Jet Propulsion Laboratory
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# Mars 2020 Return Sample Cleanliness Molecular Transport Model

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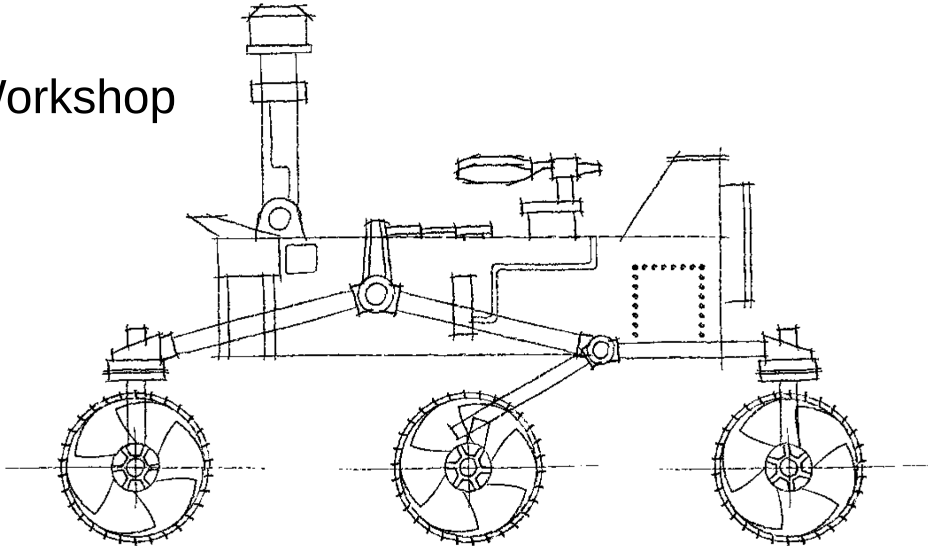
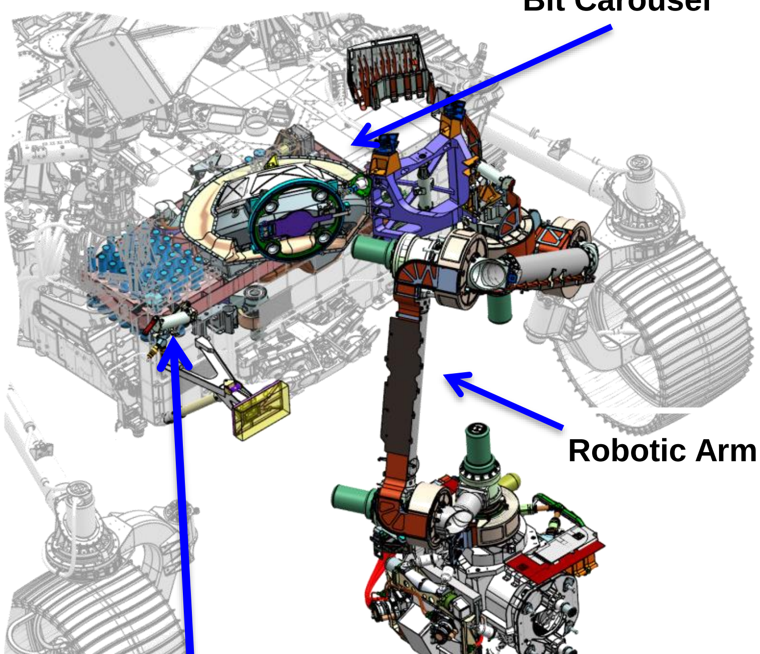


**Mars 2020** Project

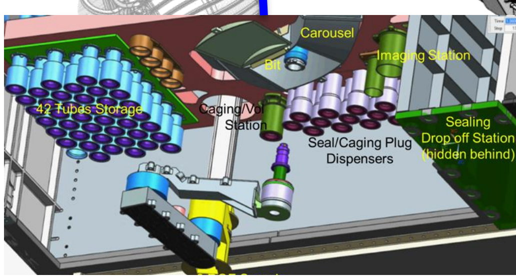
# Mars 2020 Mission has an Objective to Assemble Returnable Cached Samples for potential future Return to Earth



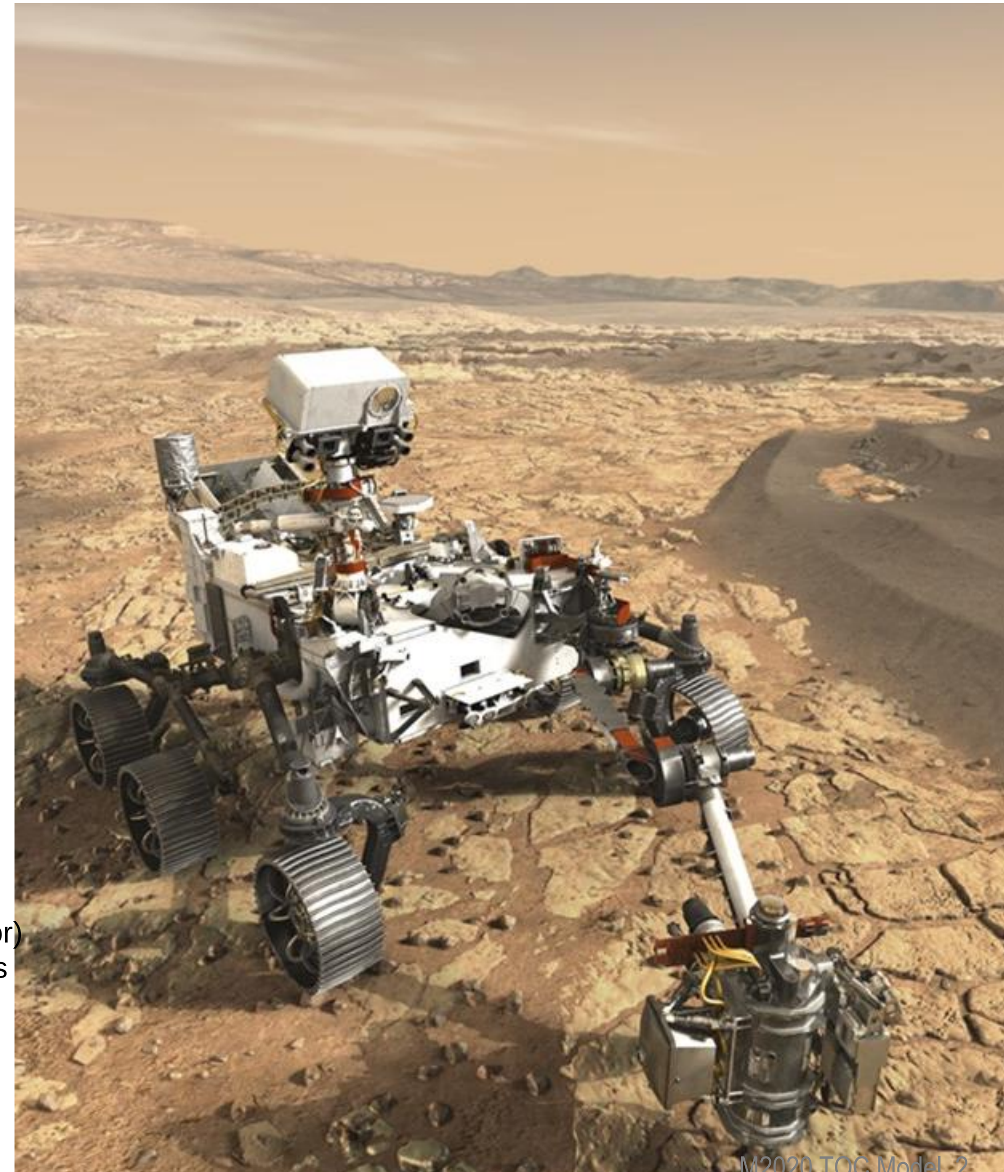
## Sample tubes are stored in the Adaptive Caching Assembly (ACA)




