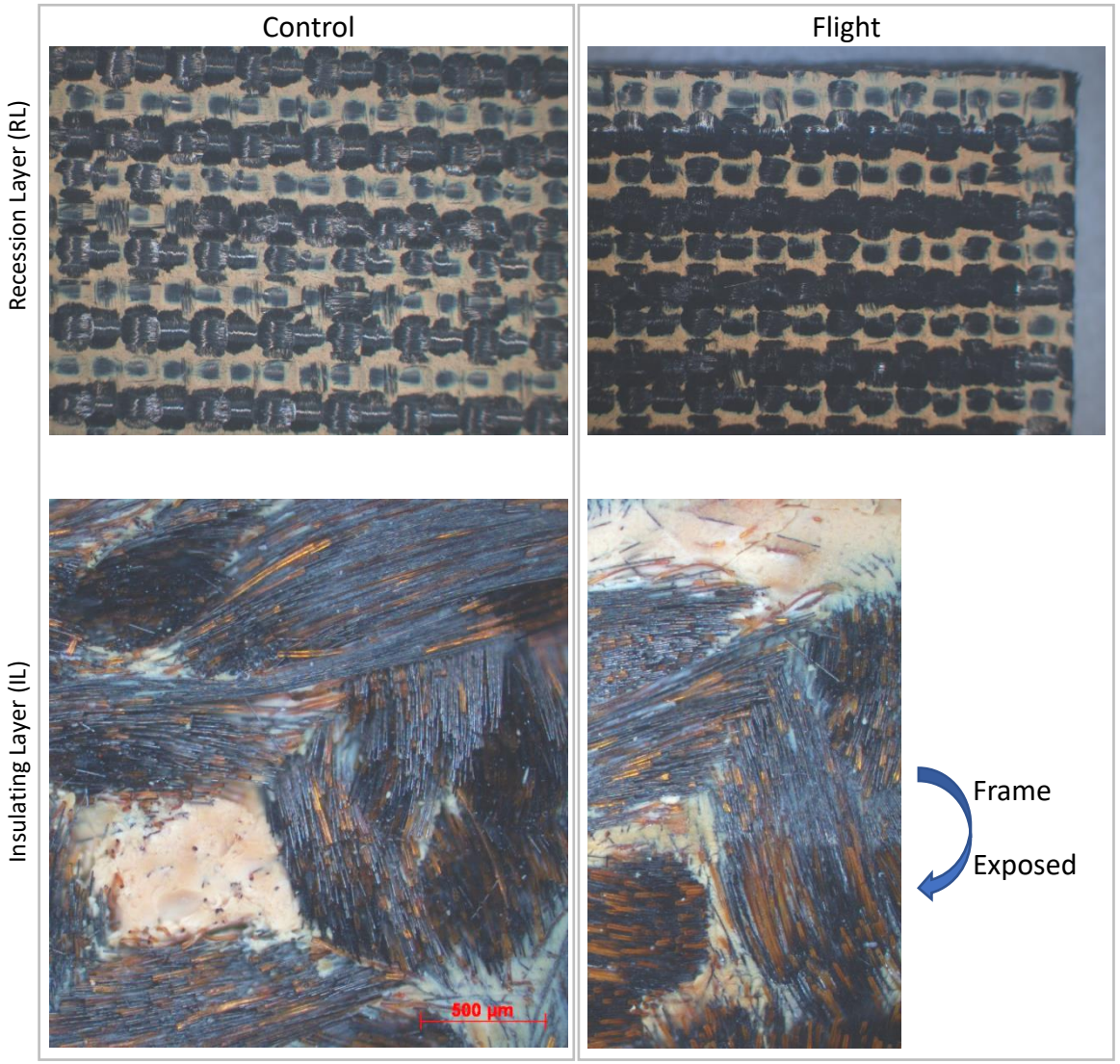
- Carbon and phenolic (like many other organics) are eroded by AO
  - Oxidation to CO, CO_2, and H_2O
- Manifest as material loss from surface with clear difference between exposed and neighboring region beneath mounting frame (lighter colored edge region in middle image below)
- Density has large impact on depth of erosion
  - Low density phenolic has much larger depth of erosion than carbon fibers
  - Pitting damage on surface of carbon fibers themselves





Acreage Erosion – HEEET

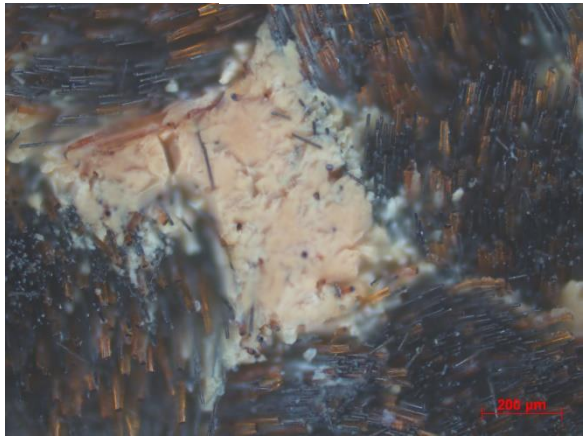
- Both RL and IL have a visible darkening where exposed, similar to PICA
  - UV caused or erosion of lighter color phenolic by AO
  - Optical properties not yet characterized
- The higher density phenolic in HEEET compared to PICA does not show a measurable recession
  - Complicated by the machined surface topology and weave-matrix spacing



