Summary of Key Findings

Planning Considerations Related to the Organic Contamination of Martian Samples and Implications for the Mars 2020 Rover

David Beaty
on behalf of the Mars 2020 Organic Contamination Panel

Presented to NRC-CAPS

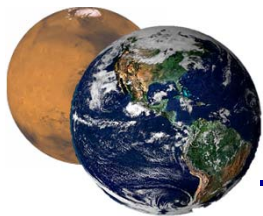Sept. 4, 2014

The presentation summarizes this white paper:

Charge to the OCP

The "Organic Contamination Panel" has been chartered with 4 primary technical tasks.

1. Based on current knowledge and capabilities, construct a list of measurements (and associated instruments/methods) anticipated to be made on the returned samples in support of objectives related to Martian organic geochemistry.

2. Determine the types and quantities of Earth-sourced organic contaminants of greatest concern, if they were on the samples. Also, specify a total organic carbon constraint.

3. Assess possible implementation approaches for recognizing and distinguishing Mars-sourced organic molecules in the samples from Earth-sourced organic molecular contamination.

4. Evaluate draft Mars 2020 mission sample organic contamination requirements and draft verification methodologies (to be provided by the Mars 2020 project).

OCP Team Roster

Primary Team

Name	Professional Affiliation	Interest/Experience
Chair		
Summons, Roger	MIT	organic geochemistry, exobiology
Sessions, Alex	Caltech	organic geochemistry, stable isotopes of organic molecules, instrument development
Technical Members		
Allwood, Abby	JPL/Caltech	astrobiology, ancient microbial biosignatures, fieldwork to laboratory
Barton, Hazel	Univ of Akron	geomicrobiology, ancient ecosystems in caves, organic geochemistry, PP; PHX and MSL
Blakkolb, Brian	JPL/Caltech	Contamination Control Engineer for M2020
Canham, John	ATK	contamination control, measurement, and effects; analytical chemistry; verification and validation; PP; surface science, analytical methods development; SAM (MSL); MOMA (ExoMars)
Clark, Benton	SSI	geochemistry, sampling strategies for contamination issues, PP; Viking and MER, OSIRIS-REX sampling system
Dworkin, Jason	GSFC	origins of life; CC for OSIRIS-REX; organics in meteorites
Lin, Ying	JPL/Caltech	chemical engineering, organic chemistry, in-situ organic molecule detection, PP, contamination control; ExoMars
Mathies, Richard	UC Berkeley	physical chemistry, laser spectroscopy, biomolecular tracers, contextual experiments for contamination
Steele, Andrew	Carnegie Inst., Wash	microbiology, meteorites, organic geochemistry; SAM (MSL), PP, 2020SDT
Facilitation		
Beaty, Dave	JPL/Caltech	Chief Cat-Herder; Mars Chief Scientist at JPL
Milkovich, Sarah	JPL/Caltech	Documentarian and Assistant Cat-Herder; M2020 science systems engineering

Expert Reviewers

Calaway, Mike	JSC--Curation	JSC curation
Des Marais, Dave	NASA Ames	Led astrobiology roadmap
Farmer, Jack	Arizona State Univ.	recognizing past life in rocks
Mahaffy, Paul	NASA GSFC	PI, MSL SAM Instrument
Oehler, Dorothy	JSC--Research	organics in Earth's geology
Sephton, Mark	Imperial College, London	Organics in meteorites
Sherwood Lollar, Barbara	University of Toronto	President, Geochemical Society

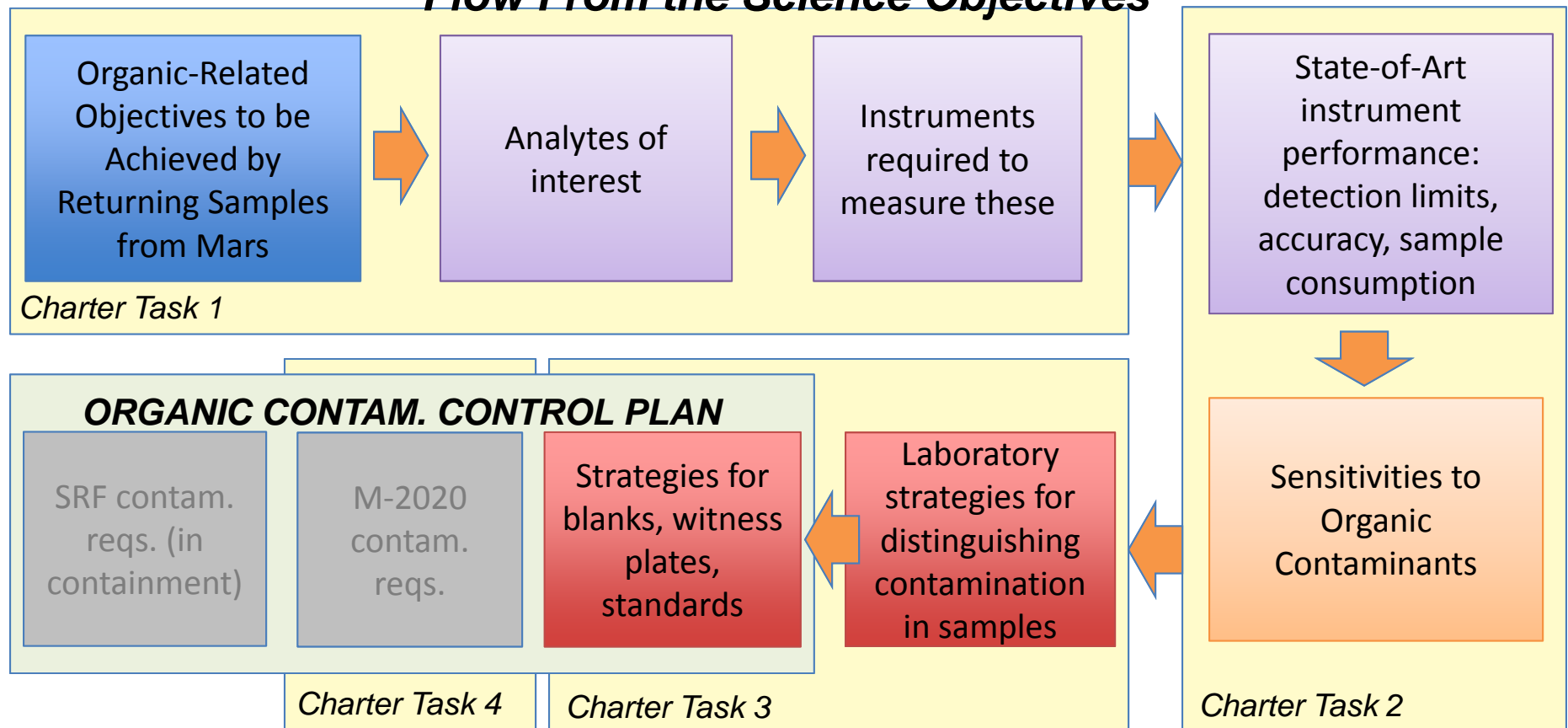## Ex Officio

Conley, Cassie	NASA HQ	NASA PPO
Farley, Ken	Caltech/JPL	Proj. Scientist, M2020
May, Lisa	NASA HQ	Mars Lead PE; MSR Program Exec
Meyer, Michael	NASA HQ	Mars Lead Scientist; MSR Prog. Scientist
Pugel, Betsy	NASA HQ	NASA HQ Planetary Protection
Wallace, Matt	JPL/Caltech	Deputy PM, M2020

Logical Flow of This Study

M2020 Organic Contamination Control Plan Needs to Flow From the Science Objectives

Organic-Related Objectives to be Achieved by Returning Samples from Mars

Charter Task 1

→ Analytes of interest

→ Instruments required to measure these

→ State-of-Art instrument performance: detection limits, accuracy, sample consumption

Charter Task 2

↓ Sensitivities to Organic Contaminants

← Laboratory strategies for distinguishing contamination in samples

ORGANIC CONTAM. CONTROL PLAN

SRF contam. reqs. (in containment) | M-2020 contam. reqs.