**Turret**
(Robotic Arm End Effector)
Corer & other instruments




**Adaptive Caching Assembly (ACA)**

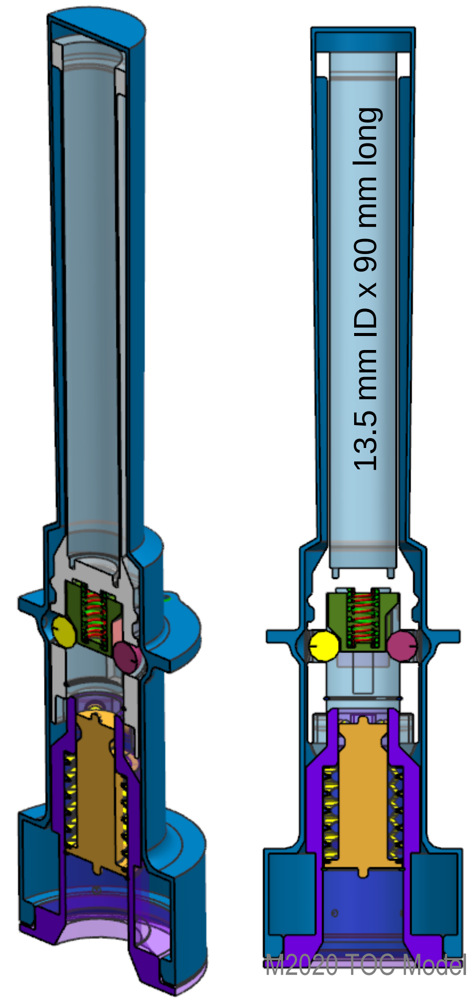


# Returnable Sample Cleanliness Requirement



- Mars 2020 Level 1 Requirement: For returned samples **less than 10 ppb total organic compounds** (TOC) and less than 1 ppb of any of a set of special organic compound known as "tier one" compounds
  – PPB estimates are made assuming a 15 g sample. For a 15 g sample, 10 PPB corresponds to a **Requirement = 150 ng per Sample Tube**
- Sample Tube interior and the Cap
  – Tube and cap sample contacting surface area ~50 $cm^2$. TOC surface density must be < 3 $ng/cm^2$
  – **TOC Requirement << Molecular Monolayer**
- Approach
  – Identify and model TOC sources
    - Materials in the ACA are the largest source of TOC
  – For each M2020 Mission phase, model TOC transport from sources to sample contacting surfaces (tube interior and cap below the seal)
  – Combine into an end-to-end model to evaluate TOC and sensitivity to assumptions

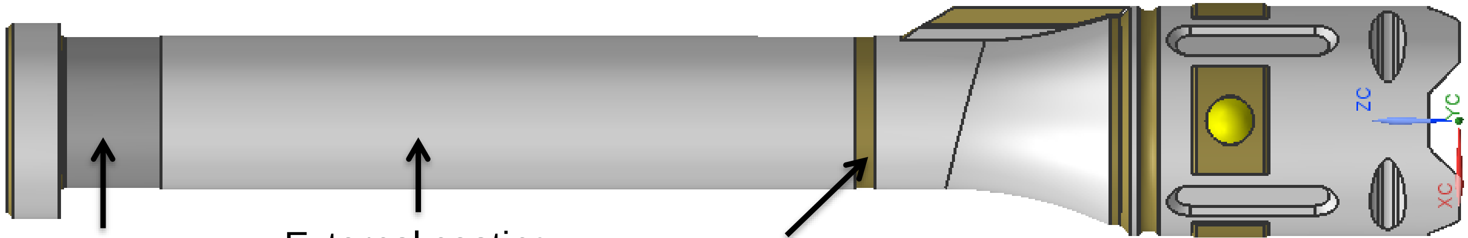
Sample Tube inside "Fluid Mechanical Particle Barrier"
**FMPB**