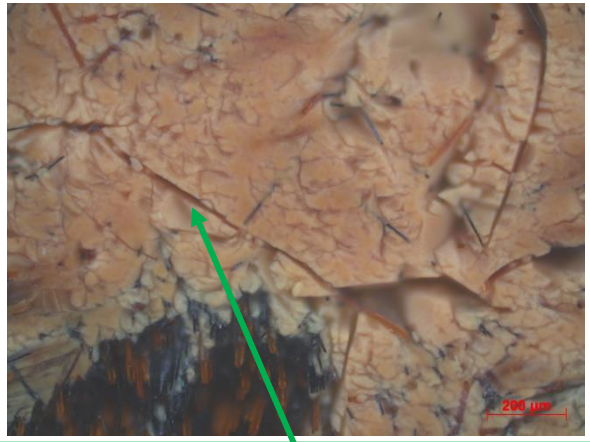
Acreage Erosion – HEEET Phenolic

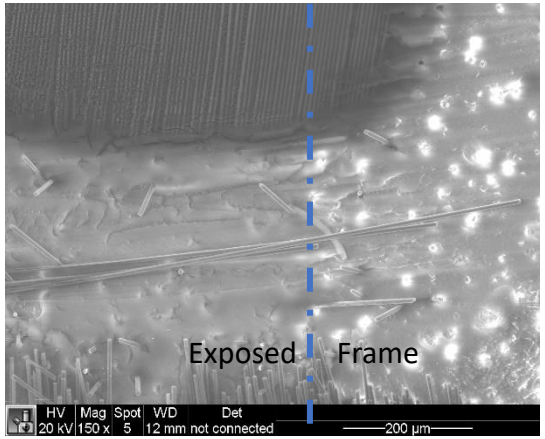
- Limited, if any, damage from LEO environment seen in phenolic matrix for flight HEEET sample
  - Some cracks and roughness in control
- No pitting
- Possible larger or increased number of cracks
- Distinctly less charging in SEM for flight vs control
  - Quantification is difficult