← Strategies for blanks, witness plates, standards

Charter Task 4 | *Charter Task 3*

The OCP was asked to provide a quantitative answer to a qualitative question

OCP Focused on M2020

	NATIVE STATE	SAMPLING ROVER	TRANSP.	SAMPLE TUBES OPENED	SAMPLES ANALYZED
	Samples on Mars	Samples affected by sampling equipment	Samples sealed	Samples affected by SRF environ.	Samples in instr.
Time	4 e9 yrs	days	10+ yrs	weeks	days
Potential for sample contamination	ZERO	HIGH	LOW	HIGH	HIGH
Timing of Requirements Needed	ZERO	**NOW**	LATER	LATER	LATER

THIS STUDY
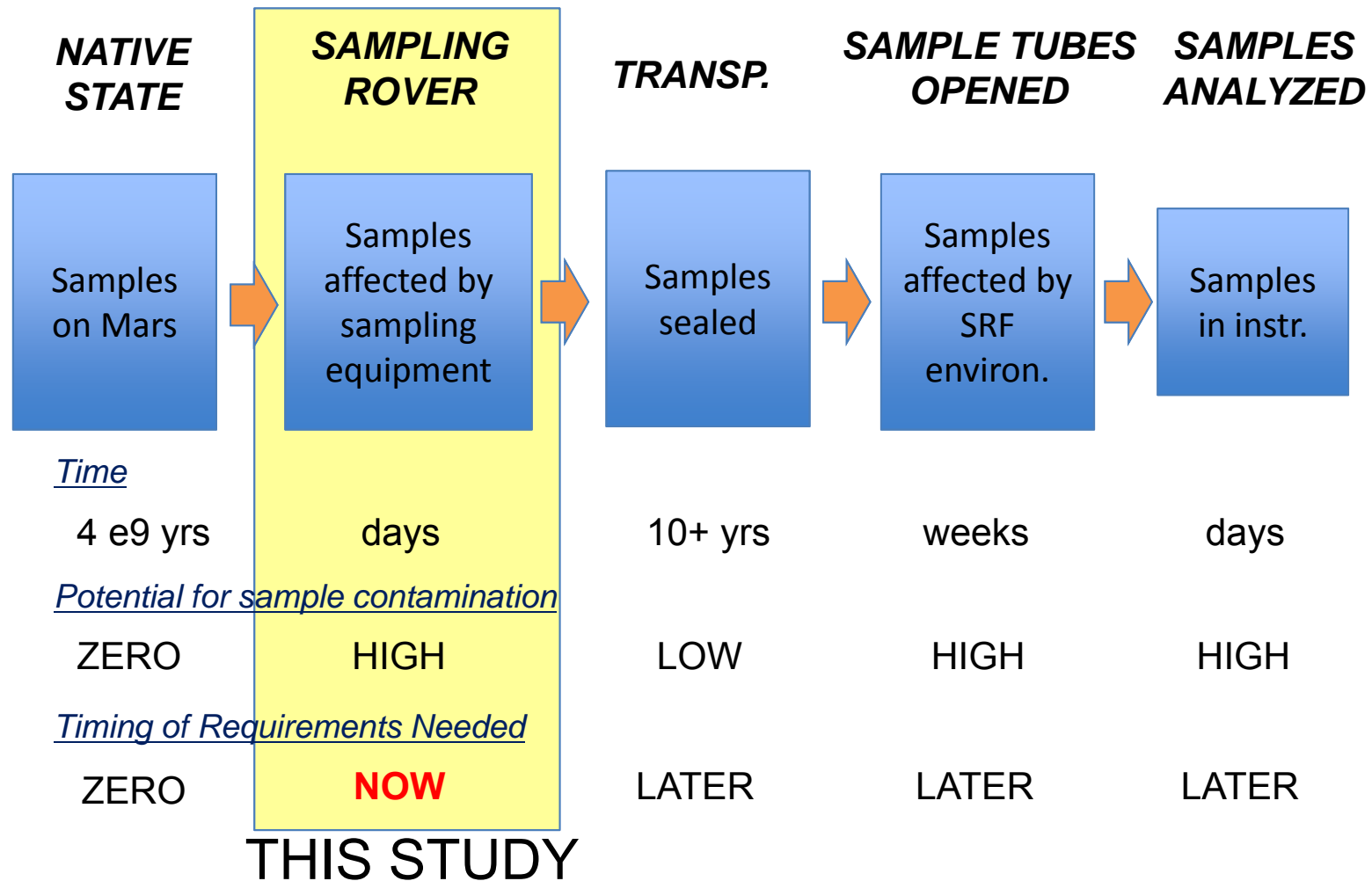
OCP Focus is on Samples not Spacecraft

M-2020

- Spacecraft Surfaces
- Organic Contamination Transfer
- SRF and analytic environment

Others determine these implications

OCP Job:
establish contamination thresholds here

Samples w. trace organic contamination → Sample-based Measurements of Organics

↓

Interpret Martian conditions

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Organic Contamination

as applied to the purposes of this committee

Any substance that significantly interferes with our ability to detect the presence of martian organic compounds or prevents our confidently determining that an organic compound is of martian and not terrestrial origin

i.e., in addition to analytes of concern, we also consider organic and inorganic compounds that may interfere with measurements of organics.

Science and PP Objectives Both Drive the Need for Organic Analyses
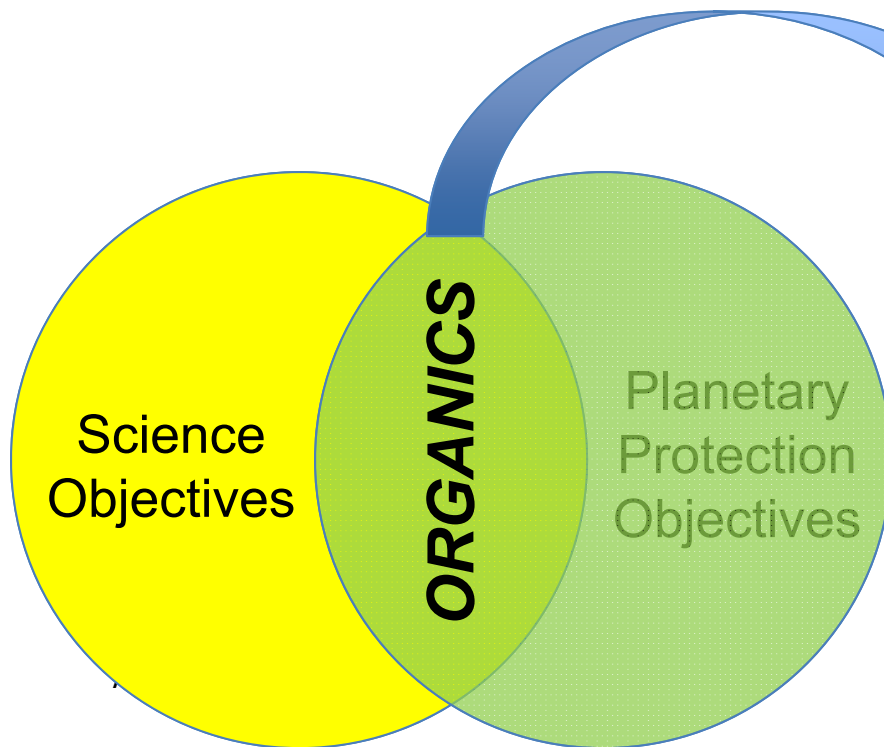
Organic Analyses
Proposed Summary of
Measurement Objectives

Science/PP Questions	Measurement Objective
Is there evidence of organic chemistry?	Determine the molecular distribution of martian organics
	Determine the chiral distribution of martian organics
	Determine the isotopic composition of martian organics
Is there evidence of extinct life?	The above measurements are directly or indirectly used to assess the evidence of extinct life
	Determine if there are spatial variations in abundance and characteristics of martian organics
Is there evidence of extant life?	The above measurements are directly or indirectly used to assess the evidence of extant martian life
	Determine the presence of large, organic polymers/biomolecules

Science Objectives

ORGANICS

Planetary Protection Objectives

Finding #5: A key subset of objectives of both science and planetary protection can be met by a common set of organic geochemical measurements of returned samples.

