Outgassing Contaminant Species Extraction, Characterization and Modeling

John M. Alred, Maxwell G. Martin, William A. Hoey, Carlos E. Soares

1 Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, U.S.A.

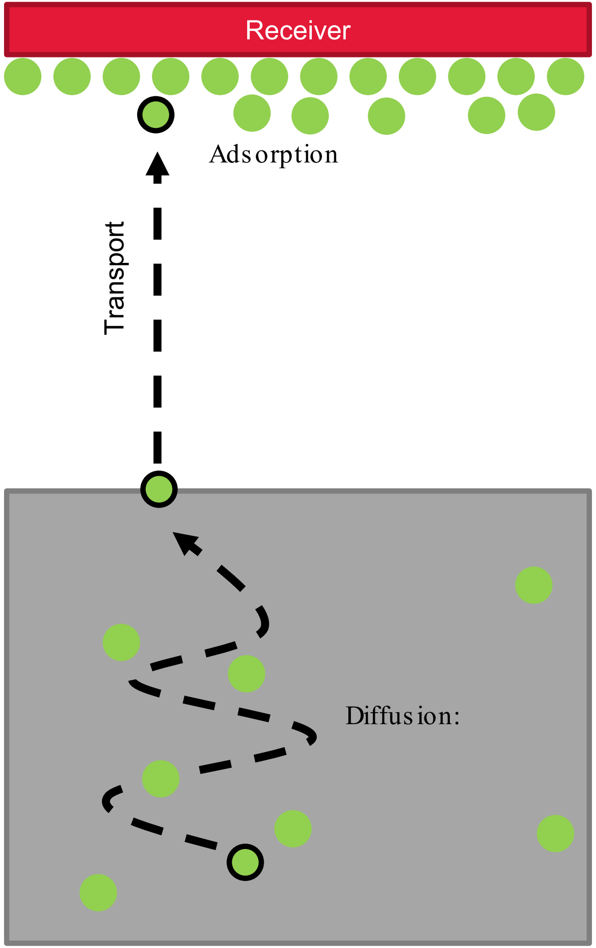
Jet Propulsion Laboratory
California Institute of Technology

Introduction

- Current and future concept space exploration missions seek to determine past and present capability to support life and presence of life outside of Earth
- Knowledge of molecular constituents outgassed from spacecraft is needed to analyze the probability of a mission to meet its science objectives
- Outgassing analysis methods are needed to further current predictive capabilities
- JPL and collaborators are currently working on the development of multispecies formulations for materials outgassing to allow more accurate extrapolation to mission conditions.

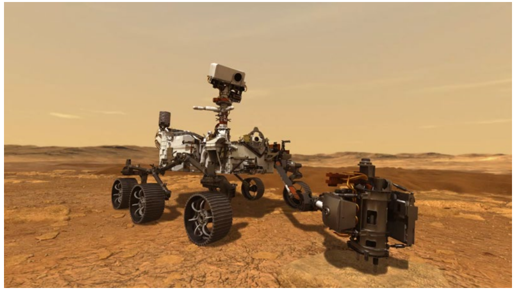
Outgassing

- Outgassing is the spontaneous evolution of atoms or molecules from a material
- Outgassing contamination is governed by several processes
  1. Diffusion of contaminant through the source material
  2. Viable Transport Mechanism
  3. Adsorption to the receiver material
  - 1,2,4 All of these physical processes have an exponential, Arrhenius, dependence on temperature
- Transport depends on environment (vacuum/continuum) and geometry
  - Continuum: Diffusion/Convection transport
  - Rarefied: Intermediate Knudsen number
  - Vacuum: Ballistic (line of sight) transport



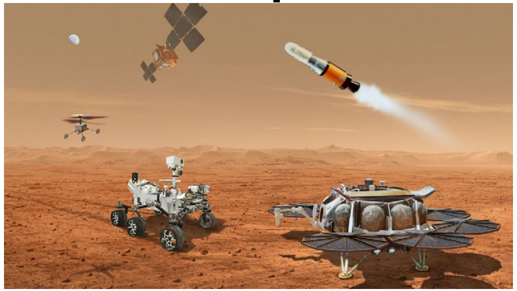
Outgassing Sensitivities Examples

Mars 2020



- Sampling Mars with objectives to detect organic signatures
- Outgassing contaminants condensing within sample tubes could jeopardize detection

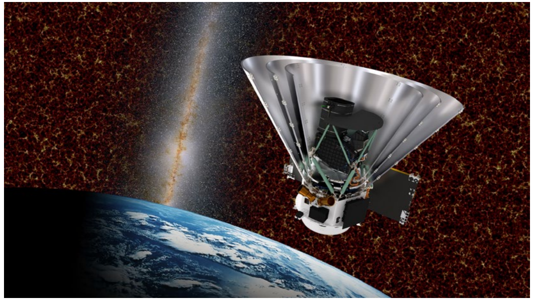
Mars Sample Return



- Returning sample tubes intended to detect organic signatures
- Outgassing contaminants leaking through sealed tubes could jeopardize scientific objectives

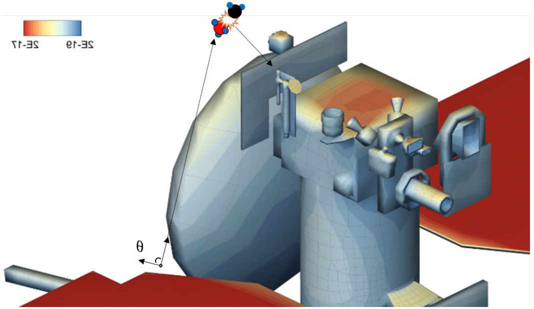
Outgassing must be characterized and quantified over the mission to guarantee scientific objectives

SPHEREx



- Scientific objectives to image biogenic molecules in the universe
- Water outgassing condensing in telescope causes severe attenuation of throughput

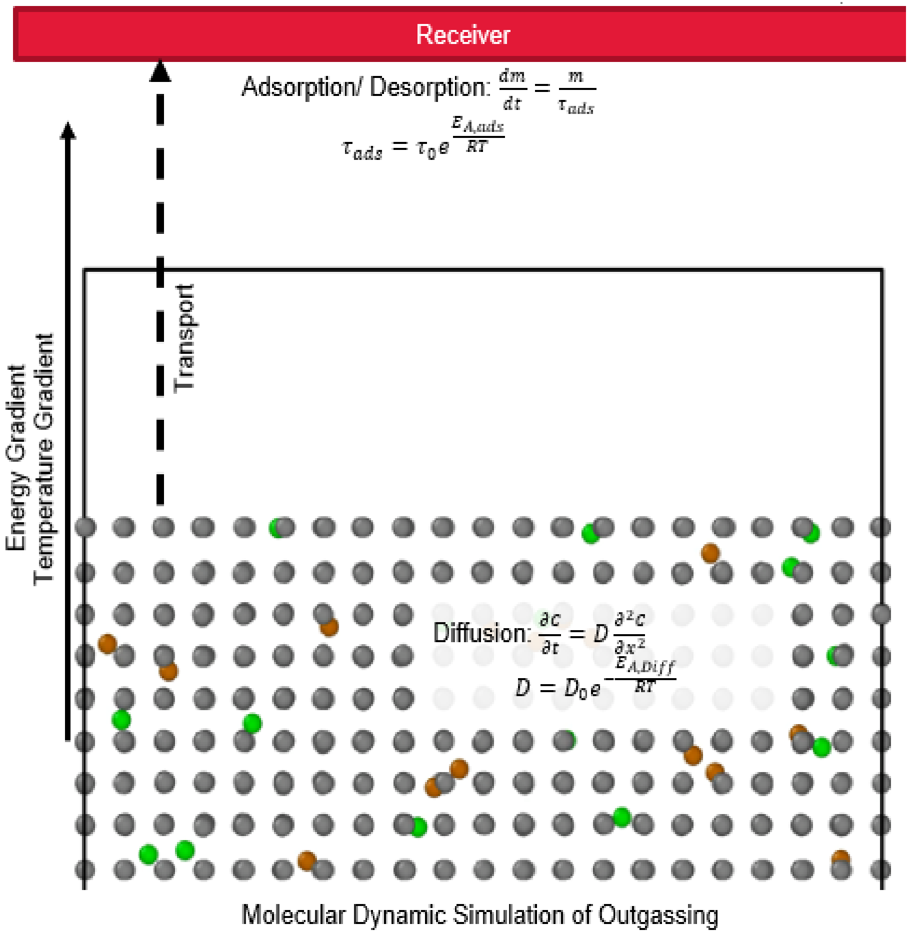
Europa Clipper



- Mass spectrometer instrument with objectives to sample Europa's atmosphere
- Outgassing contaminants reflected off atmosphere induce spurious mass spectra