# Sample Tubes, Seals, Coring Bits



***Tube Exterior***
*(unsealed)*

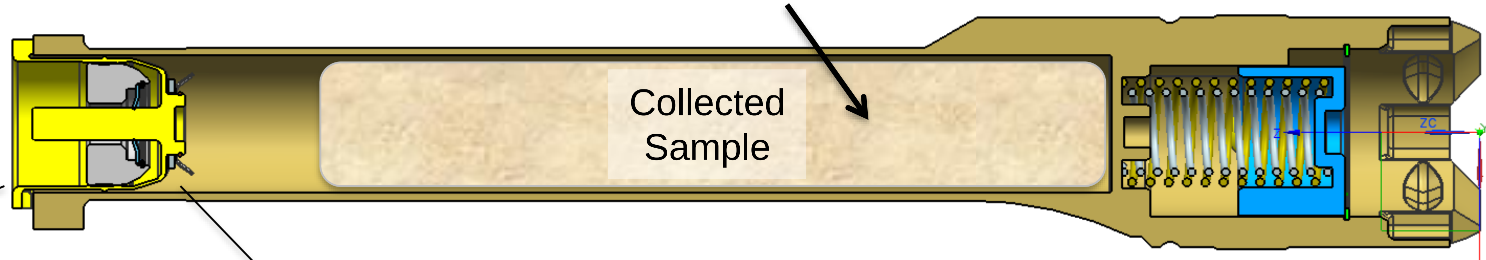


Bare Titanium

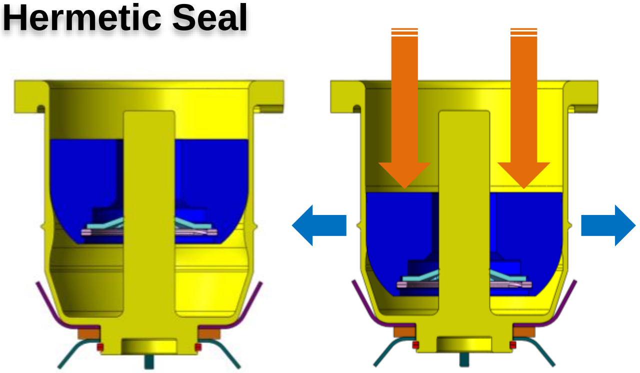
External coating
*(Alumina)*

Tube Body
*(Nitrided Ti-6Al-4V)*

***Tube Interior***
*(sealed)*



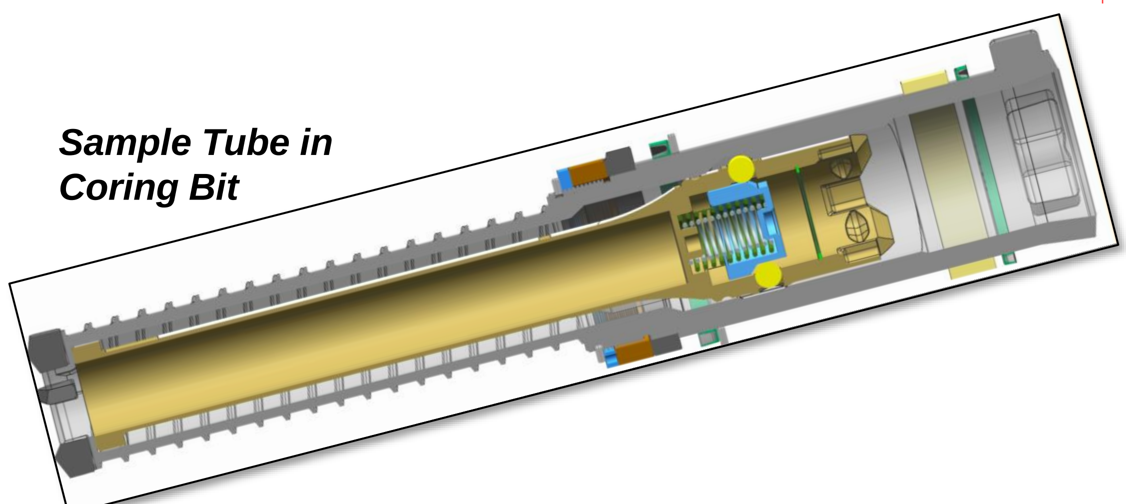

**Hermetic Seal**



Pre-Activation

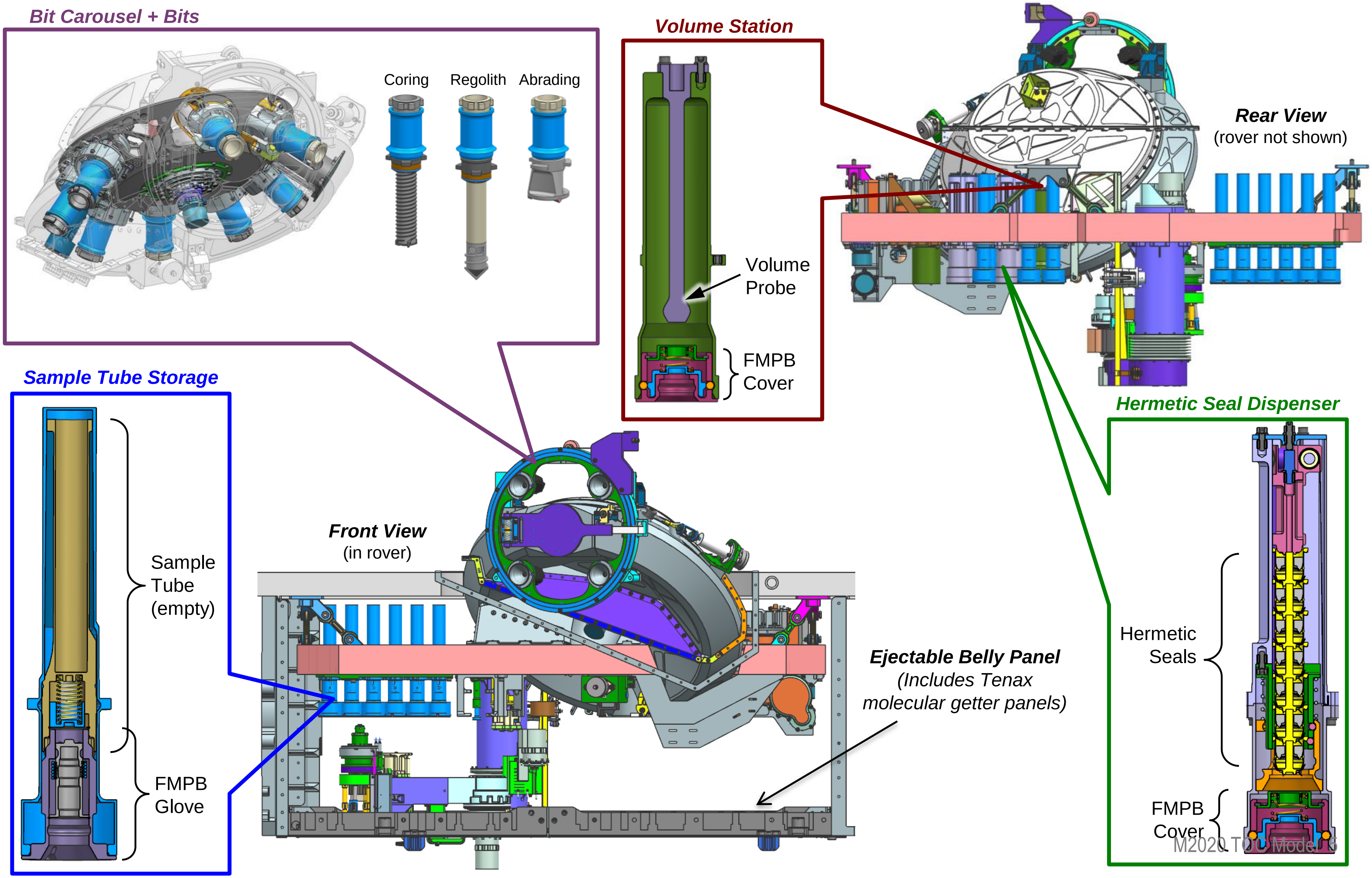
Post-Activation

***Sample Tube in Coring Bit***



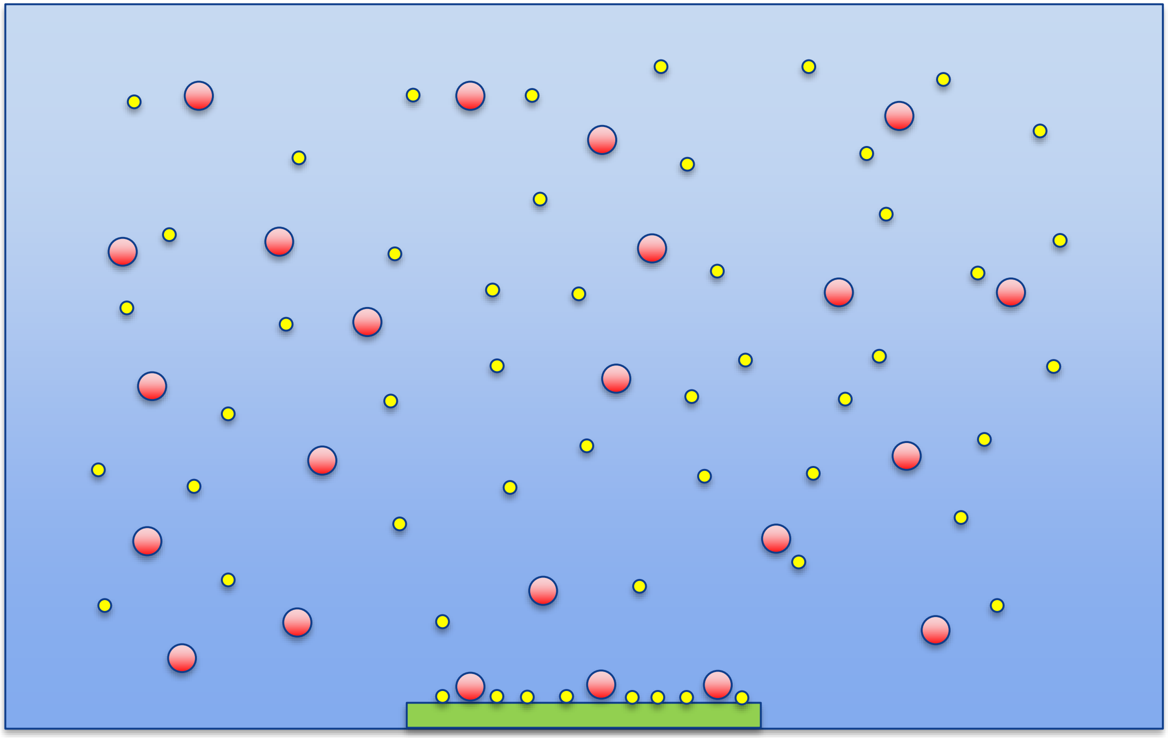
# Adaptive Caching Assembly (ACA) Hardware Details





# TOC Requirement Not Met Without Mitigation

- Large number of organic molecules in the environment
- Light molecules with hydroxyl and other polar groups can chemisorb on oxide surfaces (e.g. Ti, or Al)
- AC accumulation asymptotes in about a week to ~100 ng/cm$^2$ on a Ti-6Al-4V surface exposed in a clean room
- A Sample Tube would launch with ~ 50 x 100 = 5000 ng <u>TOC > 30X the requirement</u>