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Table 1: Potential Measurements for Returned Samples

This schematic table illustrates the structure and organization of Table 1, which is available as a separate file.

Survey Analytical Method	
Targeted Analytical Method	

Category 1: Non-Destructive, Sample Surface-Based Technique

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Example Detection Limits	Method Notes (Dependencies, Limitations, Assumptions,etc.)	Representative Contaminants (stuff we don't want in there)	References

Category 2: Slightly Destructive to Sample Surface

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Example Detection Limits	Method Notes (Dependencies, Limitations, Assumptions,etc.)	Representative Contaminants	References

Category 3: Destructive of Sample

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Example Detection Limits	Method Notes (Dependencies, Limitations, Assumptions,etc.)	Representative Contaminants	References

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Instruments and Techniques

Category 3: Destructive of Whole Sample

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions,etc.)	References
GC-ICPMS	2B	Extraction, destructive	20 pmol S as dimethylsulfide, at 0.3‰ precision;	compound must be GC-amenable	Amrani A., Sessions A. L. and Adkins J. F. (2009) Compound-Specific δ34S Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS. Analytical Chemistry 81, 9027–9034.

E X A M P L E

Finding: A huge diversity of techniques for organic analysis already exists. More will be invented. We can not predict which techniques will be used. Not all potential measurements will be possible on returned Mars samples given limited sample mass, nor will all be needed.

Finding: Because of the sensitivity of modern analytical instruments, we must accept that we will not be able to reduce all organic contaminants to non-detectable levels by all analytical techniques.

Elements of a Viable Contamination Management Strategy

- *Contamination Reduction* (#1 Below), *Contamination Characterization* (#2), and *Avoidance of Recontamination* (#3-4), are essential elements in the overall effort to achieve minimum acceptable sample quality.

STRATEGY #1
Reduce contamination at start

STRATEGY #4
Monitor the changes over time

Concentration of contaminant

STRATEGY #2
Characterize residual contamination

State of contamination at the time of sampling

STRATEGY #5
Determine contamination at time of sampling

STRATEGY #3
Minimize recontamination

0

Time
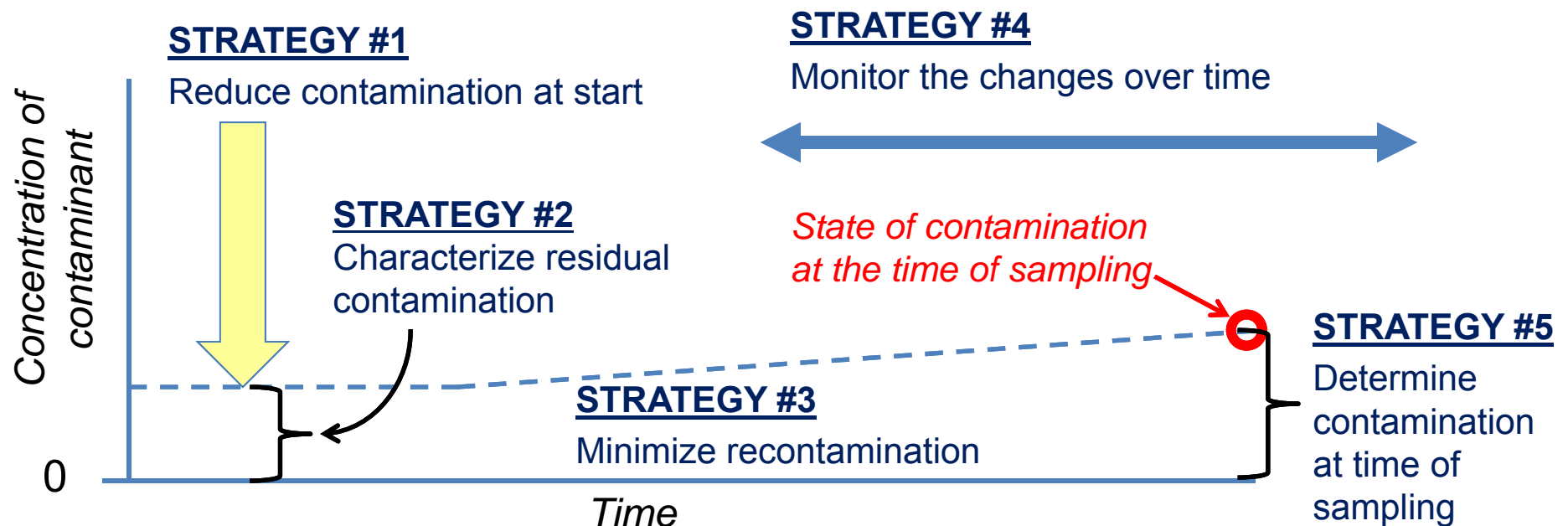
Finding #4: Our ability to interpret data from partially contaminated samples correctly depends on: 1). Minimizing contamination at the start, 2). Characterizing residual contamination, and 3). Minimizing recontamination.
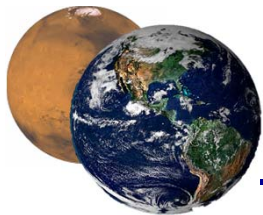
Organic Molecules of Interest

The history of the Mars surface environment is sufficiently obscure that essentially all organic molecules are of potential interest to us. Even those molecules of undoubted terrestrial origin have the potential to interfere with detection of other analytes.

Finding: We need to be concerned at some level with essentially all organic molecules as potential contaminants.
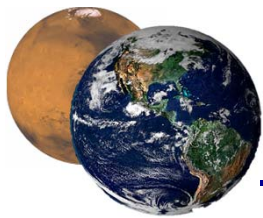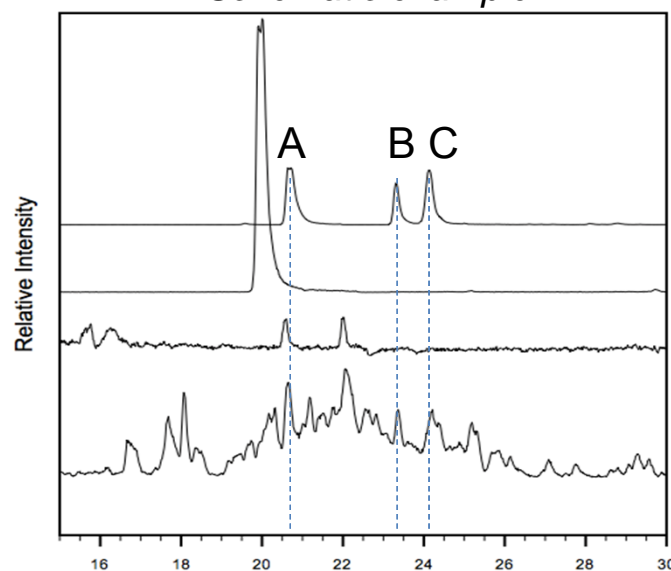
Not All Contaminants are Equal

- Certain contaminants are worse than others, if they directly interfere with analytes of interest. But this depends both on what is in samples, and what instruments/methods are used.