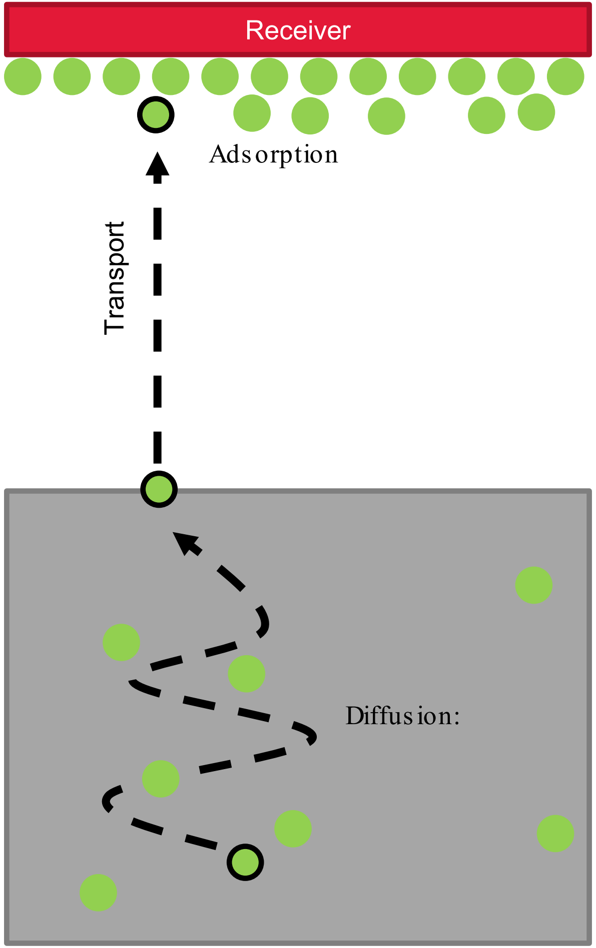
Outgassing Kinetics

- Diffusion: $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$
  - Diffusion coefficient: $D = D_0 e^{-\frac{E_{a,diff}}{RT_{source}}}$
  - Initial Concentration: C_0
- Desorption/Adsorption: $\frac{dm}{dt} = \frac{m}{\tau}$
  - Residence time: $\tau_{ads} = \tau_0\, e^{-\frac{E_{a,ads}}{R\,T_{reciever}}}$
- Variables in red are the kinetic contaminant parameters which characterize a contaminant species outgassing behavior
  - Per contaminant species: $\{C_0, D_0, E_{a,diff}, \tau_0, E_{a,ads}\}$
  - In this model desorption from source material is not considered



Outgassing Metrics tracked in MIUL

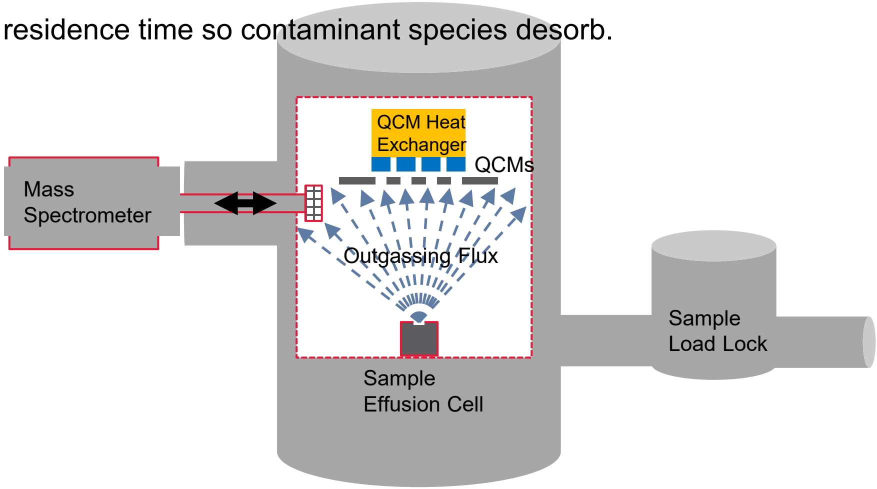
- ASTM E595 Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment
- Sample is outgassed at 125C for 24 hours
- Percent total mass loss (%TML)
  - Screening criteria <1.0%
  - Measured by mass loss of sample
- Percent collected volatile condensable materials (%CVCM)
  - Screening criteria for vacuum stable is <0.1%
  - Measured by condensation of contamination on QCM at +25C
- *Very* limited transferability of information.
  - Sample temperature is not representative of many missions
  - Measurement of %TML is often not useful for many missions. Many contaminants are not relevant
  - Temperature of QCM for %CVCM is not representative for many missions. Colder temperatures condense outgassing more readily



Detailed Outgassing Testing

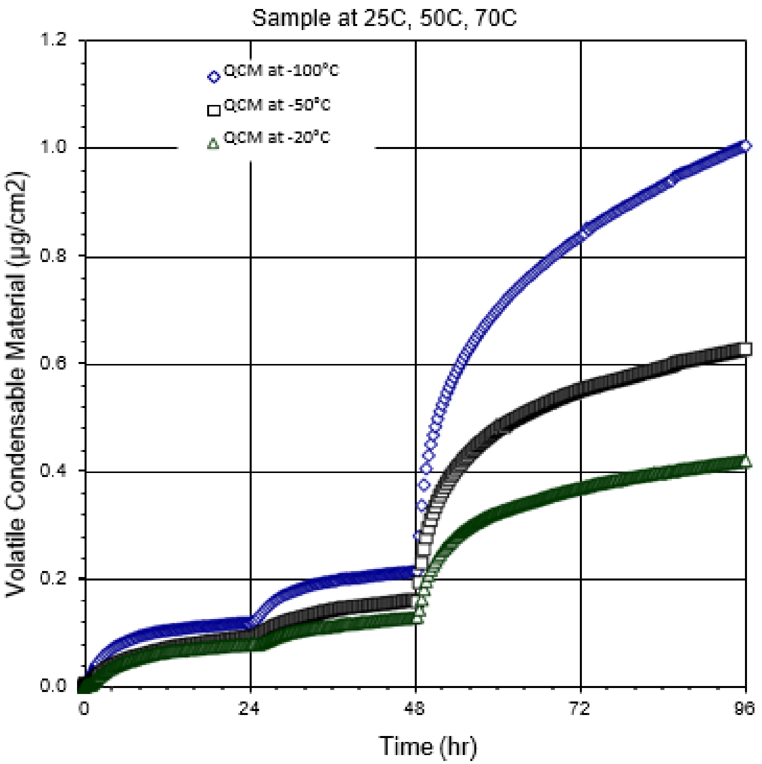
- ASTM E1559: Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials
  - More comprehensive test to study outgassing.
- Outgassing materials testing is typically performed in specialized vacuum chambers designed for precise measurements of outgassing.
- Typically two test exercises to characterize outgassing kinetics
  1. Outgassing:
     - Sample is held at constant temperature or predefined temperature steps. Controls diffusion of outgassing out of sample material
     - Multiple QCMs at different temperatures measure outgassing collection over time. Controls residence time on different QCMs
  2. Reemission / QCM Thermo Gravimetric Analysis (QTGA):
     - QCM temperature is slowly raised (1C/min). Slowly changes residence time so contaminant species desorb.