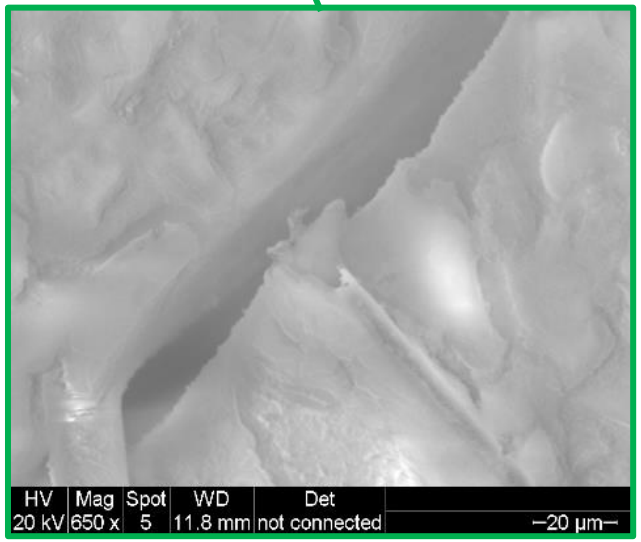
Control



Flight



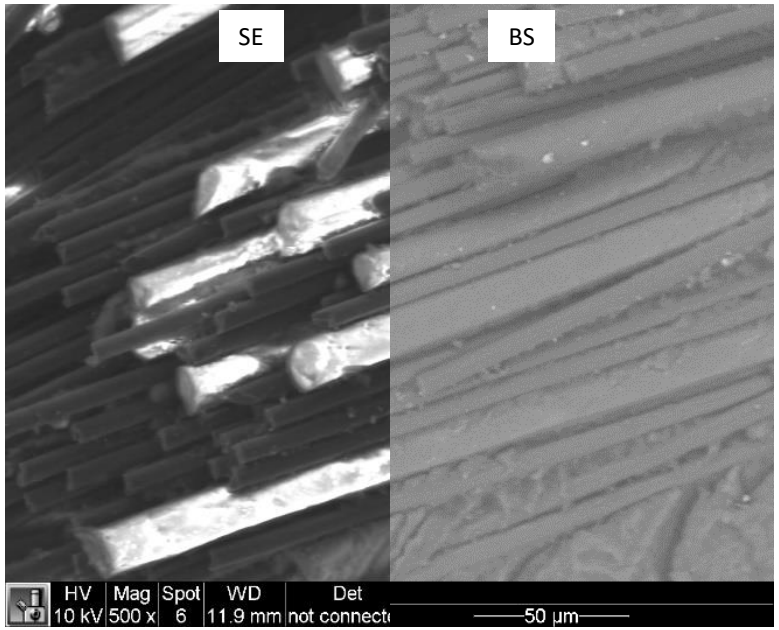




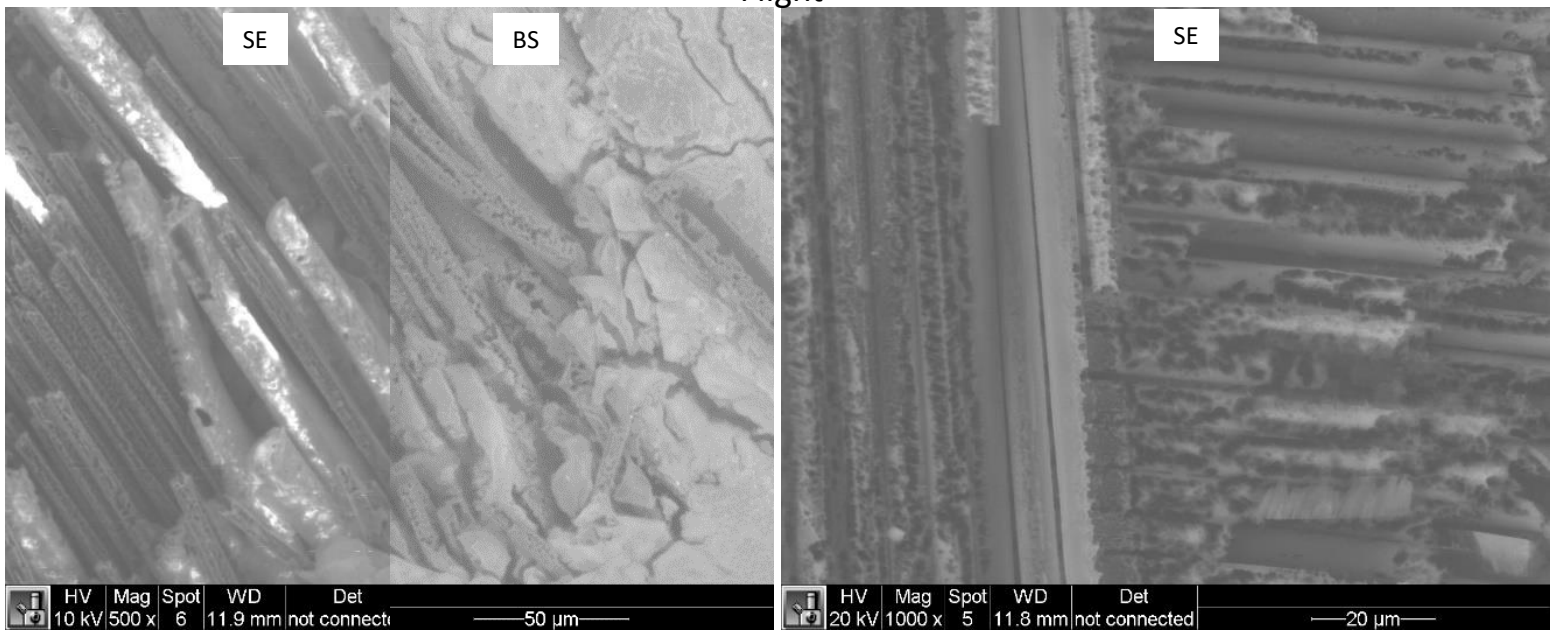
Acreage Erosion – HEEET Fibers

- HEEET contains both carbon and phenolic fibers within the yarns
- Phenolic fibers are bright in secondary electron imaging (SE) and larger diameter
- AO pitting occurs in both fibers
  - Pits are a couple microns or less in size