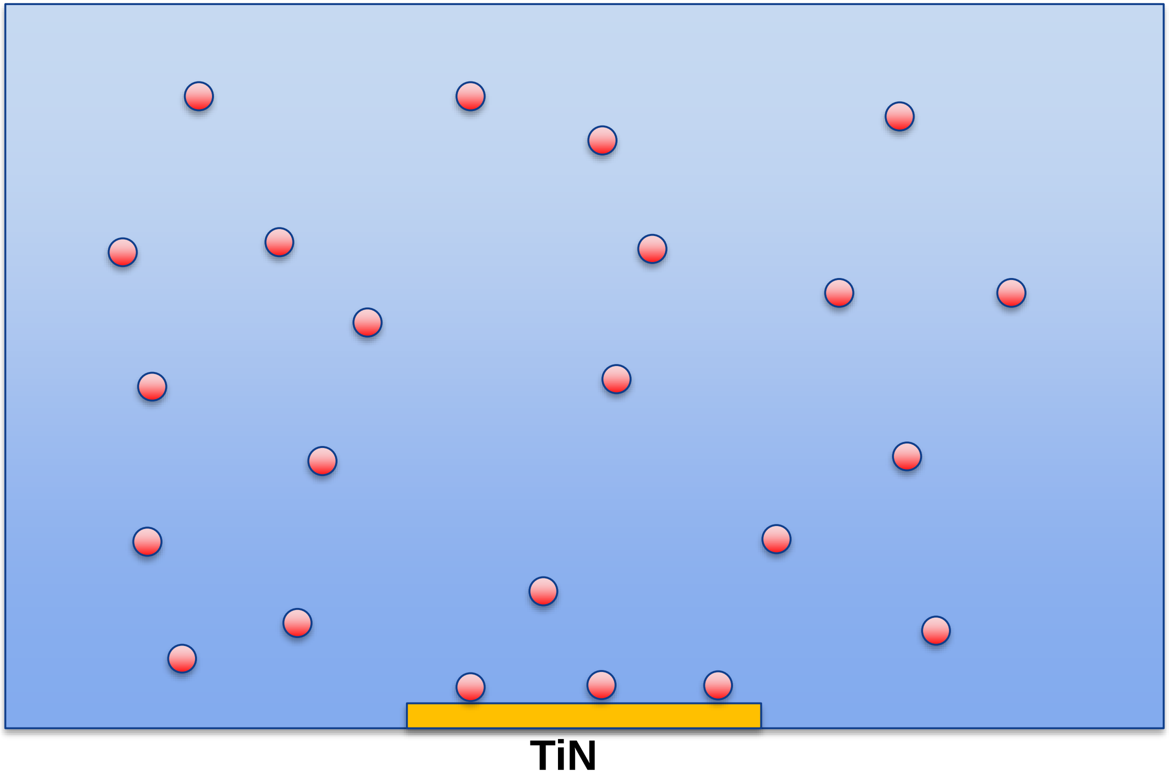


Ti-6Al-4V

# Mitigation #1: Stop Light Organic Molecules from Sticking using Titanium Nitride (TiN) Coating



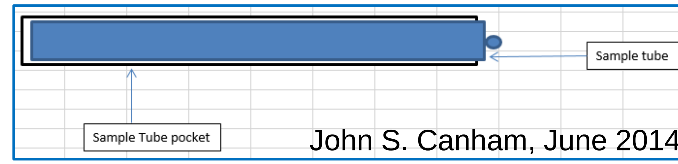
- TiN suggested by Prof. Francisco Zaera, UC Riverside
- Vapor pressure decreases exponentially with Molecular Weight → low concentration of large organic molecules (MW> 200 amu)
- Molecules can only physisorb on surfaces that are chemically inert (e.g. Au or TiN)
  - Residence time for low MW molecules is very short
- AC accumulation asymptotes in about a week to ~20 ng/cm$^2$ on a TiN surface
- A Sample Tube would launch with ~ 50 x 20 = 1000 ng TOC > 6X the requirement

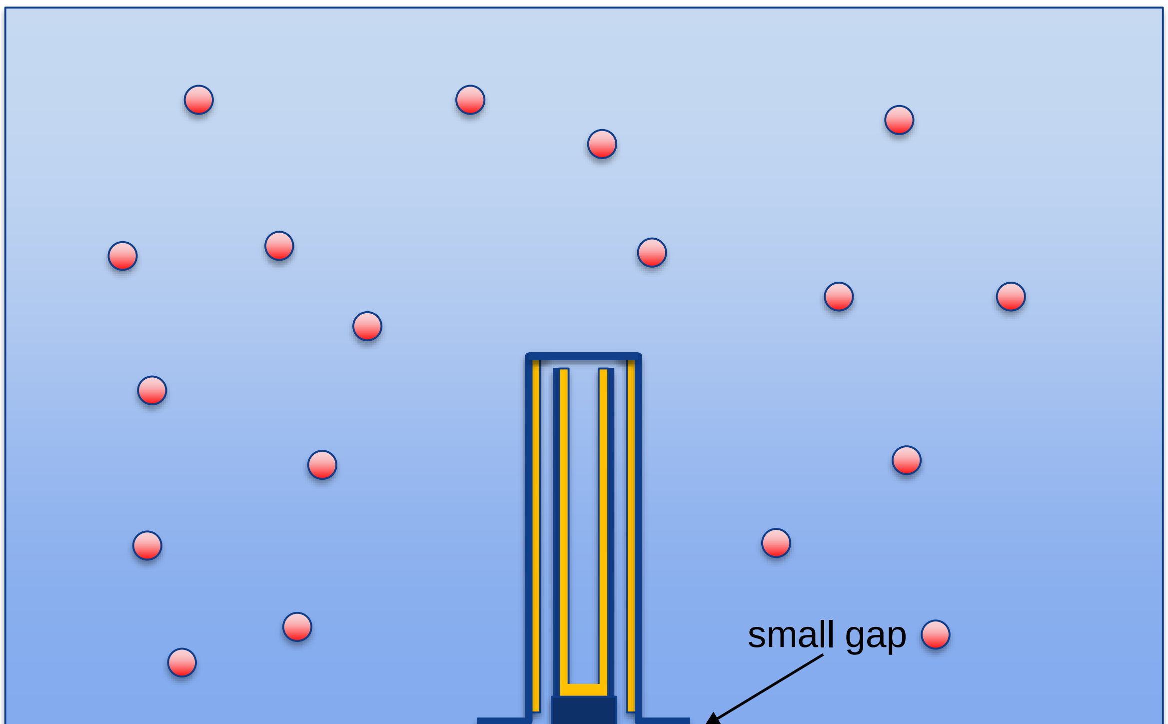


# Mitigation #2: Reduce AC Accumulation Rate with a Small Opening and a Torturous Path

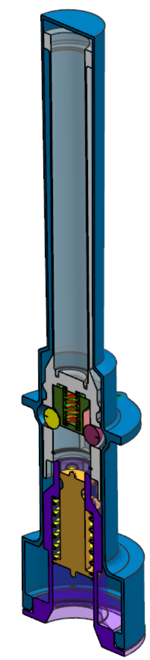


- Accumulation rate proportional to molecular flux reaching the interior surface of the sample tube
- Fluid Mechanical Particle Barrier (FMPB) reduces opening to <1% of the tube interior surface area
  - inspired by John Canham, “Contamination rate tube in pocket.xls”, June 2014
- FMPB sleeve provides another ~100 cm$^2$ to act as a “getter”




**FMPB**

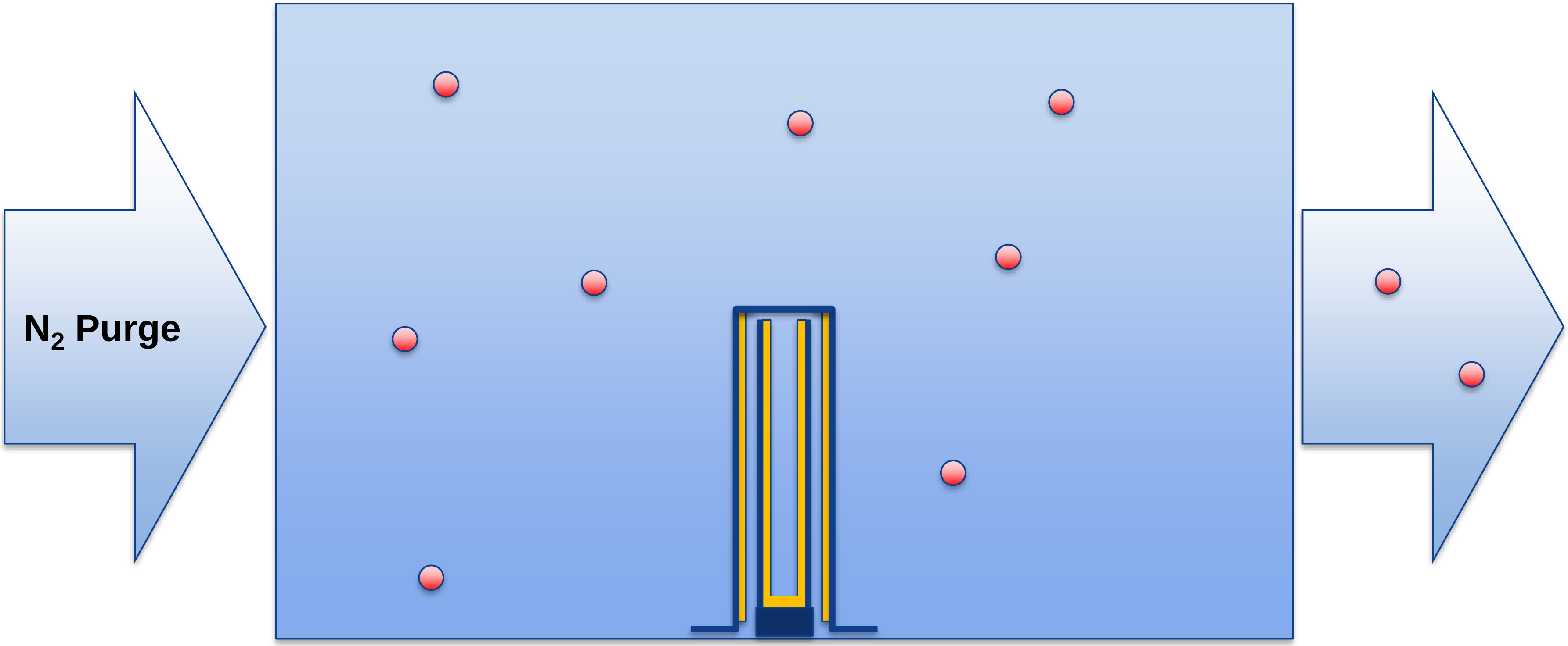


**FMPB**

# Mitigations #3 & #4: Minimize TOC Density with Low Outgassing Materials and Big TOC Sinks

- Accumulation rate proportional to molecular density near the gap at the bottom of the FMPB
- Sources: Low outgassing materials in the ACA
- Sinks: Purge in ATLO, Molecular Absorber during Cruise & Commissioning, Mars wind during Surface Operations