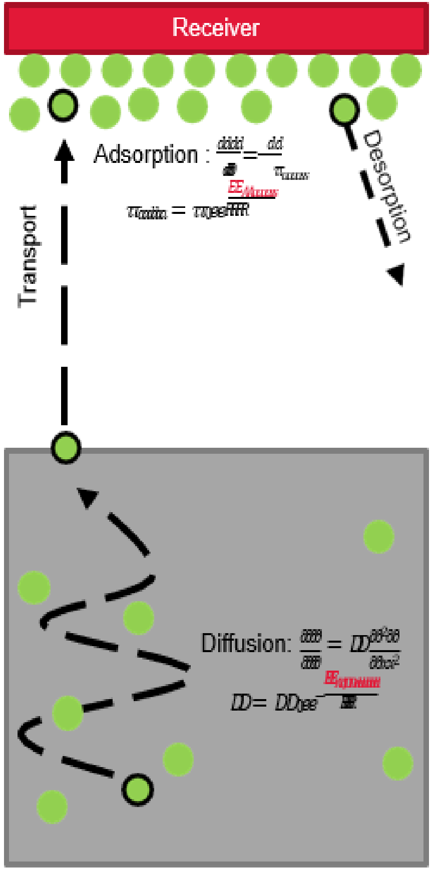
- ASTM E1559: Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials
- ECSS-Q-TM-70-52a: Kinetic outgassing of materials for space



Outgassing Test

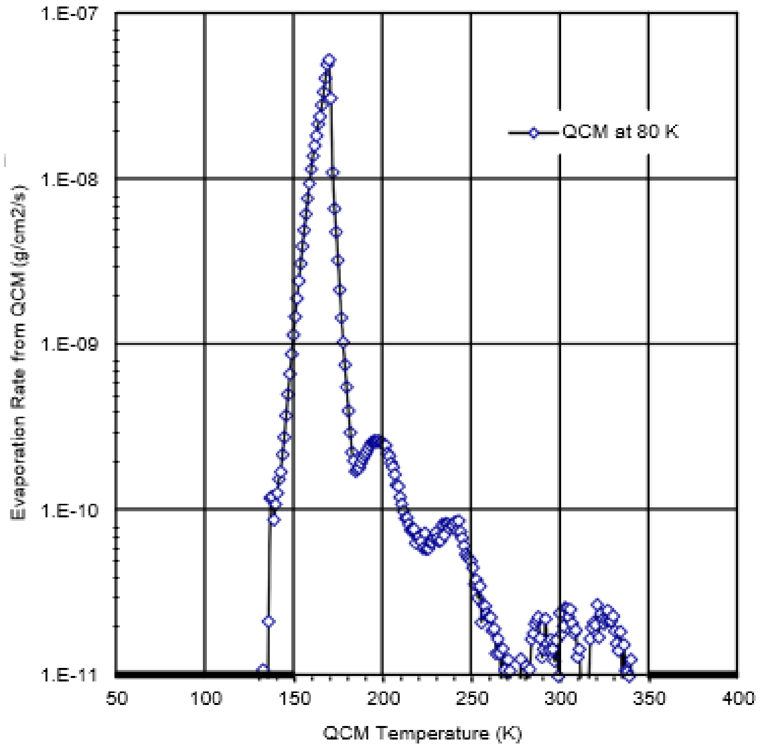
- Typical for ASTM E1559 ECSS-Q-TM-70-52a method
- Sample is held predefined temperature steps.
- Multiple QCMs at different temperatures measure outgassing collection over time
- Total accumulation on QCM provide information on initial concentrations C_0
- Net rates of accumulation on different temperature QCMs provides information on residence time: $E_{a,des}$
- Change in sample temperature probes $E_{a,diff}$

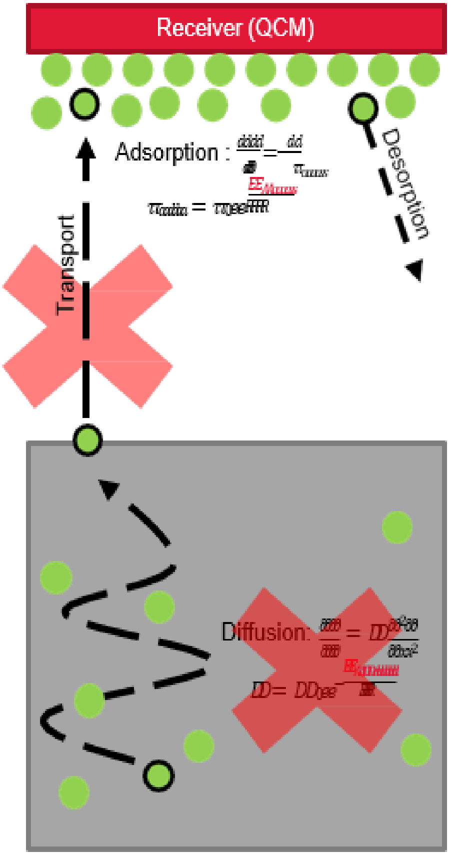




QCM Thermo Gravimetric Analysis Test

- Typical for ASTM E1559 ECSS-Q-TM-70-52a method
- Outgassing sample is removed from test chamber into load lock so QCMs are no longer accumulating
- QCM temperature is slowly raised (1C/min). Slowly changes residence time so contaminant species desorb
- Provides information on residence time in in much higher granularity, $E_{A,ads}$
- As temperature of QCM is raised slowly, contaminant species desorb sequentially due to their residence time

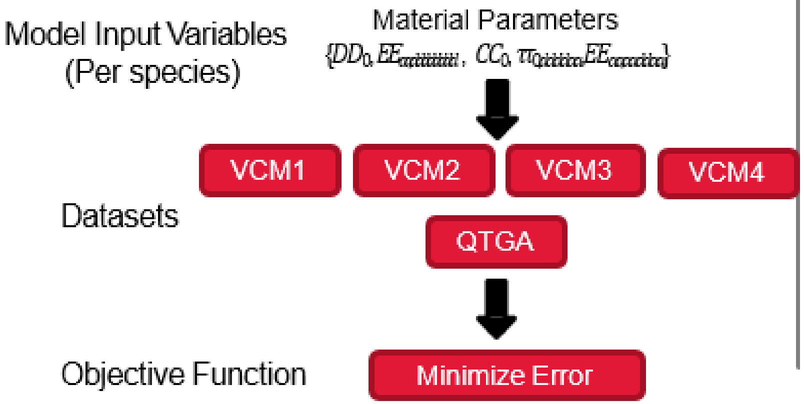


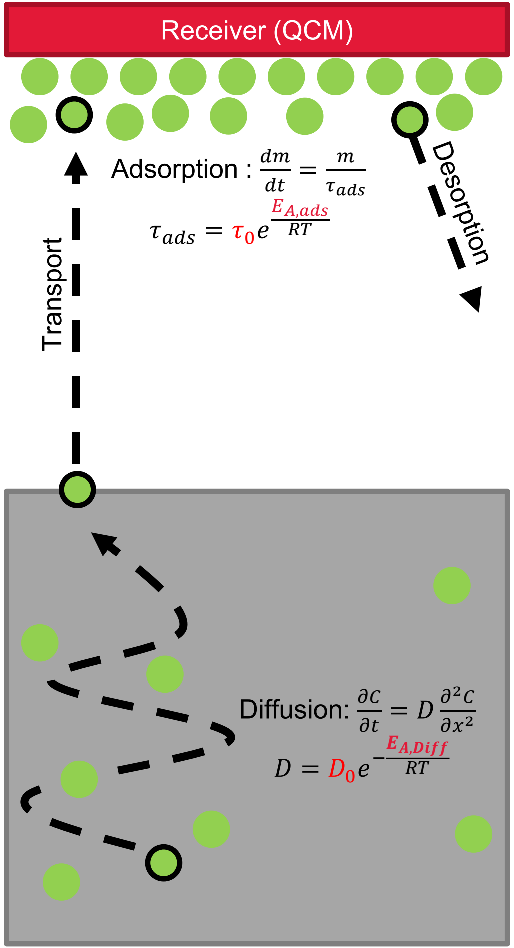


Multispecies Model Kinetic Fitting Scheme

- All available datasets are fit to minimize error between model and data
- VCMs datasets:
  - Modeling both diffusion and adsorption/desorption collection.
  - Critical to model both to describe diffusion and desorption.
- QTGA datasets:
  - At least 1 QTGA at the end of the test. May contain many QTGA datasets
  - Modeling adsorption/desorption