Control

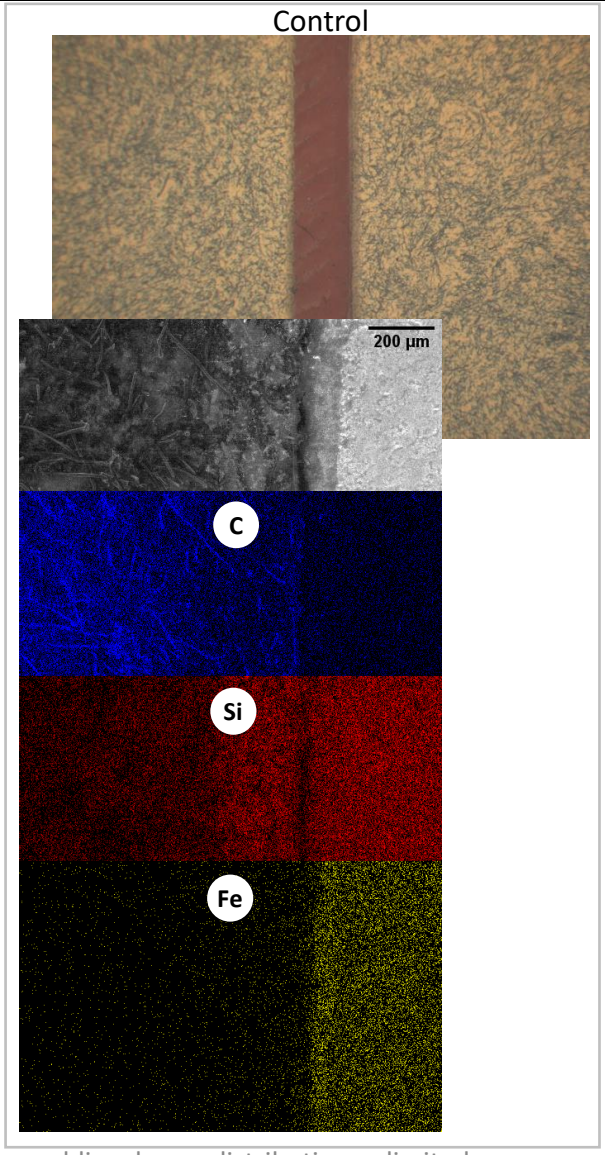


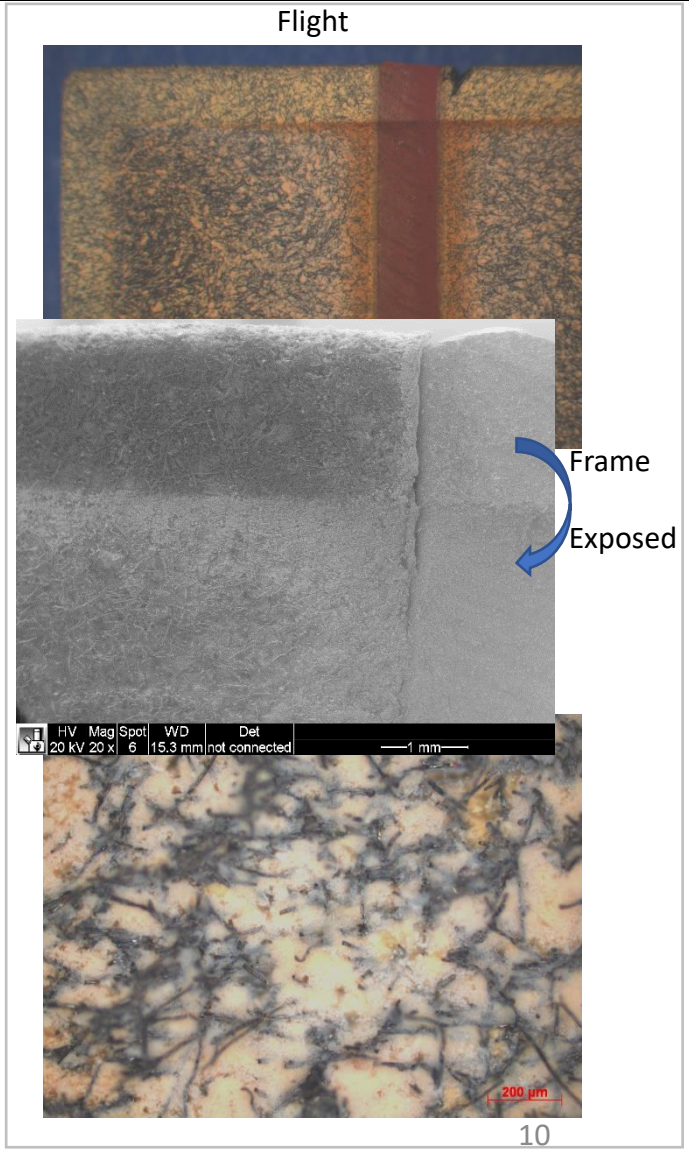
Flight



Seam PICA– RTV560

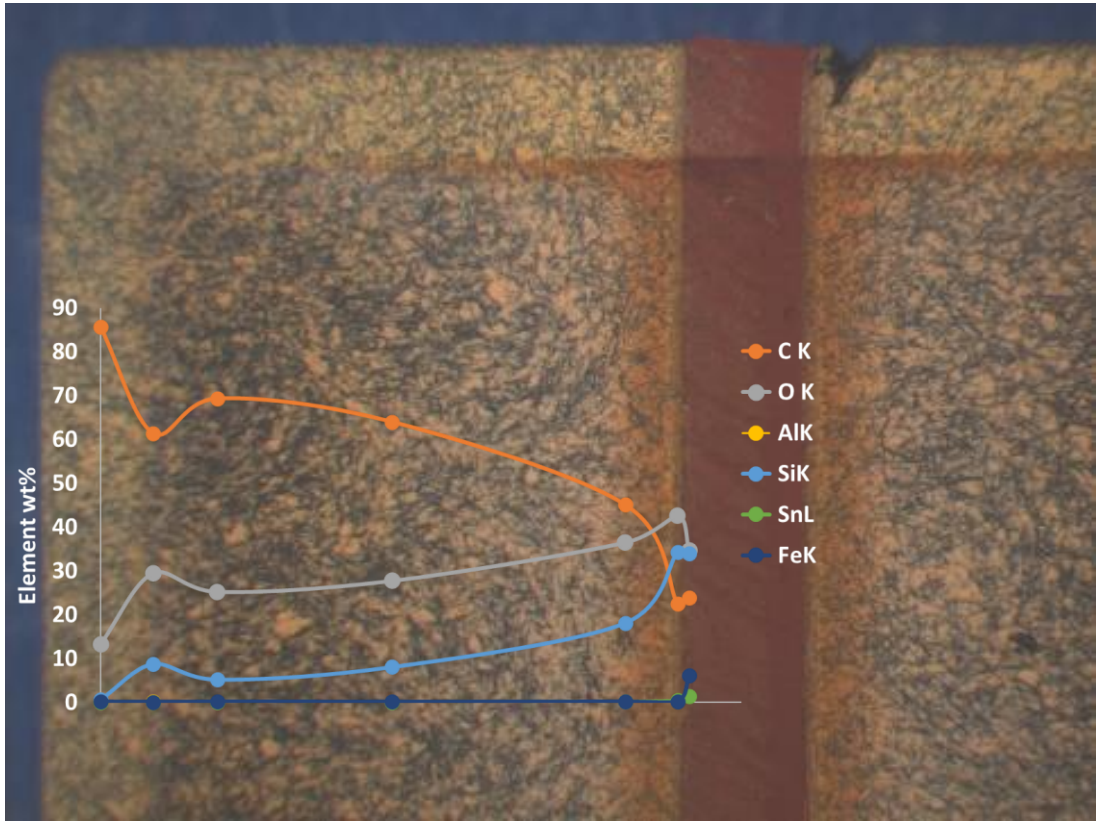
- Room temperature vulcanizing silicone with iron oxide fill and tin catalyst
- Migration of species away from seam and depositing on exposed PICA surface
  - EDS analysis on following slides
  - No change seen under frame or backside
- Less erosion of phenolic (obscured by surface film)
- Surface of PICA-RTV was machined, complicating evaluation of the interface
  - Very different stiffness and tool friction between PICA and RTV can lead to cracking