| Mission Phase | TOC Sink |
|---|---|
| ATLO | $N_2$ Purge |
| Cruise | Molecular Absorber |
| Commissioning | Molecular Absorber |
| Surface Operations | Advection & Diffusion |



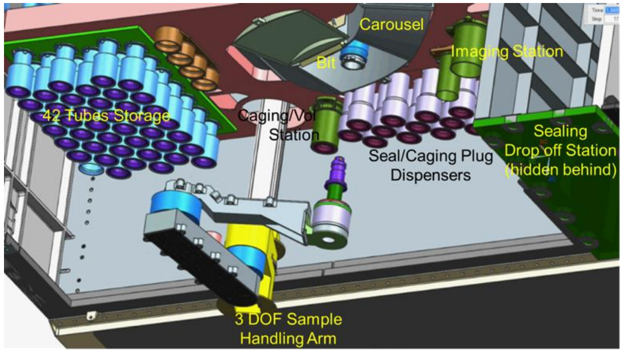

FMPB

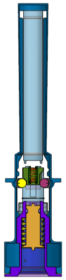
# TOC in Mars 2020 Sample Tubes: Basic Model



- Contamination
  - Sources
  - Transport
  - Sinks
- **Basic Model: Flux Balance**
  - <u>Density of TOC molecules in the ACA</u> near the FMPB flange is determined by a balance of the flux of outgassed molecules and those leaving the ACA or hitting the Molecular Absorber.
  - The flux into the FMPB is a tiny fraction of the total ACA outgassing

**ACA** (Adaptive Caching Assembly)



**FMPB**
into the gap and up to the top of the sample tube

**<u>Sources</u>**
ACA outgassing
Airborne in ATLO

**<u>Transport</u>**
Atmospheric Advection & Diffusion
Free Molecular during cruise

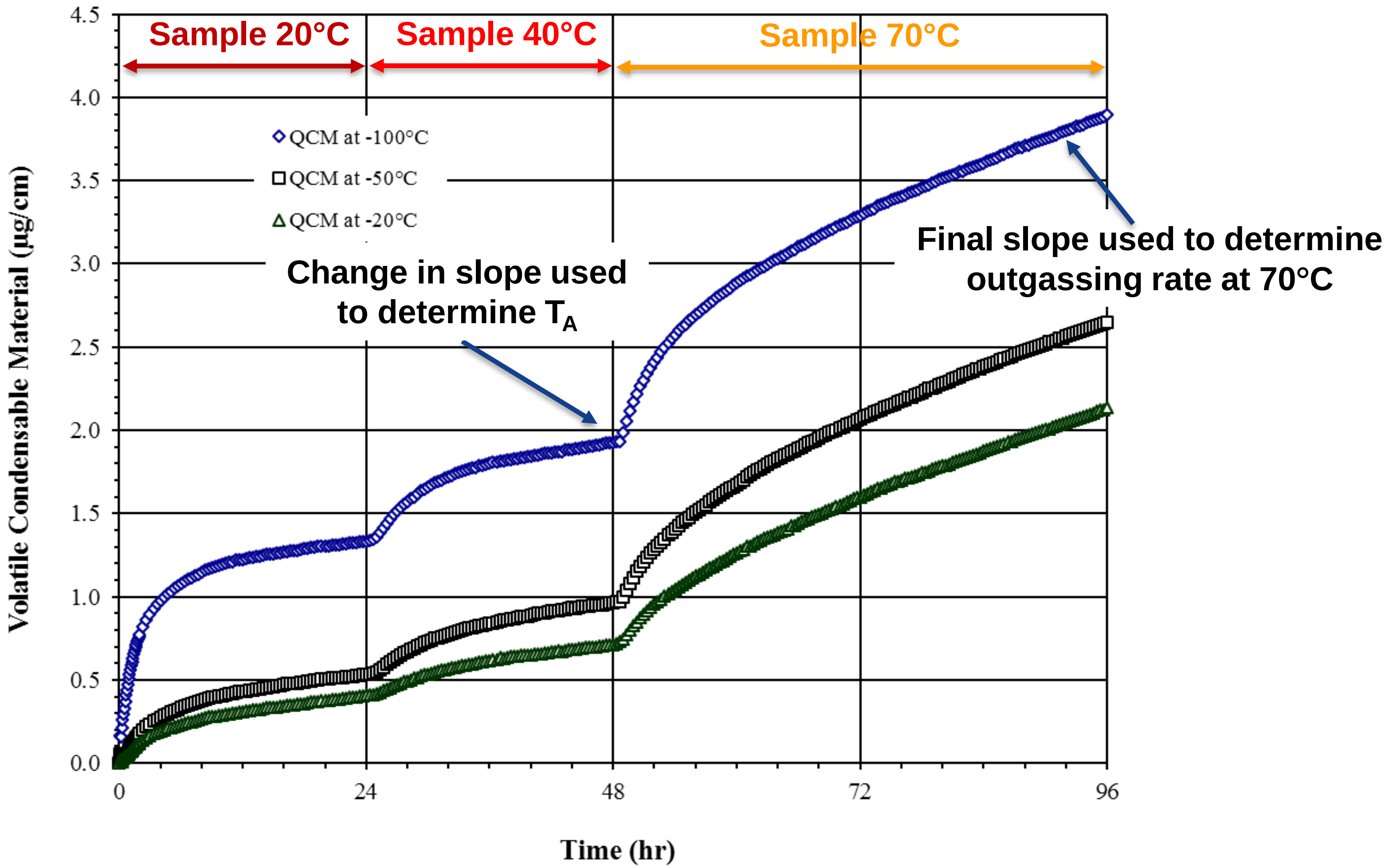
**<u>Sinks</u>**
Purge in ATLO
Molecular Absorber during cruise
Mars wind – surface Ops

$$\dot{m}_{TOC} = \rho_{TOC} \dot{V}$$

Sources

## Sample Data

External MAHLI Harness Cable at 20°C, 40°C, and 70°C.



# Outgassing Source Rates Used in TOC Analysis



**Sources**

- Rates derived from the -100°C QCM
  - Accumulation on QCM is much greater than a mono-layer
  - Only data that I have seen has binding energy of the second layer about 2/3 of the first (360 K vs 523 K)
  - Molecules that can form a monolayer on a 20°C (293 K) surface, can form multiple layers on a -70°C (203 K) surface
  - Suggests using outgassing rates derived from the -100°C QCM
- Outgassing inputs to end-to-end model

| QCM→ | | T -100°C | | T -50°C | | T -20°C | |
|---|---|---|---|---|---|---|---|
| **Materials** | **unit** | **Γ (70°C) (ng/unit/hr)** | **$T_A$(K)** | **Γ (70°C) (ng/unit/hr)** | **$T_A$(K)** | **Γ (70°C) (ng/unit/hr)** | **$T_A$(K)** |
| **Flex Cable** | **$cm^2$** | **5.4** | **12767** | **2.40** | **11554** | **1.8** | **13616** |
| **Round Wire Cable** | **$cm^2$** | **6.2** | **9246** | **5.7** | **8340** | **5.8** | **9838** |
| **Connectors** | **unit** | **257** | **9493** | **191** | **9770** | **113** | **8682** |
| **Motors** | **unit** | **14025** | **13697** | **14035** | **13417** | **13683** | **13890** |