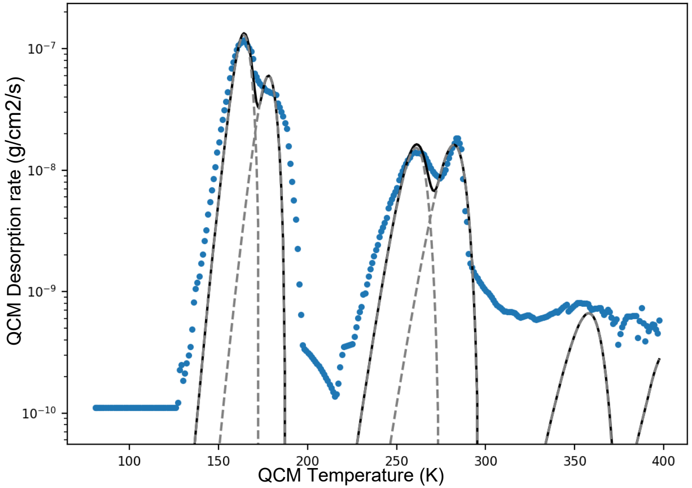
- Result from a good fit is a set of kinetic contaminant parameters (per contaminant species) which characterize outgassing from that material and adsorption/desorption

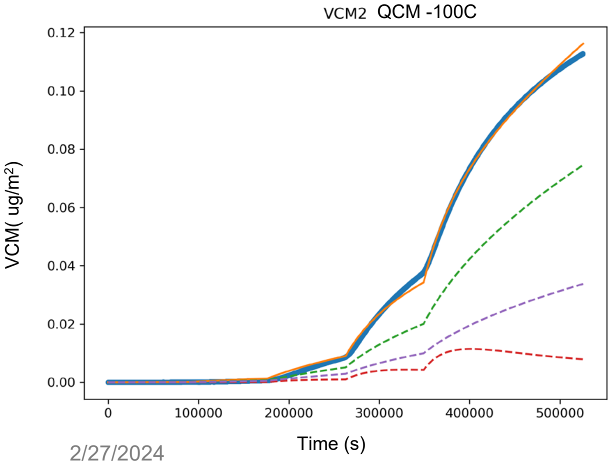


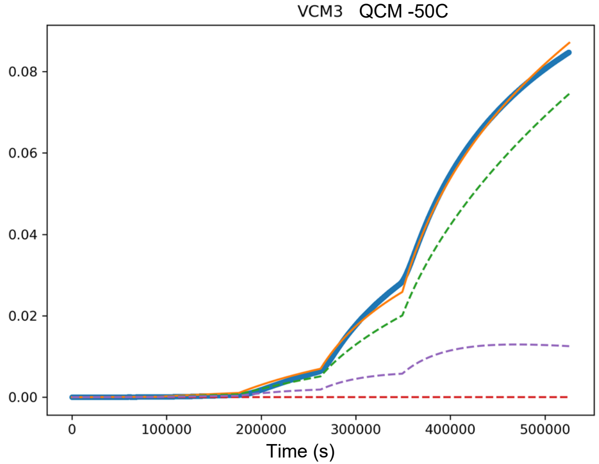


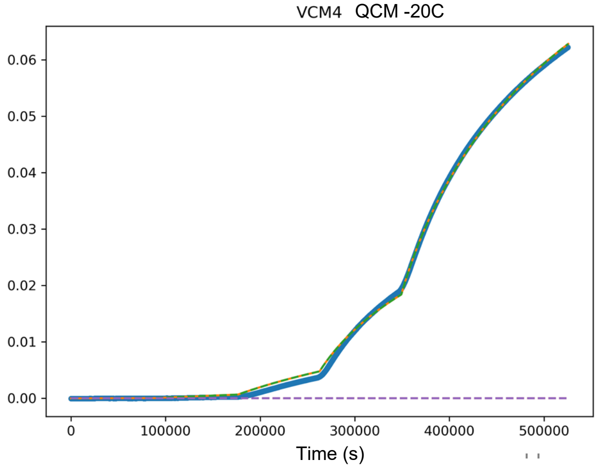
Example Multispecies Model Fit

- Test material isothermal has temperature steps at 20C 40C and 70C with QCMs collecting at 80K, -100C, -50C, -20C
- Model simultaneously reproduces key outgassing and collection features
  - QTGA and reemission residence times
  - Temperature behavior of outgassing
  - Decay of outgassing due to diffusion of contaminants
  - Collection of outgassing on different QCM temperatures





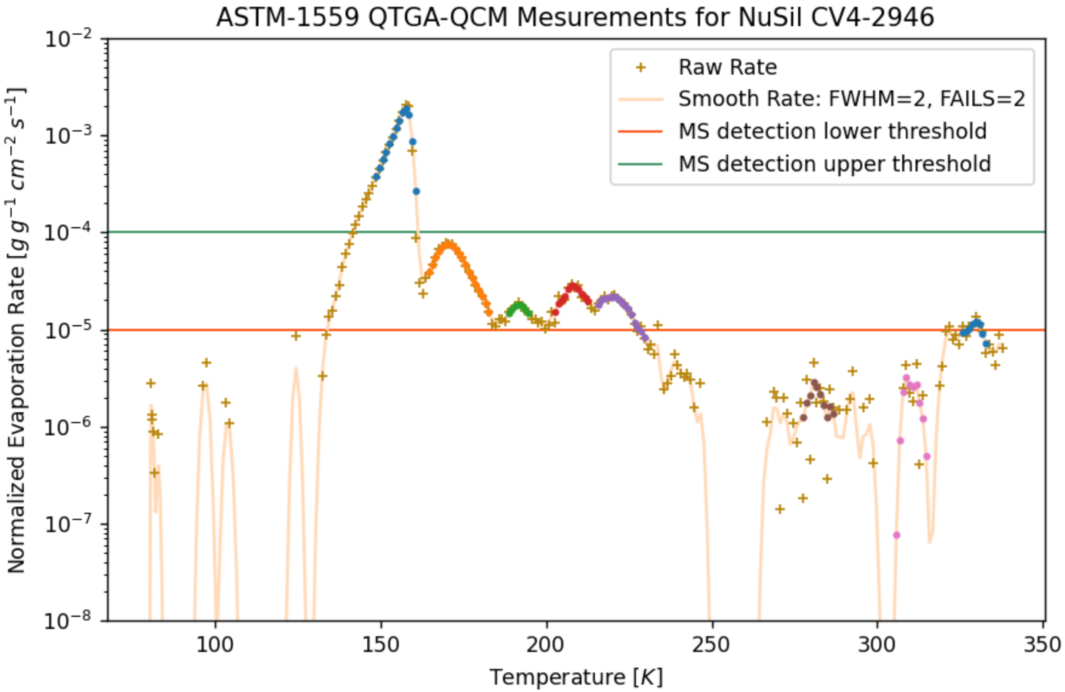




Outgassing chemistry identification

So far everything is a mathematical fit of kinetics.