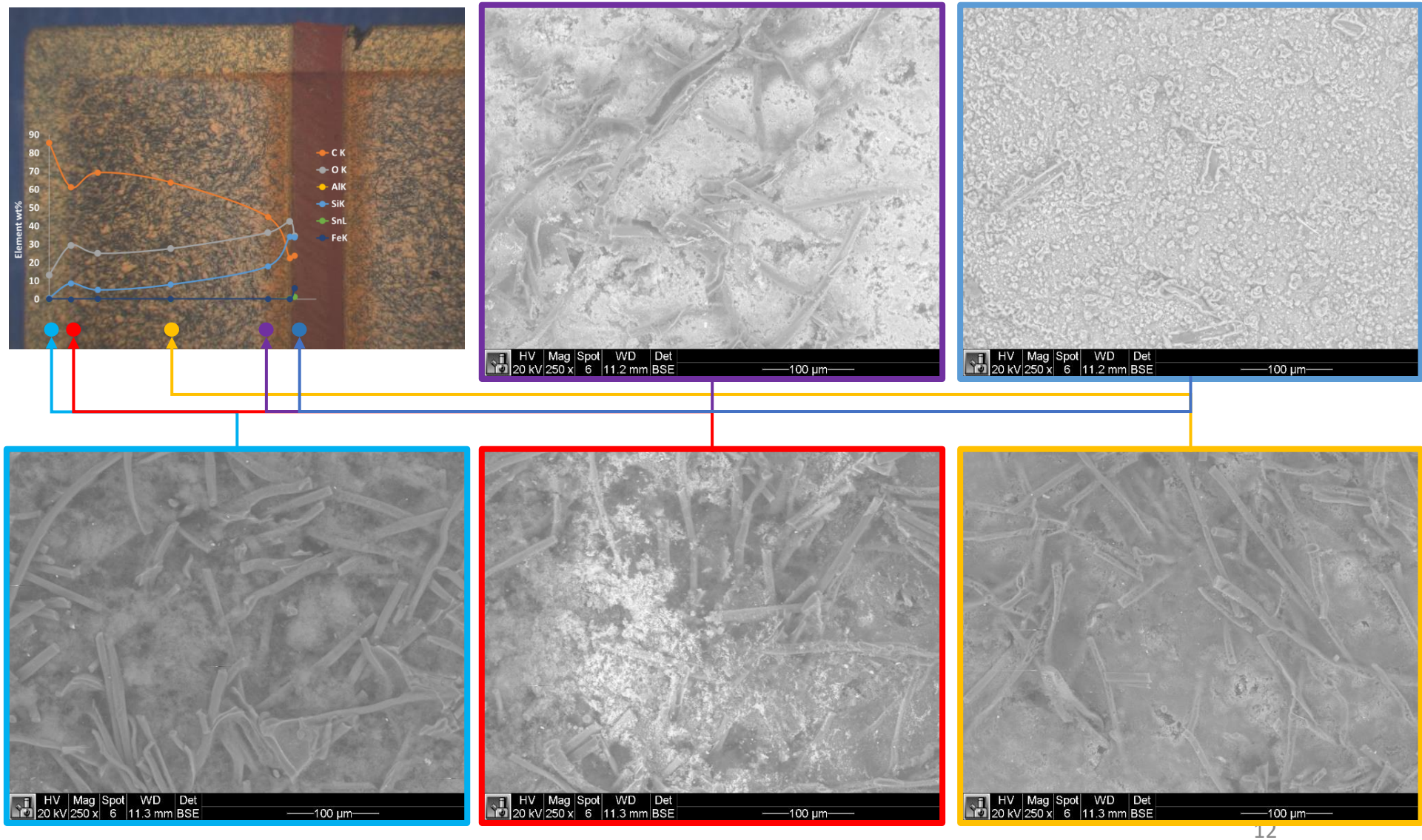
Seam PICA– RTV560

- EDS spectra collected at 500x375µm areas incrementally from RTV560 to PICA-D under frame
- Carbon decrease from PICA-D to RTV560 with Si and O the reverse trend
- Iron only measured in RTV560
- No aluminum contamination from window