- Complex contaminant profiles are, in general, much worse than a few well-characterized contaminants.

Schematic example

←Assume identification of A, B, and C is the scientific objective

←If there is one large but understood contaminant: **A, B, C detected!**

←If there are several small, but inconvenient contaminants: **B and C detected presence of A is uncertain.**

←If there is extensive diverse contamination: **inconclusive results**

Finding: Reducing specific contaminants that interfere with compounds of scientific interest is as important as reducing the total contamination burden.

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Which Contaminants Matter?

- Modern organic geochemistry:
  - Has evolved to a focus on the significance of specific molecules
- Certain molecules have a clear potential to be more problematic as contaminants than others:
  - Molecules known to exist on Mars and/or in meteorites
  - Molecules that make up life as we know it
- We adopt a two-tiered strategy for ranking contaminants:
  - <u>Tier I</u>. Contaminants of highest concern, that would directly interfere with our ability to assess the presence of extant or extinct life on Mars. Highest level of contaminant control and characterization.
  - <u>Tier II</u>. All other organic molecules. Lower level of contaminant control.
- Total Organic Carbon:
  - Is less valuable as a measurement for scientific interpretation, but is useful as a summary for implementation purposes (blanket insurance policy)

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Tier-I Compounds: Initial List

Contaminant Class	Examples	Potential Measurement Methodology	Measurement Capability	Comments/Justification	References
Nucleic acid	DNA	Fluorescence, Mass spectrometry	1 fmole	DNA is the universal signature for terrestrial life and, therefore, terrestrial contamination	Liu et al., 2013
Spores	dipicolinic acid	Fluorescence	1 pg	Bacterial spores are the most recalcitrant form of terrestrial biota	L. Krásny et al. 2013
Bacterial and fungal cell walls	N-acetylglucosamine	LCMS	1 pg	Bacterial and fungal cell wall components may be detectable after the cell is destroyed.	Schleifer and Kandler, 1972; Bartnicki-Garcia, 1968
Amino acids	glycine	LCMS	1 pg	Glycine is the most abundant amino acid in nature; abundant in fingerprints	
Amino acids	alanine	LCMS	1 pg	Alanine is chiral and abundant	
Lipids	palmitic acid	GCMS	1 pg	Most common fatty acid in bacteria and eukarya	
Lipids	squalene	GCMS	1 pg	Lipid common to all life; abundant in fingerprints	
Hydrocarbon biomarkers	pristane	GCMS	1 pg	Common component of petroleum and, therefore, petroleum-derived aerosols	
Martian organics	chlorobenzene	GCMS	<1 pg	Need at least one likely Mars-derived organic compound. Chlorobenzene is a reaction product of aromatic carboxylic acids (e.g., benzoic, phthalic) with perchlorate.	Benner et al, 2000; Biemann et al. 1977; Navarro-Gonzalez et al 2010
Martian organics	dichloromethane	GCMS	<1 pg	Identified by both Viking and MSL. May be terrestrial and/or Martian	Biemann, et al, 1977; Navarro-Gonzalez, et al, 2010.
PAHs	naphthalene	GCMS	1 pg	Most abundant and readily detectable PAH. PAHs have been detected in ALH 84001 and DaG 476 and appear to be part of the aromatic inventory of martian igneous and possible biogenic processes. Should be monitored to avoid false positive measurements	J. Clemett, et al, 1998

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Tier-I Compounds: Final List

Contaminant Class	Examples	Potential Measurement Methodology	Measurement Capability	Comments/Justification	References
Nucleic acid	DNA	Fluorescence, Mass spectrometry	1 fmole	DNA is the universal signature for terrestrial life and, therefore, terrestrial contamination	Liu et al., 2013
Spores	dipicolinic acid	Fluorescence	1 pg	Bacterial spores are the most recalcitrant form of terrestrial biota	L. Krásny et al. 2013
Bacterial and fungal cell walls	N-acetylglucosamine	LCMS	1 pg	Bacterial and fungal cell wall components may be detectable after the cell is destroyed.	Schleifer and Kandler, 1972; Bartnicki-Garcia, 1968
Amino acids	glycine	LCMS	1 pg	Glycine is the most abundant amino acid in nature; abundant in fingerprints	Salazar et al, 2012
	alanine	LCMS	1 pg	Alanine is chiral and abundant	
Lipids	palmitic acid	GCMS	1 pg	Most common fatty acid in bacteria and eukarya	
	squalene	GCMS	1 pg	Lipid common to all life; abundant in fingerprints	
Hydrocarbon biomarkers	pristane	GCMS	1 pg	Common component of petroleum and, therefore, petroleum-derived	
Martian organics	ch				000; 1977; alez et al 2010
	dic				197 ; Navarro- , 20 0.
PAHs	naphthalene	GCMS	1 pg	Most abundant and readily detectable PAH. PAHs have been detected in ALH 84001 and DaG 476 and appear to be part of the aromatic inventory of martian igneous and possible biogenic processes. Should be monitored to avoid false positive measurements	J. Clemett, et al, 19 8 Steele et al 2012
Nitrogenous compound	urea	LCMS		Important to pre-biotic chemistry	Esther, et al, 2008
Short-chain carboxylic acid	Acetic acid	GCMS			
Polyhydroxy compound	Glycerol	GCMS			
Hydroxy carboxylic acid	Pyruvic acid	LCMS or GCMS		Metabolite of sugars and important metabolic intermediate	
Linear hydrocarbons	N-Heptacosane	GCMS	10 ng/g		

Added Based on Expert Reviewer Feedback

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Allowable Levels of Contamination

Three possible approaches to deducing limits:

What analyte concentrations do we expect?
Acceptable levels a function of signal/background ratio

What concentrations can we measure?
Cleaning below this limit cannot easily be verified

What level of cleanliness can we achieve?
Cleaning below this level may not be possible or practical

Compare to find optimal levels

What analyte concentrations do we expect?

- ## Martian meteorites
  - Amino acids detected at levels of **few ppb** (Callahan et al., 2013)
  - Organic carbon in inclusions in igneous minerals has been measured in multiple martian meteorites at levels of **10 to 20 ppm** TOC.

- ## In situ analysis (rovers, landers)
  - Viking GCMS: less than **1 to 10 ppb** of any individual complex organic compound present in soils
    - Lab experiments with perchlorate are consistent with up to **6.5 ppm** organics in soil at Viking sites (this is disputed by the GCMS P.I. and collaborator)
  - MSL: **~150-300 (ppb)** CBZ identified in Cumberland GCMS analyses. Only trace CBZ levels detected in Rocknest and blanks (**< 10 ppb**). Reported by Freissinet et al. (2014)

- ## Conclusion: highly uncertain, but most likely in **low ppb** range for most kinds of molecules, and TOC in the **ppm** range.

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What level of cleanliness can we achieve?

How clean can a metal surface be?

- It is possible to reduce the quantity of organic molecules on metal surfaces to near-zero, for example, by oxidative heating

- However, clean metal surfaces exposed to air quickly (within minutes/hours) acquire a layer of adventitious carbon (AC), typically ~20 to 100 ng/cm^2. The phenomenon is well documented in the literature (e.g., Ref. 1-5)

- Rate and amount of formation is highly variable, and depending on precursor concentrations, substrate, configurations, and environmental conditions

JPL test data suggests an asymptotic time dependence for the formation of AC.