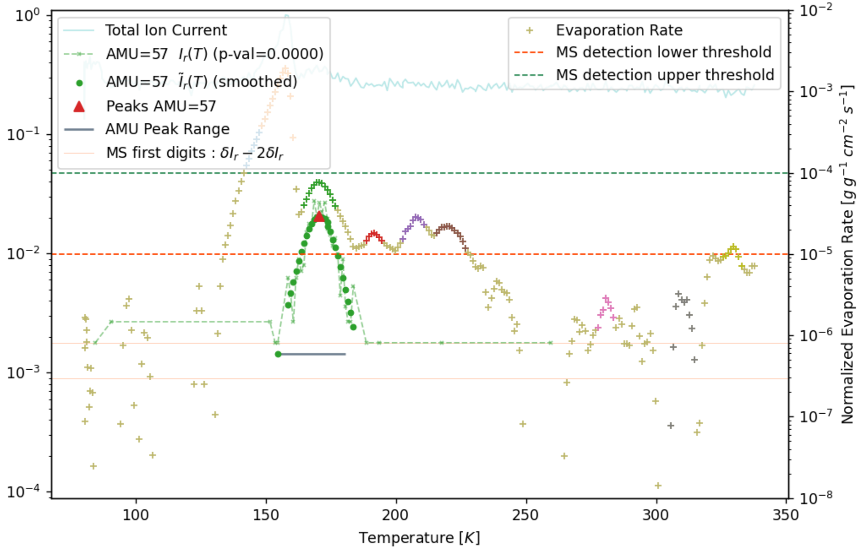
Recognizing species through desorption rate physical separation

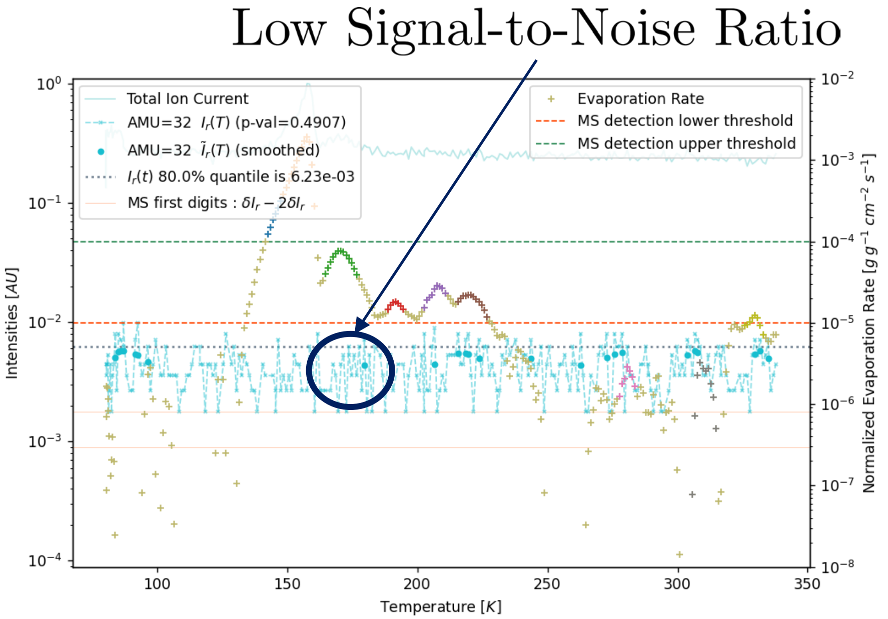


Controlled temperature gradient helps **separate species** in the **QTGA section** of the 1559 test

Filling the gap between 1559-QTGA and experimental spectrum

What makes a mass channel relevant to an outgassing species

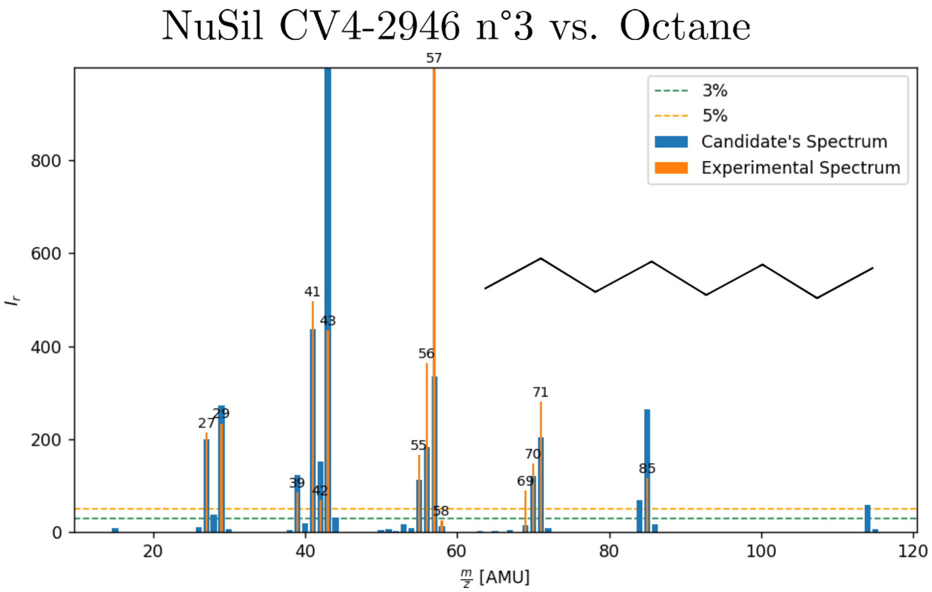




Correlation between **MS** and **QCM** **signals indicate** that a mass **channel** is **relevant**

What information can be inferred from a mass spectrum

Working with indirect information about a chemical species



Method	Score	Rank
RMSLE 3%	-2.364	6
Spec2Vec 3%	2.209	2
MS2DeepScore 3%	1.320	2
Composite 3%	**1.393**	**2**

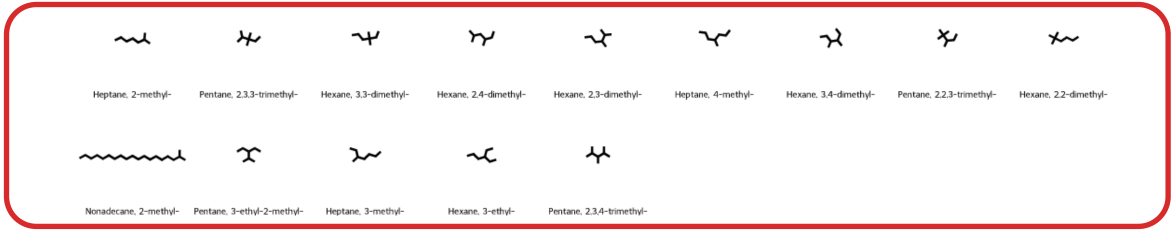
Diverse Scores → Unique <u>Composite Score</u>

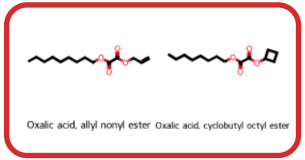
<u>Florian Huber et al.</u>, 2021

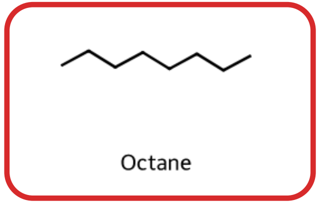
Spectrum similarity used as a proxy for molecular similarity helps us determine what the contaminants are most likely to be

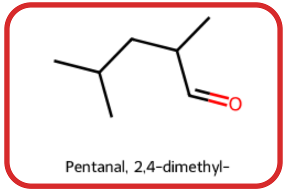
How to make sense of the result

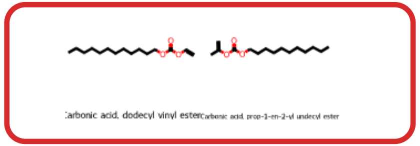
In the end, what can be known of a given outgassing species











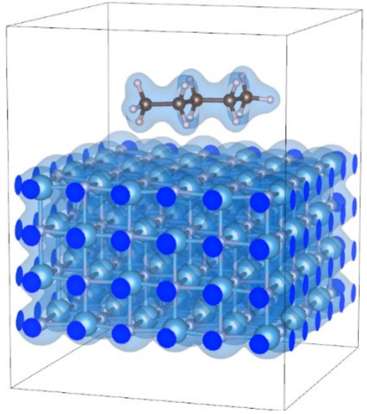
- Similar Top Ranking Results
- Few and related molecular groups
- Relative Confidence

Molecular clustering allows for a **comprehensive understanding** of an outgassing **species' identity**