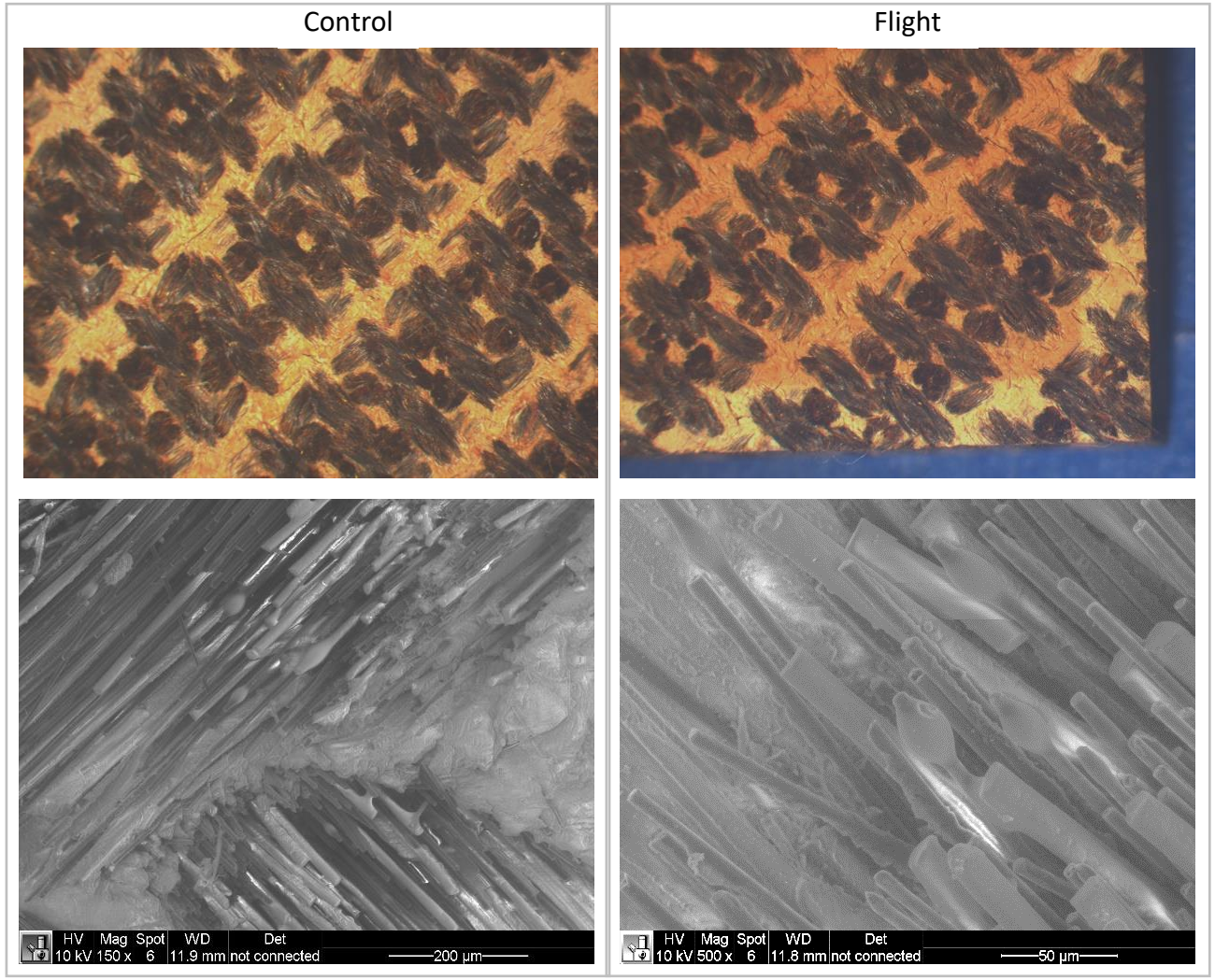
Seam PICA– RTV560

- Film more apparent in SEM
- Silica accumulation next to frame
- Low molecular weight silicone is most likely migrating species
  - Convert to silica film upon AO interaction
  - Is volatile silicone present everywhere or is AO/UV-C needed to generate?
- If red is iron, what species is mobile?



Coating HEEET–NuSil

- Nusil 1144-0 is a silicone coating designed to provide AO protection and be low outgassing
- Initial interest was dust control
- Qualitatively less overall darkening than non-coated samples
- Less AO pitting on fibers
- Droplets on some fibers indicative of less-than-ideal wetting or excess application
  - No droplets/excess on phenolic matrix



Implications for Missions and Heatshield Design

- Aerothermal performance of heatshield acreage material
  - Erosion from AO is small in comparison to heatshield thickness and design margins
  - No indication of macroscopic cracking to impact structural integrity
  - Through thickness thermal conductivity not likely affected by limited surface effects
  - NuSil coating retards erosion, however correct surface loading and aerothermal impact need to be considered
- Change in optical properties (darkening) for acreage materials could result in higher solar absorption
  - Might impact vehicle temperature in flight/orbit, especially if traveling closer to sun
  - Thermal control coatings exist but need to consider impact on aerothermal performance
- Tile seams
  - No clear loss of performance of RTV560 as a seam however not directly evaluated
  - Likely impact on optical and other surface properties from RTV560, though not always negative

Future Work

- Quantification of PICA-D erosion
  - Micro-CT to resolve relief in cross-section around sample frame for difference between fiber and phenolic matrix behavior
  - Beneath silica film adjacent RTV560 seam
- HEEET IL spectroscopy for solar absorbance
  - Multiple measurement statistics to capture weave size scale and orientation
  - Comparison with NuSil coated flight and control
- Mechanism for species migration from exposed RTV560
  - Formation and transport of volatile silicone and silica film (or other species)
  - If red portion is iron, what is migrating species?
  - Does NuSil behave similarly or, if not, would an overcoat protect from RTV560 migration?

Questions?

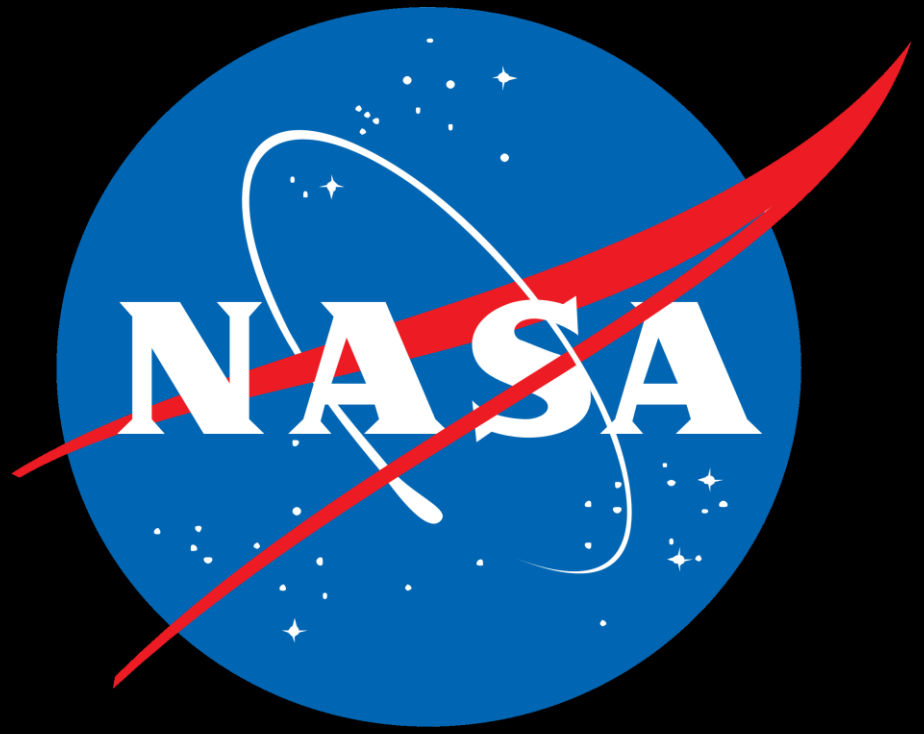
References & sources:

https://www1.grc.nasa.gov/space/iss-research/misse/

https://science.nasa.gov/technology/technology-highlights/protecting-future-planetary-missions-from-extreme-heat