Hydrocarbon film formation on clean metal surfaces over time

Flow bench AC experiment

Std cleanroom witness plate: 3 week exposure: 50ng/cm2

MSL: 23ng/cm2 "at launch"

1. Siegbahn K, et al. Nova Acta Regiae Soc. Sci. Ups 1967; IV: 20.
3. T.L. Barr, S. Seal, J. Vac. Sci. Technol. A 13(3) (1995) 1239.
4. P. Swift, Surf. Interface Anal. 4 (1992) 47.
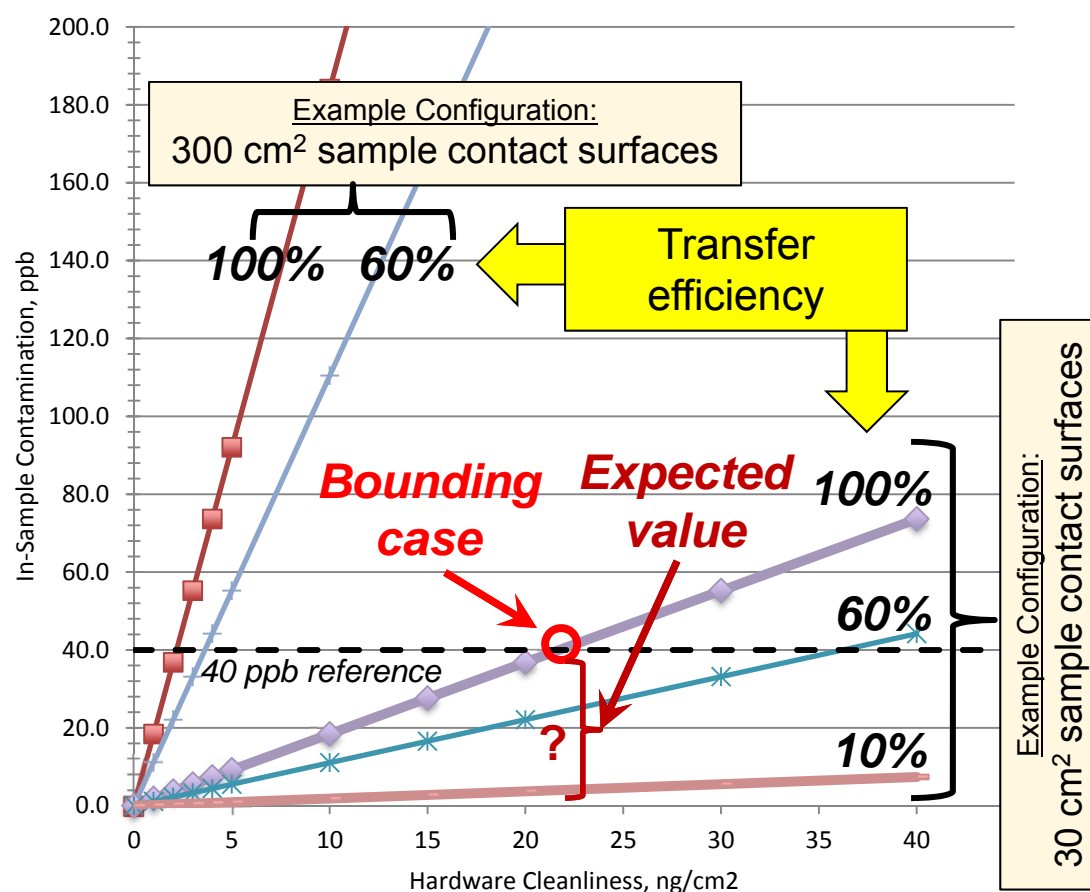5. H. Piao, N.S. McIntyre, Surf. Interface Anal. 33 (2002) 591.
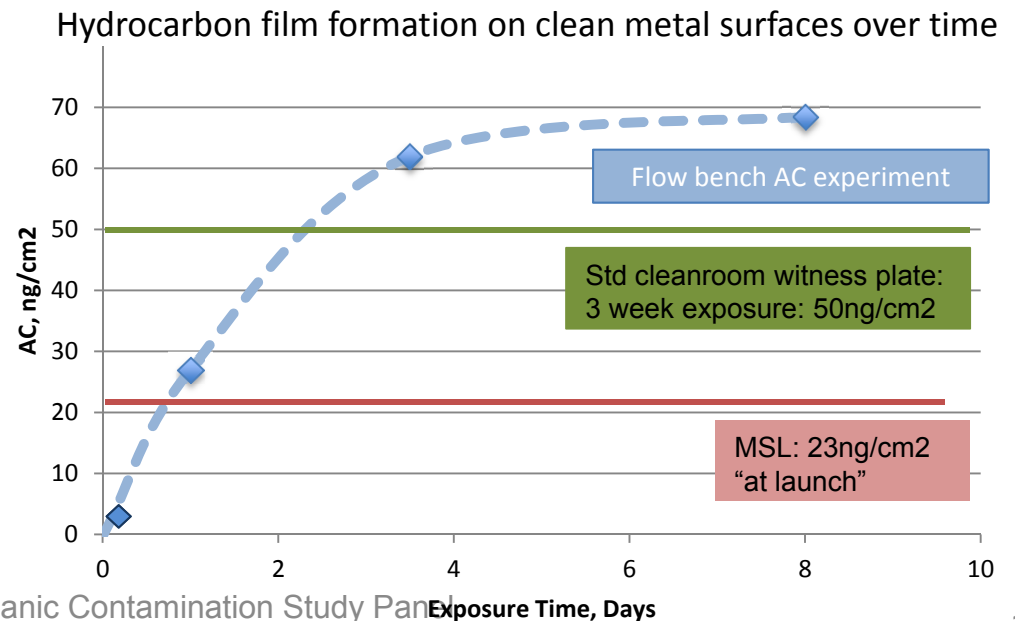
Translating Cleanliness Levels From Metal Surface Values to Rock/Soil Values

$$ppb = \frac{h/w \; cleanliness \; level(ng/cm^2) \; \times \; surface \; area \; of \; the \; sample \; that \; contacts \; h/w(cm^2) \times transfer \; efficiency}{Mass \; of \; sample \; core(g)}$$

- Assume sample mass = 16 g
- Contaminant contact transfer efficiency (%) is dependent on sample-hardware configuration.
    - A range of 10% to 100% is presented to illustrate the proportional dependence of in-sample contamination to this parameter.

Finding: In the case of a system with sample contact surfaces of 30 cm², and contaminated with with 20 ng/cm² organic carbon, collected samples would have a theoretical maximum of 40 ppb organic contaminants, and an expected concentration of an unknown amount less than 40 ppb, depending on transfer efficiency.

Generic contaminant transfer models

Chart axes: In-Sample Contamination, ppb (y-axis, 0.0 to 200.0) vs. Hardware Cleanliness, ng/cm2 (x-axis, 0 to 40)

Example Configuration: 300 cm² sample contact surfaces — 100% 60%

Transfer efficiency

Bounding case — Expected value — 100% 60% 10%

40 ppb reference

Example Configuration: 30 cm² sample contact surfaces

Proposed Contamination Thresholds: Summary of Key Technical Inputs

What Do We Expect?

Highly variable by compound

Could be ≥ low ppb levels for certain important compounds, lower for trace compounds

TOC > 10-20 ppm, variable by sample

What Can We Measure?

1 ppb general, <0.1 ppb for some targeted methods, ppt levels for some specific analytes

Sensitivity controlled mainly by blanks, not by instrument detection limits

Reasonable lower limit ~1 ppb

How Clean Can We Achieve?