- Outgassing Source Term in the end-to-end model

$$\dot{m}_{TOC} = \sum_{sources} A_i \Gamma_i(T)$$

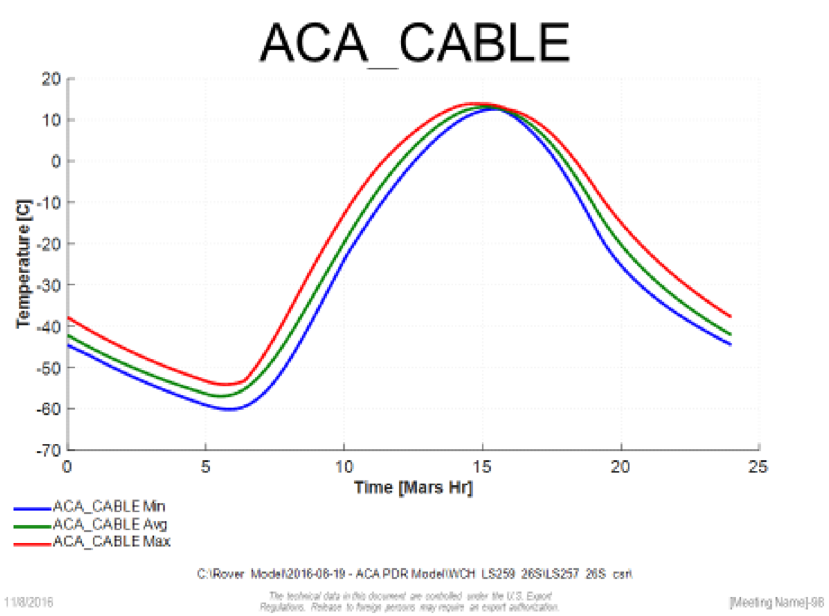
$$\Gamma(T) = \Gamma(T_0)\frac{\exp\left(-\frac{T_A}{T}\right)}{\exp\left(-\frac{T_A}{T_0}\right)}$$

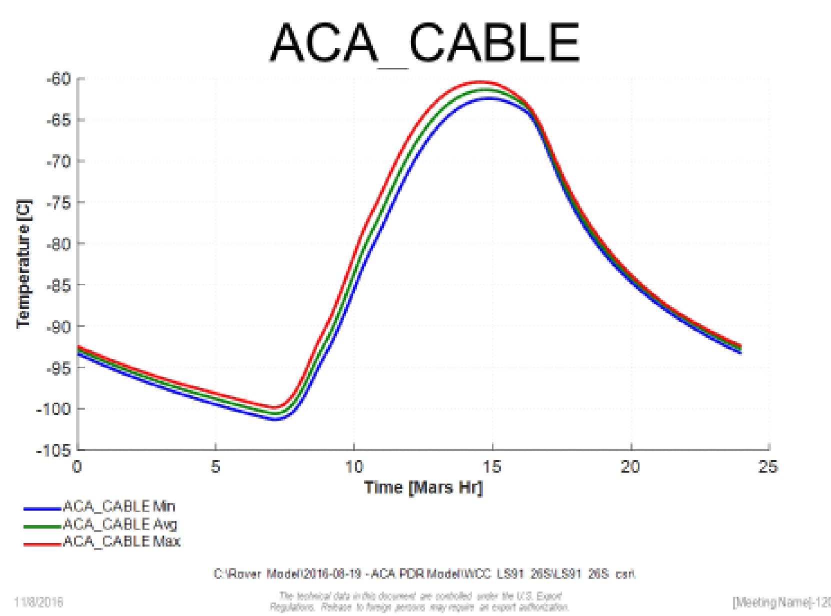
# ACA Temperatures: Surface of Mars

**Sources**

- Matt Redmond & Eddie Farias, “H_Section_CCMD and Sealing Station - 2016-09-06.pptx”
- Cables produce a large fraction of ACA outgassing
- Spreadsheet model adds +10°C for margin

| Case | WCH/BPoff | WCC/BPoff |
|---|---|---|
| T_max(°C) | 25 | -55 |
| T_min(°C) | -50 | -90 |



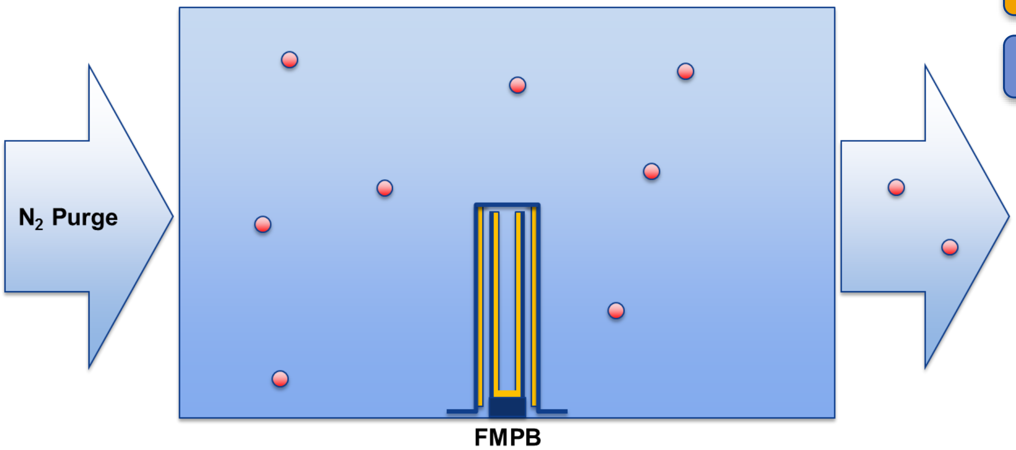
# Transport & Sinks by Mission Phase

Transport

Sinks

Density of TOC molecules in the ACA is determined by balancing the flux of outgassed molecules with those leaving the ACA

$$\rho_{TOC} = \frac{\dot{m}_{TOC}}{\dot{V}}$$




| Mission Phase | TOC Transport | TOC Sink | |
|---|---|---|---|
| ATLO | Advection/Diffusion | $N_2$ Purge | $\dot{V} = \dot{V}_{purge}$ |
| Cruise | Free Molecular | Molecular Absorber | $\dot{V} = \frac{\bar{c}}{4} A_{MA}$ |
| Commissioning | Diffusion | Molecular Absorber | $\dot{V} = u_{dif} A_{MA}, \quad u_{dif} \approx \frac{D_{Mars}}{\ell}, \quad \ell \approx 0.2\,m$ |
| Surface Ops | Advection/Diffusion | Mars Atmosphere | $\dot{V} = u_{wind}^{effective} A_{bellypan}, \quad u_{wind}^{effective} \approx 0.02\,u_{wind}$ |

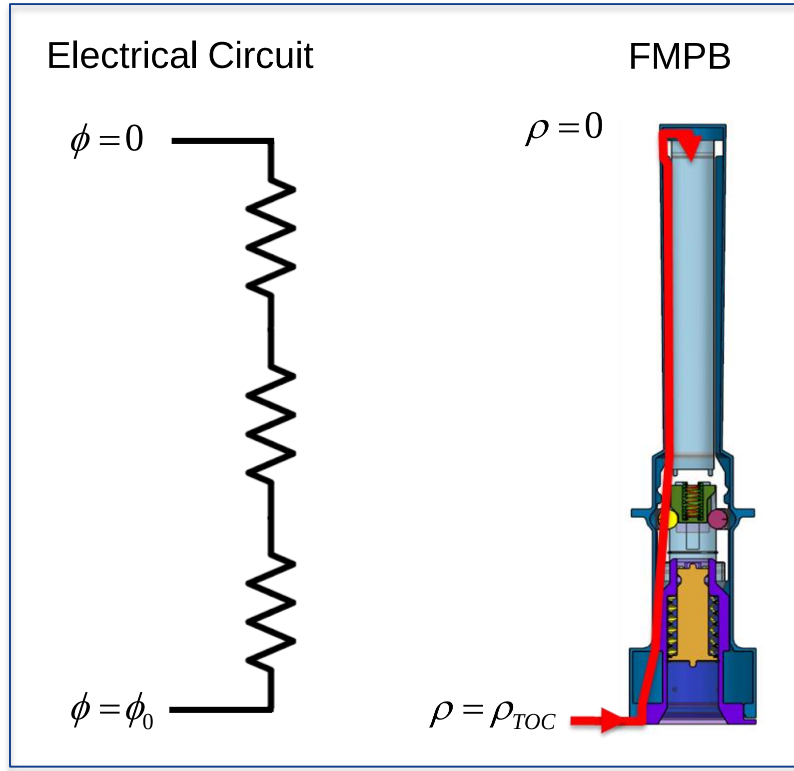
# TOC into the FMPB: Flow Resistances Add