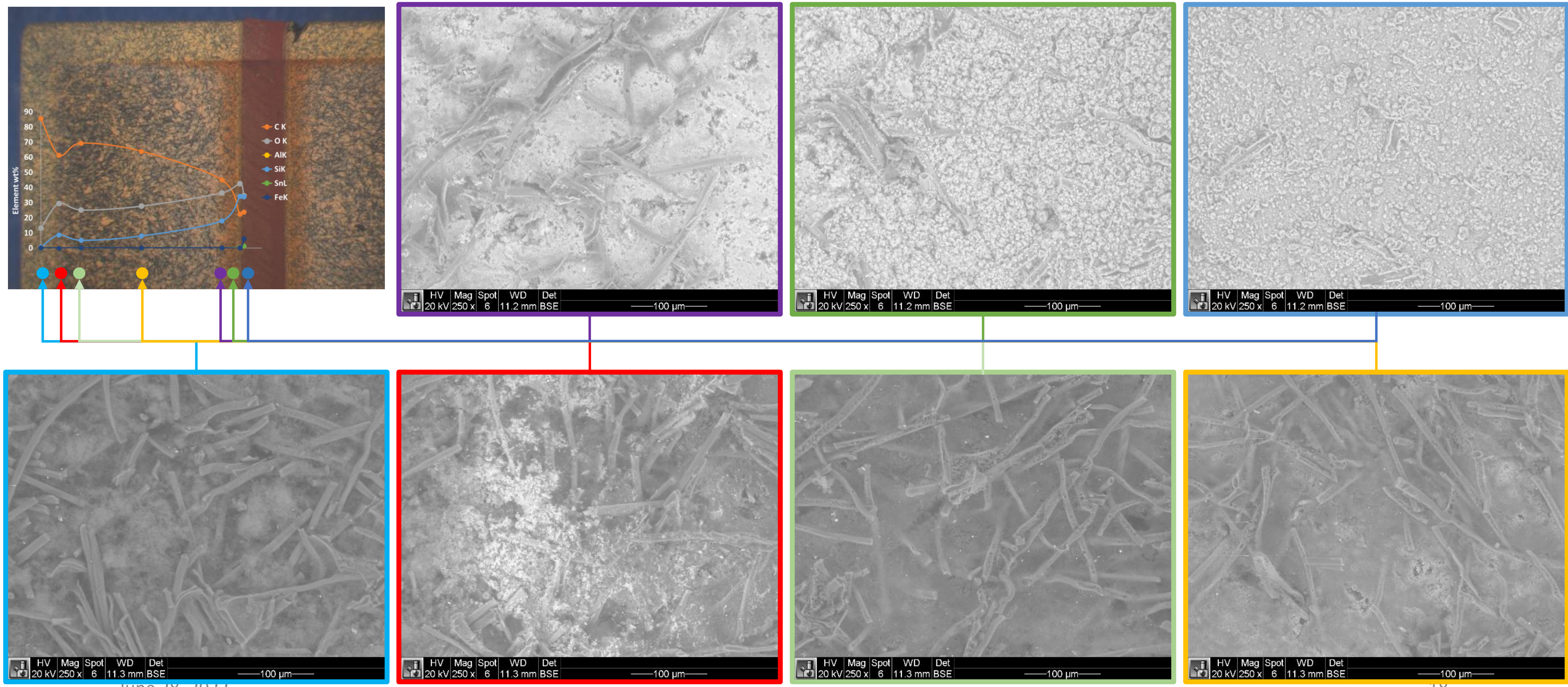
Ellerby, Don, and Ethiraj Venkatapathy. "Heatshield for Extreme Entry Environment Technology (HEEET): Development Status." New Frontiers Program Technology Workshop. No. ARC-E-DAA-TN30985. 2016.

National Aeronautics and Space Administration



Ames Research Center
Entry Systems and Technology Division

Seam PICA– RTV560



Coatings – AZ93

- AZ93 is a ZnO white pigment bonded with potassium silicate
  - Fully ceramic oxide system
- Slight darkening under frame
  - No Al detected by EDS
  - Likely in fact bleaching of exposed as appearance under the frame is similar to control
- Reflectance in UV-visible increased slightly on flight
- Fewer dark inclusions in flight than control
  - Could cause increased reflectance
  - Yet to be identified but organic contamination would be removed by AO
  - Possibly sourced from HEEET substrate
- Few cracks in flight surface which might be associated with damage from clamping in frame