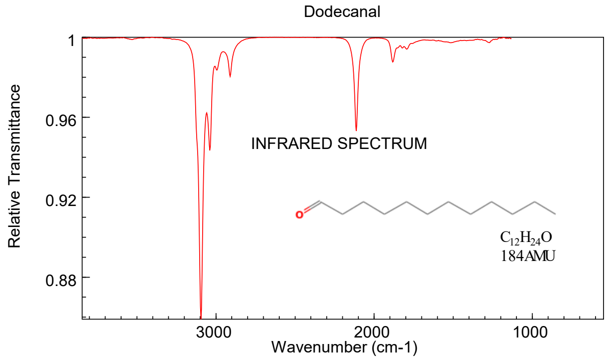
Mass Spectrometry Benefits

- By connecting kinetic multispecies model to mass spectrometry the kinetic contaminant parameters, $\{D_0,\ E_{a,diff}\ ,\ C_0,\ \tau_{0,des}, E_{a,ads}\}$ of outgassing molecules can be determined
- This kinetic multispecies model allows the capability of extrapolating outgassing for specific mission time and temperature conditions
- Knowledge of the contaminant chemical composition allows for a much more comprehensive understanding of the effects of outgassing contamination on scientific objectives
    - Molecular properties such as IR or UV spectra can be used to assess the impact to optical instruments and throughput (Example: SPHEREx, CGI, Psyche/DSOC)
    - Chemical composition can be assessed for the impact on sampling missions and detection of organics (Examples: Mars 2020, Mars Sample Return, Europa Lander)
    - Chemical composition can be assessed for the impact on mass spectrometers flown on missions intending to study atmospheric composition (Example: Cassini, Europa clipper)
- Additionally with the knowledge of chemical composition molecular properties can be calculated directly using computational material science techniques
    - Density functional theory was used to calculate the adsorption energy, $E_{A,ads}$, to TiN, the low surface energy coating in the Mars 2020 sample tubes[1]

DFT simulation of alkane adsorption to TiN



NIST IR Adsorption Spectra

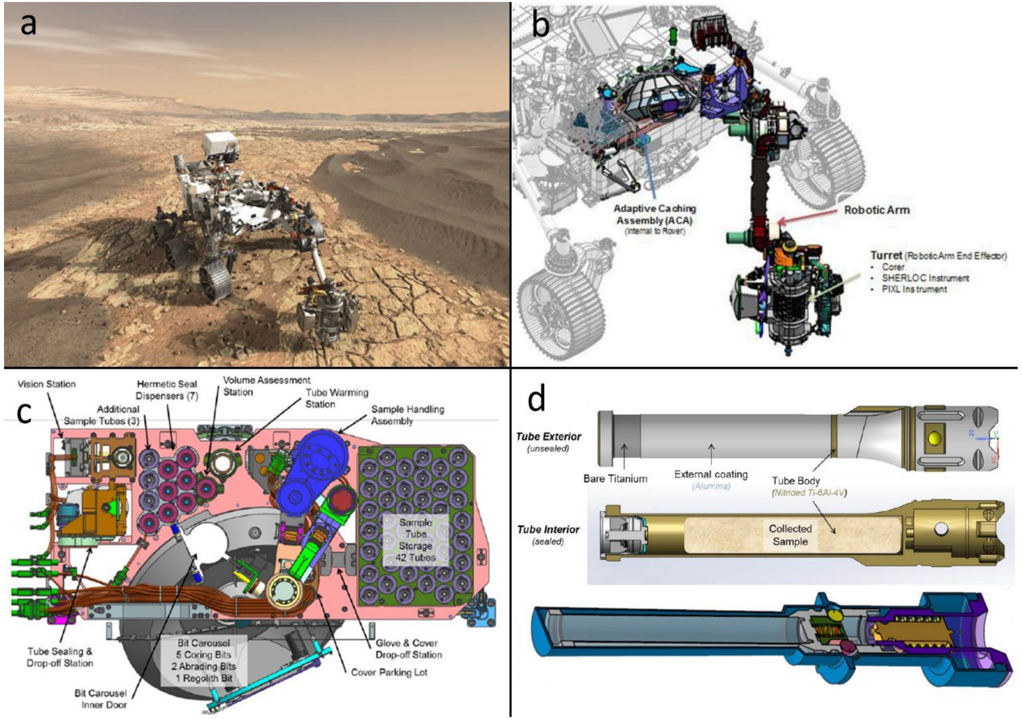


NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

1. Alred, J.M., Martin, M.G, Hoey, W.A., Wong, A.T., White, L.M., Boeder, P.A., Cofer, S.A., Dias-Ribeiro, A., Soares, C.E., "Predicting Terrestrial Contamination of the Mars 2020 Sample Caching System with Novel Multispecies Outgassing and Transport Models," Proc. SPIE 11489, Systems Contamination: Prediction, Control, and Performance 2020, 1148904, 21 August 2020.

Mars Example: Guaranteeing Detection

- Scientific requirement of less than 10 parts per billion (PPB) Total Organic Carbon (TOC) of terrestrial origin within the cached samples
- Each sample is nominally 15g which means less than 150ng of contamination can be tolerated
- This is less than a single layer of adsorbed contaminant molecules within the sample tubes
- More complicated than just cleaning sample tubes before launch. Outgassing can easily exceed this budget

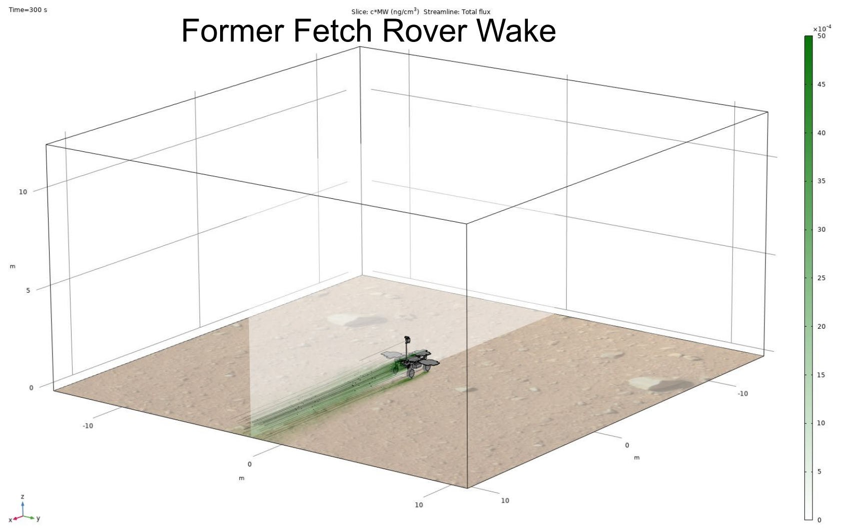


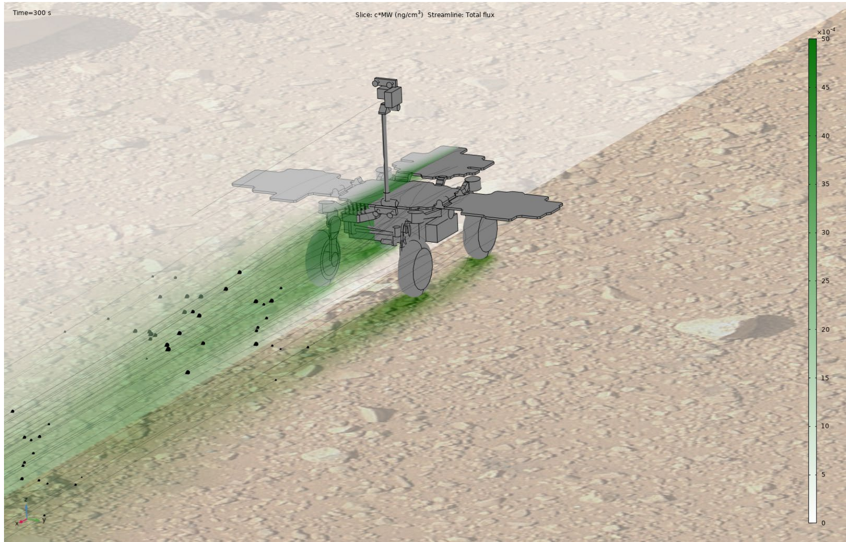
1. Alred, J., Martin, M., Hoey, W., Wong, A., White, L., Boeder, P., Cofer, S., Dias-Ribeiro, A., Soares, C., 2020. “Predicting Terrestrial Contamination of the Mars 2020 Sample Caching System with Novel Multispecies Outgassing and Transport Models.” Proceedings vol. 11489, Systems Contamination: Prediction, Control and Performance; 1148904.