Variable, depending on compound abundance

ppt levels possible for specific compounds

~40 ppb limit from adventitious carbon

Unless aggressive measures to prevent recontamination
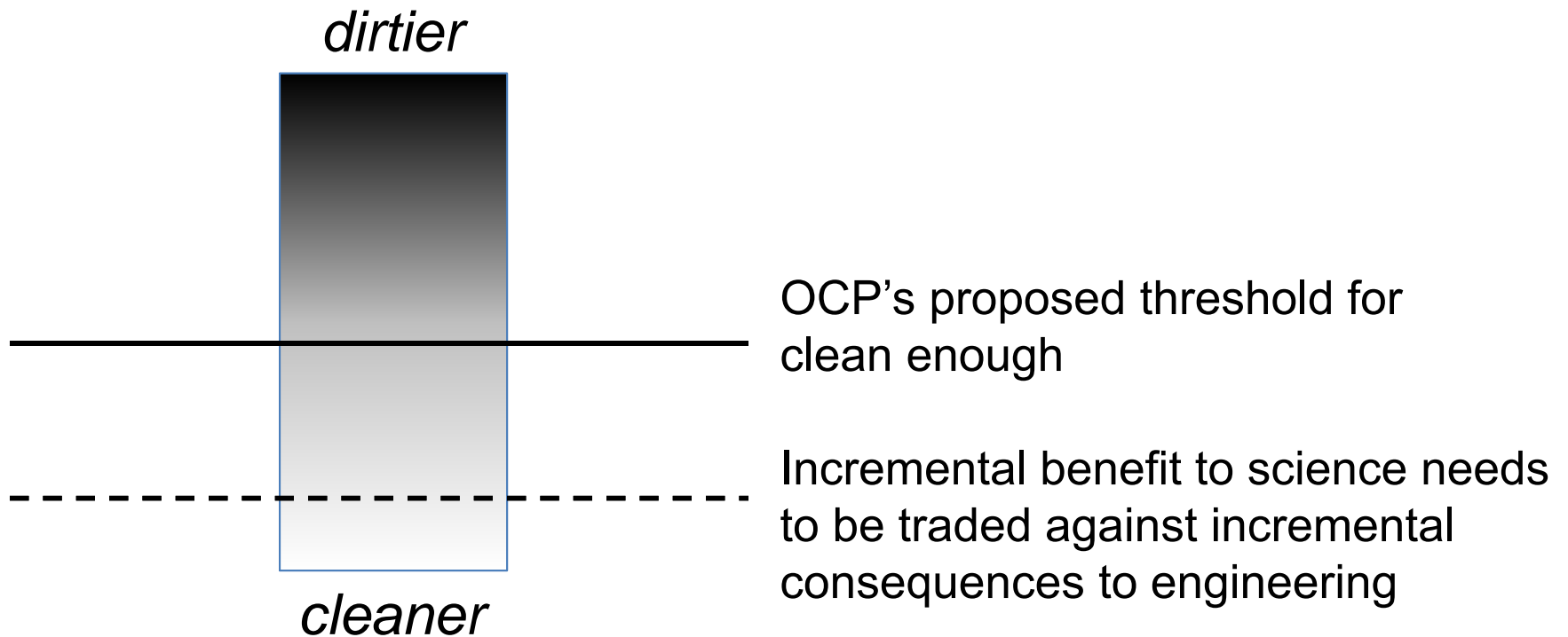
OCP's Definition of "How Clean is Clean Enough"?
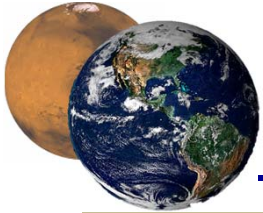
A 3-tiered definition is proposed:

1. For highest-priority organic molecules (Tier 1), set a standard that is most stringent: **1 ppb**. In some cases individual molecules may be chosen to represent a compound class. We have the highest confidence that these molecules would be important to interpreting martian geochemistry if they were returned.

2. For lower-priority organic molecules (Tier 2), set a more relaxed standard: **10 ppb**

3. Establish a limit for Total Organic Carbon (TOC) to monitor the sum of all organic molecules: **40 ppb**. This will help to recognize "surprises" in the form of contaminants not being specifically tracked.
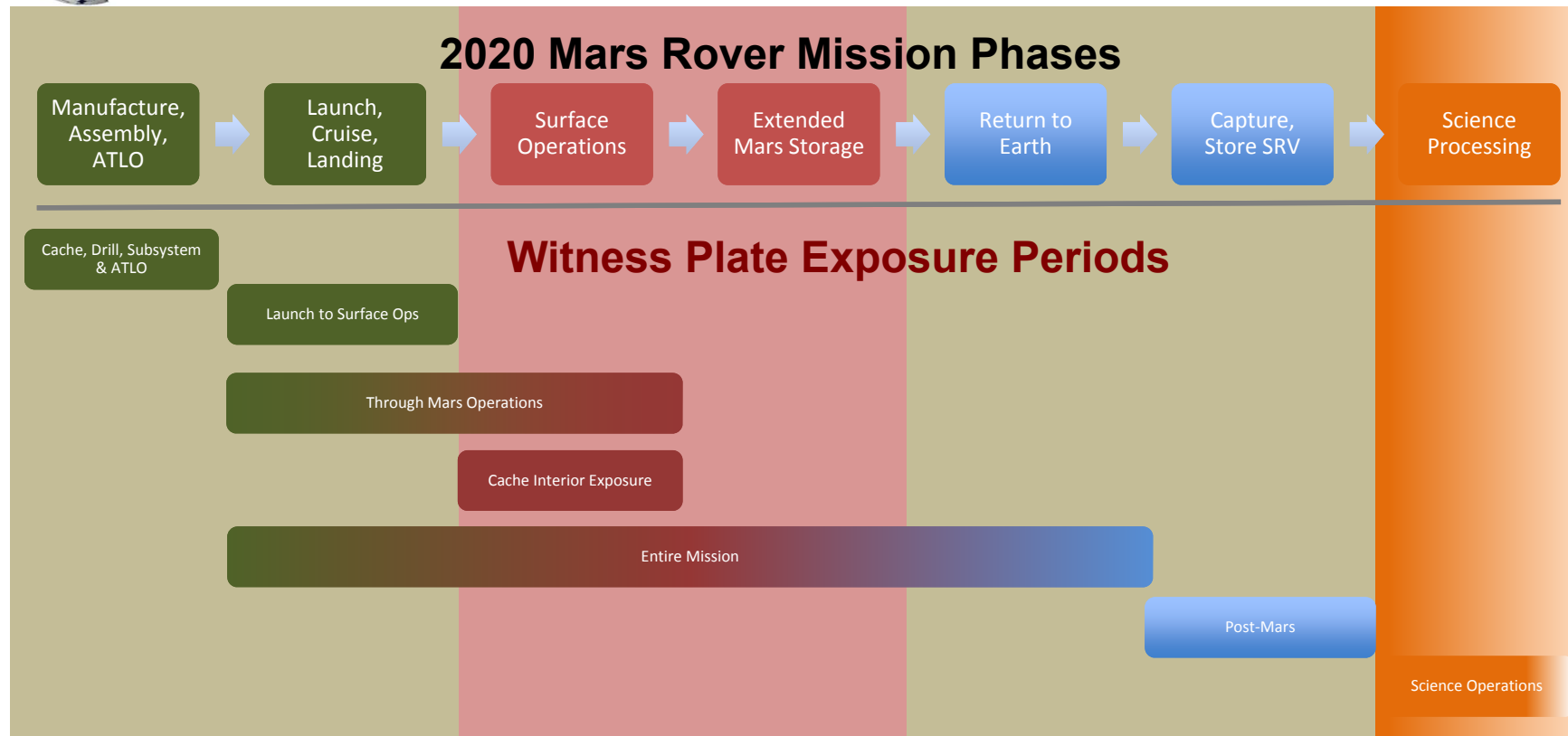
Cleaner is Better!

dirtier

OCP's proposed threshold for clean enough

Incremental benefit to science needs to be traded against incremental consequences to engineering

cleaner

Finding: Since we don't know the concentration of the organic molecules of interest in the martian samples that might be returned by MSR, there is an unquantifiable scientific reward relating to detectability above background that would progressively be increased the cleaner the samples are. The scientific rewards must be balanced against the technical risks.