Transport

- Ohm's Law is a diffusion equation
- Torturous path modeled as a series of flow resistances

| | Ohm's Law | Mass Diffusion |
|---|---|---|
| basic equation | $j = \sigma \nabla \phi$ | $j = D \nabla \rho$ |
| | $\nabla \phi = \eta\, j$ | $\nabla \rho = \frac{1}{D} j$ |
| | $\Delta \phi = R\, I$ | $\Delta \rho = R\, J$ |
| series resistance | $\phi = I \sum R$ | $\Delta \rho = J \sum R$ |
| circuit current | $I = \frac{\phi}{\sum R}$ | $J = \frac{\rho}{\sum R}$ |



# Diffusion Rate into the Sample Tube

- Mass diffusion equation

  $j = D\nabla\rho$ where *j* is the mass flow density

- Mass flow through a single gap

  (assuming nothing sticks to the walls)

  $J = 2\pi\, r\, h\, D\dfrac{\Delta\rho}{L}$ where r is the tube radius, h the gap height, and L the gap length

- Flow resistance, η, through a gap is

  $\Delta\rho = \eta\, J$

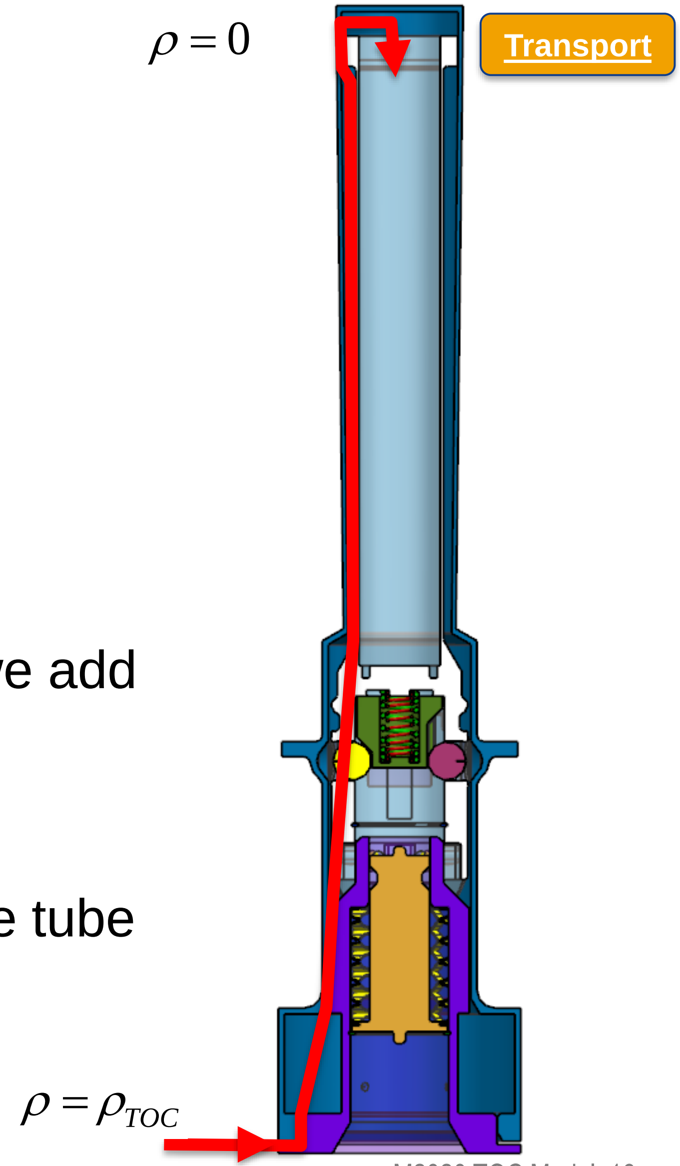
  $\eta \equiv \dfrac{L}{2\pi\, r\, h}\dfrac{1}{D}$

- Since the FMPB has multiple gaps in series, we add the flow resistances

  $\eta_{FMPB} \equiv \dfrac{1}{D}\sum_i \dfrac{L_i}{2\pi\, r_i\, h_i} = \dfrac{1}{D} R_{FMPB}$ $R_{FMPB} \equiv \sum_i \dfrac{L_i}{2\pi\, r_i\, h_i}$

- The mass flow rate to the interior of the sample tube

$$J_{FMPB} \equiv \frac{\rho_{TOC}}{\eta_{FMPB}} = \frac{D}{R_{FMPB}}\rho_{TOC}$$



# Data and Analysis Combined in the M2020 TOC End to End Spreadsheet



- Values and formulas in the spreadsheet are described in this presentation
- Light blue cells are Inputs, e.g. **purge** | **1.0** | liter/s
- Buttons perform calculations, e.g. **Cruise**

**Mission TOC Past FMPB Inside Tube**

| Phase | FMPB | FMPB_2 | |
|---|---|---|---|
| Cleaning | 4 | 0.5 | ng |
| ATLO | 7 | 13 | ng |
| Cruise | 1 | 1 | ng |
| Commission | 2 | 4 | ng |
| Surface Ops | 8 | 15 | ng |
| Total | 22 | 34 | ng |

| | | |
|---|---|---|
| Open Tube WCH | 2.58 | ng/sol |
| Volume Probe | 5 | ng |

**Mission Duration Inputs**

| Phase | Duration | |
|---|---|---|
| ATLO | 90 | days |
| Cruise | 217 | days |
| Commission | 30 | sols |
| Surface Ops | 1000 | sols |
| Total | 1363 | days |

**Mission Parameter Inputs**

| | | |
|---|---|---|
| u_wind | 0.10 | m/s |
| purge | 1.0 | liter/s |
| Initial_Clean | 0.1 | ng/cm2 |
| A_MA | 0.10 | m2 |
| A_BP | 0.36 | m2 |
| Diff_Mars | 6.00E-04 | m2/s |
| Diff_Earth | 5.00E-06 | m2/s |
| Diff_Dist | 0.2 | m |

| | | |
|---|---|---|
| purge | 0.17 | lb/min |

**Past FMPB**

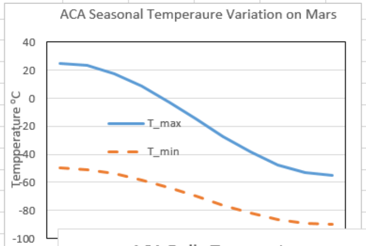
| | |
|---|---|
| Diffusion | 26 |
| Cruise | 1 |
| Past FMPB Total | 27 |

| Case -> | WCH/BPon | WCH/BPoff | CBE/BPon | WCC/BPoff | ATLO |
|---|---|---|---|---|---|
| T_max °C | -10 | 25 | -20 | -55 | 20 |
| T_min °C | -50 | -50 | -60 | -90 | 20 |
| Outgassing (ng/sol) | 1.83E+02 | 7.53E+03 | 4.94E+01 | 2.40E-01 | 2.15E+04 |
| BP on / Purge on (T/F) | T | F | T | F | T |
| rho_TOC (wind 0.100 m/s) | 6.88E+00 | 2.29E+00 | 1.86E+00 | 7.31E-05 | 2.43E+02 |
| FMPB Diffusion (ng/sol) | 2.61E-01 | 8.68E-02 | 7.04E-02 | 2.77E-06 | 7.48E-02 |
| FMPB_2 Diffusion (ng/sol) | 4.91E-01 | 1.64E-01 | 1.33E-01 | 5.22E-06 | 1.41E-01 |
| Open Tube (ng/sol) | | 2.58E+00 | | 8.24E-05 | |