Mars Example

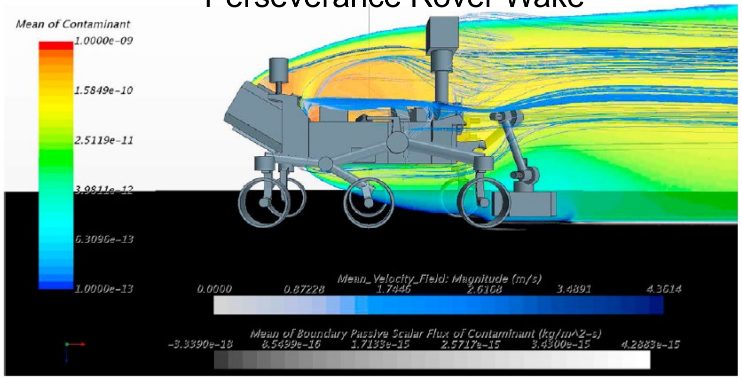
- Can contaminate hardware used to sample
- Can contaminate Martian samples
- All contamination effects to science had to be tracked to verify Mars 2020 and MSR science requirements

Former Fetch Rover Wake



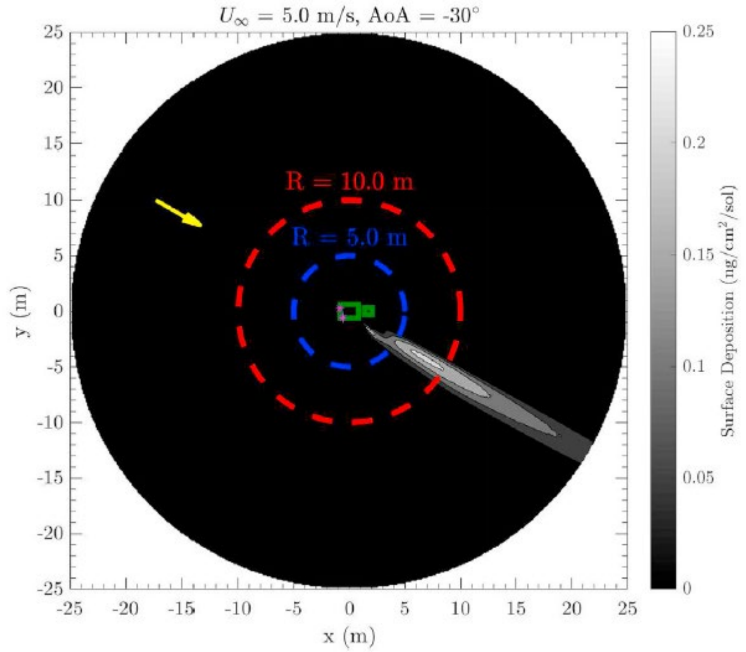


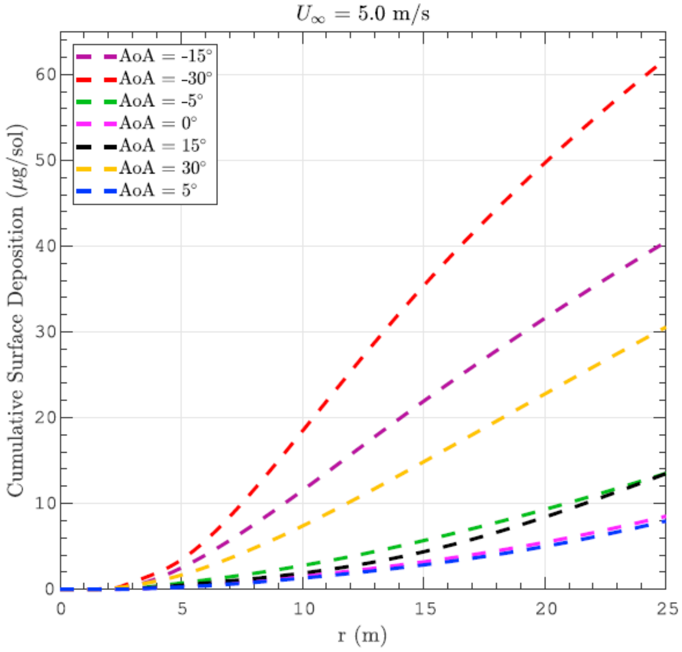
Perseverance Rover Wake



Mars Example

- The perseverance rover could potentially contaminate a sampling site
- Depends on Mars wind speed and wind direction
- This influenced loiter times limits when the Perseverance rover is allowed to be near a sampling site

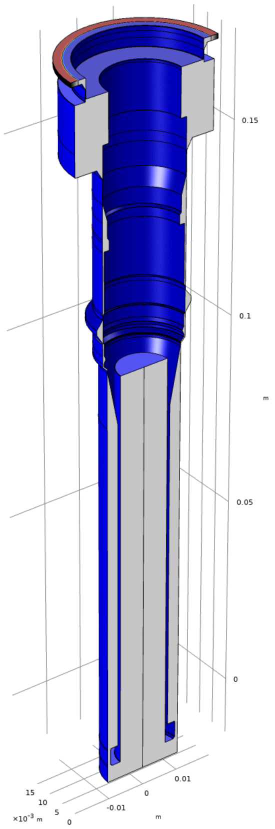


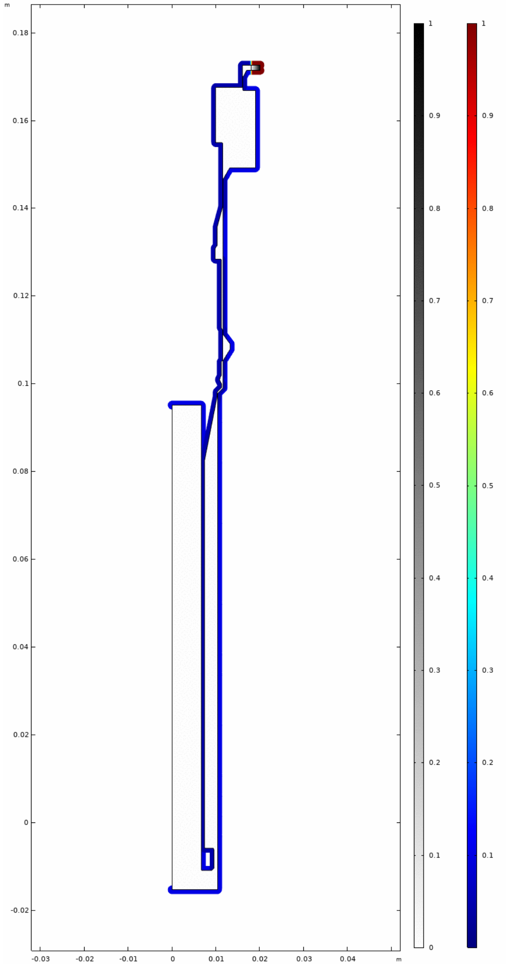


Rabinovitch, J., & Katz, I. (2019). Surface deposition of molecular contaminants in the mars 2020 rover wake. *Planetary and Space Science*, *168*, 1-14.