The Importance of Witness Plate Planning

2020 Mars Rover Mission Phases

| Manufacture, Assembly, ATLO | → | Launch, Cruise, Landing | → | Surface Operations | → | Extended Mars Storage | → | Return to Earth | → | Capture, Store SRV | → | Science Processing |

Witness Plate Exposure Periods

- Cache, Drill, Subsystem & ATLO
- Launch to Surface Ops
- Through Mars Operations
- Cache Interior Exposure
- Entire Mission
- Post-Mars
- Science Operations

EXAMPLE

Finding: In order to track the introduction of contaminants, the witness plate strategy would need active control over witness plate exposure during discrete mission phases. An example is shown here. The exposure timing is left to the M2020 science team.
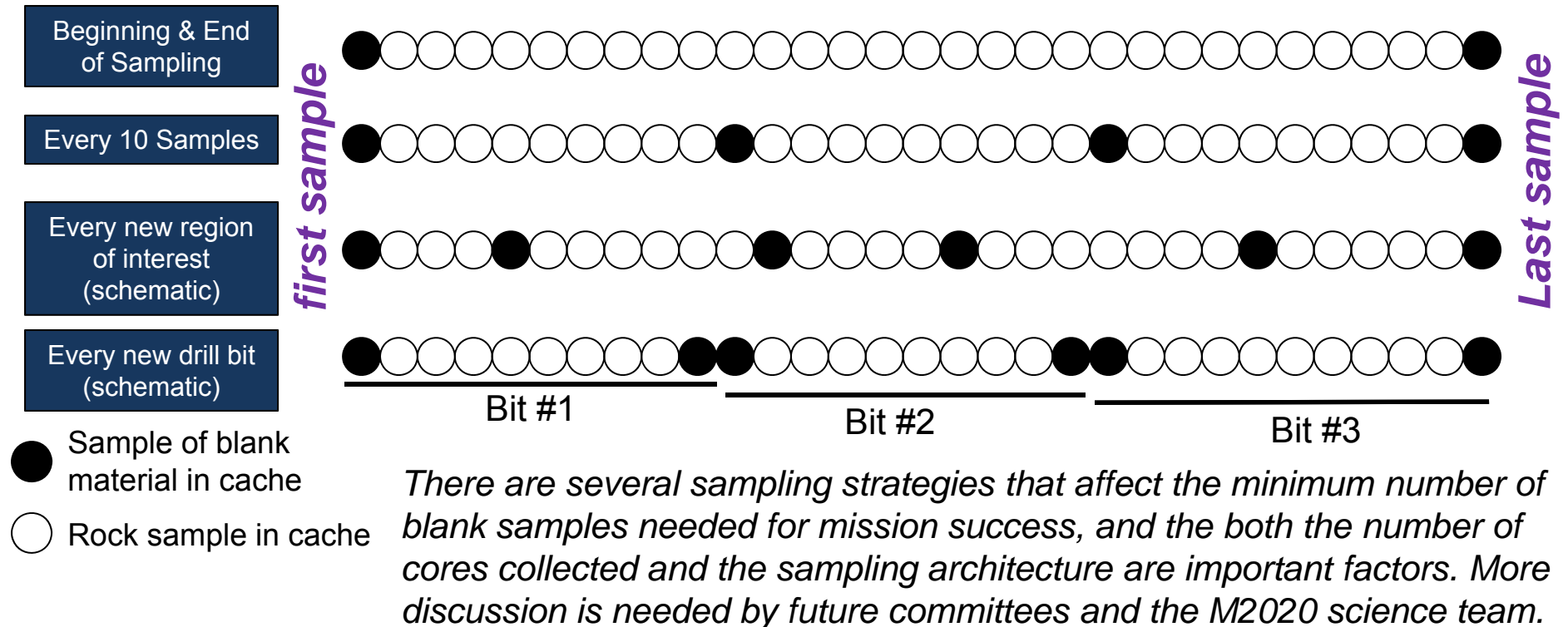
Blanks

Strategies For Blanks

Beginning & End of Sampling

Every 10 Samples

Every new region of interest (schematic)

Every new drill bit (schematic)

⬤ Sample of blank material in cache

◯ Rock sample in cache

Sequence of sample acquisition

first sample

Last sample

Bit #1   Bit #2   Bit #3

There are several sampling strategies that affect the minimum number of blank samples needed for mission success, and the both the number of cores collected and the sampling architecture are important factors. More discussion is needed by future committees and the M2020 science team.

Finding: The return of *in situ* drilled procedural blanks are a critical part of the science of this mission.
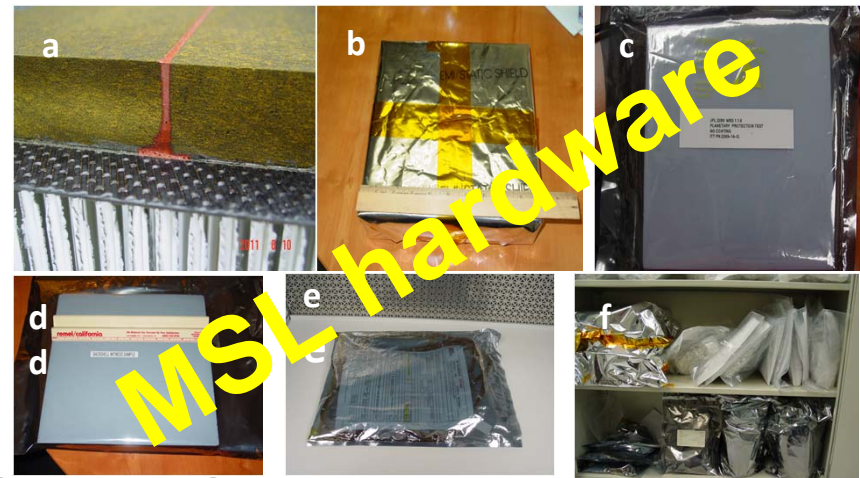
Archive Facilities Needed

- A **<u>systematic approach, and necessary supporting facilities</u>**, should be established to preserve and curate inorganic, organic, and Planetary Protection-related samples

  – These archived materials are necessary to compare against compounds that may be found in the samples

- The samples will arise from spacecraft assembly, contamination control, and verification processes prior to flight

- Analyses of these samples may occur during the M-2020 mission, and afterwards as reference samples during post-flight analyses

JSC Curation Complex

JPL Planetary Protection Archive

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Conclusions

1. We expect that returned Mars samples would have detectable amounts of Earth-sourced contaminants. These must be characterized. This characterization is the first step of the science to be performed on returned samples, and should be done to the same quality.

2. Organic analysis of samples contaminated to varying degrees is a standard practice. It is possible to measure molecules of interest in the presence of contamination. These strategies may be applied to returned martian samples.

3. OCP has proposed an estimate of the minimum acceptable amount/character of organic contamination on returned martian samples. However, cleaner would be better!