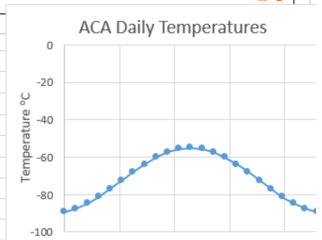
**Surface Sol** **Surface Operations**

| | Mission | WCH | WCC |
|---|---|---|---|
| Mars Years | 1.50 | 25 | -55 |
| sols/year | 668 | -50 | -90 |
| Outgassing (ng) | 7.04E+05 | | |
| Mission TOC (wind 0.100 m/s | 2.14E+02 | | |
| FMPB Diffusion (ng) | 8.1 | | |
| FMPB_2 Diffusion (ng) | 15.3 | | |

| Average | | |
|---|---|---|
| 7.04E+02 | | |
| Daily (ng/s | T_max | T_min |
| 7.53E+03 | 25.0 | -50.0 |
| 6.12E+03 | 23.0 | -51.0 |
| 3.34E+03 | 17.4 | -53.8 |
| 1.27E+03 | 8.5 | -58.2 |
| 3.58E+02 | -2.6 | -63.8 |
| 8.03E+01 | -15.0 | -70.0 |
| 1.59E+01 | -27.4 | -76.2 |
| 3.26E+00 | -38.5 | -81.8 |
| 8.39E-01 | -47.4 | -86.2 |
| 3.33E-01 | -53.0 | -89.0 |
| 2.40E-01 | -55.0 | -90.0 |



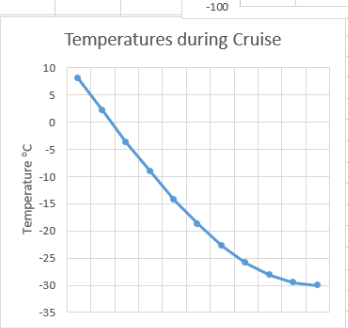

| ACA_Outgassing Rate | 3.33E-05 | ng/hr | | | T_ACA | -90.0 | | | |
|---|---|---|---|---|---|---|---|---|---|
| Materials | unit | Data (ng/un | T(data) | T_E | units/ACA | T_ACA | Flux(ng/unit/hr) | Flux (ng/hr) | source |
| Flex Cable | cm2 | 5.4 | 70 | 12767 | 3696 | -90.0 | 3.94E-14 | 1.45E-10 | data |
| Round Wire Cable | cm2 | 6.2 | 70 | 9246 | 3391 | -90.0 | 3.63E-10 | 1.23E-06 | data |
| Connectors | unit | 257 | 70 | 9493 | 20 | -90.0 | 7.95E-09 | 1.59E-07 | data |
| Motors | unit | 14025 | 70 | 13697 | 7 | -90.0 | 9.63E-12 | 6.74E-11 | data |
| Camera | cm2 | 10 | 70 | 9000 | 457 | -90.0 | 1.09E-09 | 4.97E-07 | estimated |
| Other | cm2 | 1.00 | 50 | 8000 | 5321 | -90.0 | 5.90E-09 | 3.14E-05 | estimated |
| | | | | | | -90.0 | 0.00E+00 | 0.00E+00 | |




| | | |
|---|---|---|
| t_Cruise | 5208 | hr |
| Outgassing (ng) | 1.90E+05 | ng |
| T_CruiseMax | 8 | °C |
| T_CruiseMin | -30 | °C |
| Total per FMPB | 0.96 | ng |
| Total per FMPB_2 | 1.44 | ng |

**Cruise**

| T Cruise°c |
|---|
| 8.0 |
| 2.1 |
| -3.7 |
| -9.3 |
| -14.3 |
| -18.9 |
| -22.7 |
| -25.9 |
| -28.1 |
| -29.5 |
| -30.0 |




| ACA Temperature | | | | | |
|---|---|---|---|---|---|
| T_max | -55.0 | | VProbeArea | 5 | cm2 |
| T_min | -90.0 | | VProbeConta | 20 | ng/cm2 |
| n_time | 24 | | VProbeTrans | 5% | |
| hrs_per_sol | 24.617 | hrs | A_Flange | 4.52E-05 | m2 |
| s_per_sol | 8.86E+04 | | uDiffEarth | 2.50E-05 | m/s |
| s_per_day | 8.64E+04 | | uDiffBP | 3.00E-03 | m/s |
| | | | ng_to_kg | 1.00E+12 | |

| Tube_Interior | 40 | cm2 | Tube_ID | 13.5 | mm |
|---|---|---|---|---|---|
| R_FMPB | 1.40E+03 | 1/m | R_FMPB_X | 9.12E+02 | |
| J_FMPB | 5.07E-06 | | J_FMPB_X | 5.41E-06 | |
| FMPB rate | 1.69E-10 | ng/hr | | | |
| Total Cruise per FMPB | 8.79E-07 | ng | Total Cruise per FMPB_X | 1.03E+00 | ng |

**Sample Tube FMPB Dimensions**

| Gap | r | h | L | L/(r*h^2) | Resistance (1/m) |
|---|---|---|---|---|---|
| Flange | 18 | 0.4 | 4 | 1.4 | 88 |
| A | 16 | 0.1 | 2.5 | 15.6 | 249 |
| B | 15 | 8 | 16.4 | 0.0 | 22 |
| C | 23 | 0.25 | 20 | 13.9 | 554 |
| Long | 15 | 2.5 | 100 | 1.1 | 424 |
| Top | 15 | 0.4 | 2.5 | 1.0 | 66 |

# Backup

# TiN Chosen for Sample Tube Surfaces Because it Accumulates Low Levels of AC



- TiN suggested by Prof. Zaera
- TiN collects much less TOC than other surfaces
- A small percentage of organic molecules in the air stick to TiN
- Asymptotic accumulation much lower on good TiN surfaces
- TiN will oxidize at high temperatures
  - Tests on TiN showed coating failed after heating to 500°C
  - Peer reviewed literature (from Zaera) and shows TiN oxidizes at 500 °C but should be stable at 350°C

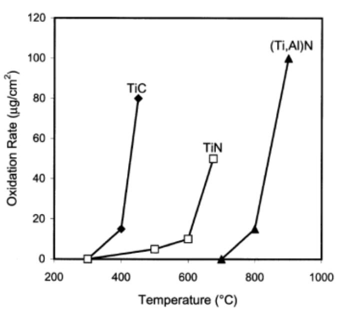



Fig. 12. Oxidation rate of hard coatings in step stress tests [51].

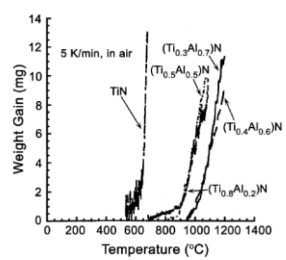
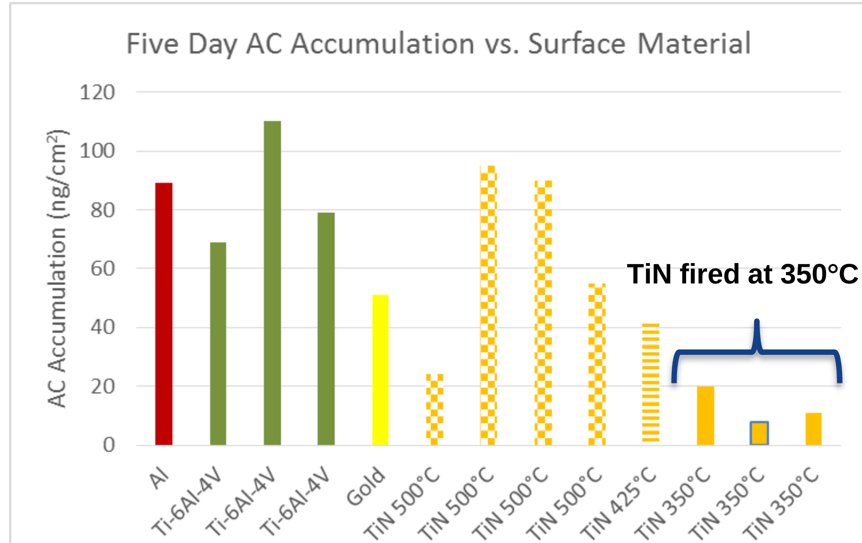



Fig. 13. Oxidation curves as a function of the Al concentration in the $(Ti_{1-x}Al_x)N$ films [29].

PalDey & Deevi, "Single layer and multilayer wear resistant coatings of (Ti,Al)N: a review", Materials Science and Engineering A342 (2003) 58-79




Mark Anderson, "Tube_TiN_Status_3-29-16.xlsx, Mark Anderson, "Adventitious Carbon Accumulation on TiN –AHT May 16, 2016 Batch", 6/7/2016