Mars Example

- Simulation of contamination transport Atmospheric environment
  - Diffusion transport regime
- Contamination is mainly adsorbed by the high energy surfaces and cannot diffuse into the sample intimate surfaces
- It is expected that the sample tubes remained at their as-cleaned cleanliness
  - Pending updating analysis with flight data
- This is expected to significantly improve estimates over the previous model





Conclusions

- Framework for the comprehensive modeling of outgassing generation and effects has been under active development
- Physics of outgassing
  - Activation energies of processes control conditions under which contamination can be generated and accumulated
- Multispecies model
  - Determination of outgassing constituents
  - Extrapolation of each species outgassing to mission condition
- Transport models
  - New end-to-end calculations combing the measured and characterized outgassing rate of the ACA with the calculated surface properties of the sample tubes
- For the example of Mars 2020 all of these culminate into the estimate of the terrestrial contamination of the samples guaranteeing unambiguous future detection of Martian based organics samples

Jet Propulsion Laboratory
California Institute of Technology

Recent Relevant Publications by JPL

Europa Clipper:

- *Soares, C., Wong, A., Hoey, W., Fugett, D., Anderson, J., Alred, J., Thorbourn, D., 2022. "High-Energy Radiation Induced Outgassing Testing and Modeling for Jovian System Missions."* *Presentation, ISMSE 15.*
- Ricchiuti, V., Fugett, D., Soares, C., 2022. "Modeling of Contamination Vent Path for Outgassing Components Underneath Thermal Blankets on Europa Clipper." Presentation, SPIE Optical Engineering + Applications Conference, San Diego, CA.
- Fugett, D., Soares, C., Wong, A., Anderson, J., Ricchiuti, V., Hoey, W., 2022. "Contamination Control Approach to Mitigating Radiation Induced Outgassing on Europa Clipper." Proc. IEEE Aerospace Conference.
- Anderson, J., Wong, A., Fugett, D., Hoey, W., 2020. "Modeling Radiation Influence on Spacecraft Materials Outgassing." Proc. IEEE Aerospace Conference.
- Soares, C., Hoey, W., Anderson, J., Ferraro, N., 2019. "Spacecraft Return Flux Considerations for Missions Targeting Detection of Organics with Mass Spectrometers." Proc. 70th International Astronautical Congress.
- Soares, C., Wong, A., Fugett, D., Hoey, W., Alred, J., Ferraro, N., Thorbourn, D., 2019. "High-Energy Radiation Testing and Effects on Spacecraft Materials Outgassing." Proc. 70th International Astronautical Congress.
- Wong, A., Fugett, D., Thorbourn, D., Martin, E., Hoey, W., et al. 2019. "Evaluating the *In Situ* Outgassing Characteristics of Silicone Adhesives in a Europa-Like Environment." Presentation, Applied Space Environments Conference, Los Angeles, CA.
- Hoey, W., Anderson, J., Soares, C., 2019. "State-of-the-Art Modeling of Contaminant Transport in Vacuum Chambers and Space Environments." Presentation, Applied Space Environments Conference, Los Angeles, CA.

Psyche Asteroid Mission:

- Martin, M., Alred J., Hoey, W., Ly, C., Soares, C., 2022. "Contamination Control Program for the Psyche Asteroid Mission." Presentation, SPIE Optical Engineering + Applications Conference, San Diego, CA.
- Martin, M., Hoey, W., Alred, J., Soares, C., Ferraro, N., 2021. "Understanding Spacecraft Test Environments in JPL's Twenty-Five-Foot Space Simulator." Presentation, Applied Space Environments Conference, Los Angeles, CA.
- Martin, M., Hoey, W., Alred, J., Soares, C., 2020. "Novel Contamination Control Model Development and Application to the Psyche Mission." Proc. IEEE Aerospace Conference.
- Martin, M., Wong, A., Hoey, W., Alred, J., Boeder, P., Soares, C., 2019. "Advancements in Monitoring and Operating Thermal Vacuum Environmental Test Chambers for Next-Generation Space Exploration Hardware." Presentation, 66th International Symposium of the American Vacuum Society, Columbus, OH.

Recent Relevant Publications by JPL

Mars 2020 Perseverance:

- Wong, A., Martin, M., Hoey, W., Soares, C., Hurst, K., Roberts, E., Perkins, R., Maltais, T., Shiraishi, L., Boeder, P., Alred, J., 2022. “Understanding Sampling Hardware Cleanliness from Perseverance Lessons Learned, and Forward Approach to Biosignature Missions.” Proc. AIAA SciTech Conference.
- Alred, J., Martin, M., Hoey, W., Wong, A., White, L., Boeder, P., Cofer, S., Dias-Ribeiro, A., Soares, C., 2020. “Predicting Terrestrial Contamination of the Mars 2020 Sample Caching System with Novel Multispecies Outgassing and Transport Models.” Proceedings vol. 11489, Systems Contamination: Prediction, Control and Performance; 1148904.
- Katz, I., Anderson, M., White, L., Boeder, P., Hoey, W., 2018. “Mars 2020 Sample Cleanliness Molecular Transport Model.” SPIE Opt. Eng. + Appl. Proceedings 10748, Systems Contamination: Prediction, Control and Performance 107480A.
- Soares, C., Hoey, W., Anderson, J., Anderson, M., Boeder, P., Ferraro, N., Liao, S., Sylvia, M., 2018. “Spacecraft Contamination Control Challenges for Space Missions with Organic Compound Detection Capabilities and for Potential Sample Return.” Proc. International Symposium on Materials in the Space Environment.

SPHEREx Observatory:

- Alred, J. M., et al., 2022. “Modeling Contaminant Outgassing and Free Molecular Transport Processes for the Cryogenic SPHEREx Observatory.” Presentation, 32nd International Symposium on Rarefied Gas Dynamics (RGD32).
- Alred, J. M. et al., 2021. “Designing a Decontamination Solution for the Low-Earth-Orbit, Cryogenic SPHEREx Mission,” Proc. IEEE Aerospace Conference.

Europa Lander Mission Concept:

- Hoey, W., Soares, C., Alred, J., Anderson, J., Martin, M., Shallcross, G., Wong, A., 2022. “Spacecraft Engine Plumes in Near-Vacuum: Earth’s Moon and Beyond.” Presentation, 32nd International Symposium on Rarefied Gas Dynamics (RGD32).
- Conte, A., Hoey, W., Wong, A., Soares, C., Grabe, M., Hepp, C., 2022. “Europa Lander Plume-Induced Contamination: Monopropellant Thruster Plumes Modeling in STG-CT High-Vacuum Chamber.” *(Manuscript in review)*
- Hoey, W., Lam, R., Wong, A., Soares, C., 2020. “Europa Lander Engine Plume Interactions with the Surface and Vehicle.” Proc. IEEE Aerospace Conference.
- Lam, R., Maghsoudi, E., Hoey, W., 2019. “Numerical Study of Lander Engine Plume Impingement on the Surface of Europa.” Proc. 66th JANNAF Propulsion Meeting / 37th Exhaust Plume and Signatures (EPSS) Meeting.

Recent Relevant Publications by JPL

Gateway:

- *Hoey, W., Soares, C., Martin, M., Shallcross, G., Steagall, C., Worthy, E., 2022. "A Predictive Model of Lunar Gateway Molecular Contamination." Presentation, ISMSE 15.*

Roman Space Telescope Coronagraph Instrument (CGI):

- Sylvia, M., Martin, M., Anderson, M., Cardines, J., Aldrich, D., Zhou, C., Hoey, W., Soares, C., 2021. "Contamination Requirements and Mitigation Strategies for the Nancy Grace Roman Coronagraph Instrument (CGI)." Presentation, 2021 NASA Contamination, Coatings, Materials, and Planetary Protection Workshop ().

Fairing Particle Redistribution:

- Alred, J. M., et al., 2022. "Particle Contamination Launch Redistribution and Effects on the Low-Earth-Orbit Infrared SPHEREx Telescope." Presentation, SPIE Optical Engineering + Applications Conference, San Diego, CA.
- Hoey, W., Shallcross, G., Martin, M., Soares, C., Cooper, M., 2022. "Launch recontamination: planetary protection models for particle transport in spacecraft payload fairing environments." Presentation; 44th Committee on Space Research (COSPAR).
- Shallcross, G., Hoey, W., Soares, C., Cooper, M., 2022. "Launch recontamination: the evaluation of particle adhesion and removal mechanisms in spacecraft payload fairing environments." Presentation; 44th Committee on Space Research (COSPAR).
- Hoey, W., Alred, J., Anderson, J., Martin, M., Soares, C., Droz, E., Shallcross, G., 2021. "Toward Predictive Models of Launch Ascent Depressurization and Induced Particle Redistribution." Presentation, 2021 NASA Contamination, Coatings, Materials, and Planetary Protection Workshop ().
- Anderson, J., Hoey, W., Alred, J., Soares, C., Brieda, L., 2020. "Space Launch Vehicle Transient Particle Redistribution Modeling and Implications for Optically Sensitive Payloads." Proceedings v. 11489, SPIE Systems Contamination: Prediction, Control and Performance; 114890D.