4. M-2020 should carry out systematic planning in the areas of witness plates, archive facilities, and blanks/standards.

BACKUP

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Instruments and Techniques

Category 1: Non-Destructive, Sample Surface-Based Technique

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Deep UV Raman/Fluorescence Spectroscopy	1A, 2C	Non-destructive. No surface preparation required.	Raman: Aromatics <10-4 w/w (<100 ppm) Aliphatics <10-4 w/w (<100 ppm) 50 um/spot at 1 to 10s per spot Fluorescence: Aromatics <10-6 w/w (<ppm) Single cell sensitivity (~2 pg carbon) [6] 50 um/spot at 1s per spot	Performance can be enhanced with longer integration times. Sensitivities depend on organic species and are matrix dependent. Surface roughness can be handled based on optical system with hit against sensitivites or integration times. Quantification is difficult	[1] Beegle, et. al., Lunar and Planetary Institute Science Conference Abstracts 45: 2835.[2] Ghosh, et. al, Applied Spectroscopy 66 (9): 1013–21. [3] Tuschel, David D, Aleksandr V Mikhonin, Brian E Lemoff, and Sanford A Asher. 2010. "Deep Ultraviolet Resonance Raman Excitation Enables Explosives Detection." Applied Spectroscopy 64 (4), 425–32.[4] Bhartia, et.al., International Society for Optics and Photonics. 83581A–83581A–9.[5] Johnson, et.al., Astrobiology 11 (2): 151–56. [6] Bhartia, et. al.,.Applied and Environmental Microbiology, 2010, 78(21), p 7231-7237)
Confocal Raman Spectroscopy at up to 360nm micron spatial resolution	1A, 2C	Non-destructive. Benefits from thin section, polished surface prep. Or can be fresh fracture surface with contour following confocal optics.	Lower limit from ~0.1 to 1 wt. % per spot analysis (30s) [1] with absolute detection limit correlated to number of analyzed spots. <50 ppm graphic carbon [1] Single cell detection sensitivity. [2]	Detection limits strongly dependent on laser wavelength, target species. 532 nm excitation provides non-quantitative detection of hematite, beta-carotene. Raman spectra are subject to organic and mineral background fluorescence, which can be mitigated by time-gating. Careful consideration for laser wavelength and power to avoid sample damage. Quantification is difficult	[1] Wang, et. al.Journal of Geophysical Research, 108(E1), 5005 [2] Ref TBD
FT-IR Spectroscopy	1A, 2C	Non-destructive. Benefits from thin section and polished surface prep, but can be used on unprepared surfaces. Ideally KBR pellets are made of samples.	Lower limit ~5 ppm for specific targets 10 um/spot >200 min per spot [1]	Not sensitive to graphitic carbon. Samples are ideally crushed and made into KBR windows [2] Quantification is difficult	[1] Ref TBD [2] General approach for FTIR in literature. [2a] Bhaskar, Nature and Science, 2009;7(5), 45-51 (Dergoan H5 Chondrite) [2b] Matrajt, et. al., Astronomy & Astrophysics, 416(3), 2003, 983-990 (Tagish Lake Meteoirte) [3] Anderson, et. al., Review of Scientific Instruments, 76, 034101 (2005)
IR Reflectance Spectroscopy	1A, 2C	Non-destructive.	Lower limit typically ~0.5-1 wt. % per spot analysis, with absolute detection limit correlated to number of analyzed spots.	Sensitive to only specific organic species. Ideal for rapid mineral context. Quantification is difficult	[1] Not used actively for organics detection

Category 2: Slightly Destructive to Sample Surface

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Laser desorption-MS	1A, 2A, 2C	Vacuum exposure, polished thin section or fresh fracture surface, laser beam damage	Semi-quantitative, wide range of sensitivites including sub-fmol.	Specific to PAH or other large conjugated systems. No chromatography, so no distinction of isomers or enantiomers.	
Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)	1A, 2A, 2B, 2C	Vacuum exposure, polished thin section or fresh fracture surface, ionization damage	Non quantitative, low ppb sensitivity. Very sensitive to surface contamination. Maps organic and inorganic species. For isotopes: ppt sensitivity, 50nm spatial resolution 1 - 5 per mil isotopic resolution dependent on instrument and isotope.	Provides context of isotopes. C, N, S, D/H	
LAL Assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.		Gram-negative microbes only. Insensitive to gram-positive microbes.	
ATP luminometry	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	Proportional to microbial metabolic activity	Insensitive to spores	
Microbial plating assay	2F	Wipe, swap, extraction. Sample exposed to water/solvent, wipe/swab detritus.	~0.01% maximum sensitivity to abundance of microbial flora		

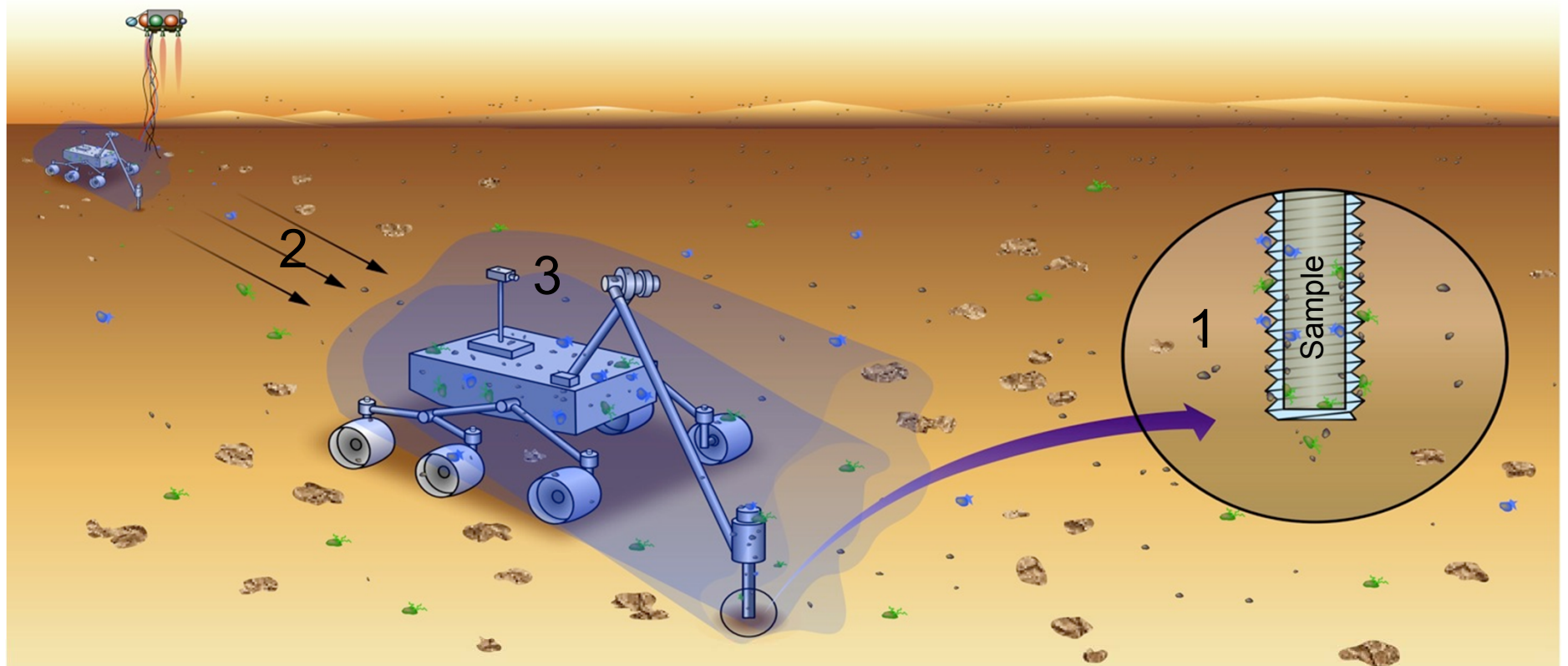## Category 3: Destructive of Whole Sample

Analytical Method	Objectives Addressed	Sample Requirements and Degradation	Performance Characteristics and Detection Limits	Method Notes (Dependencies, Limitations, Assumptions, etc.)	References
Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO2.	Splitting to NPD detectors, nitrogen may be accessible.	
Total inorganic carbon and total organic carbon	1B, weight % abundance of organic carbon	Both non acid and acid digestion used to separate inorganic from organic	~1-10 ppb in 1 ml of gas or about 1E-11 to 1E-12 g of CO2 (??)	Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, … kind of tough to say in general. Evolved compounds other than CO2 can be detected.Nitrogen can be done at the same time. Need nitrogen perhaps even D/H.	
Microfluidic Capillary Electrophoresis	2A, 2D, 2F		1 to 10 ppb following extraction, derivatization	Process blanks?	
GC/MS FAME using cyanopropyl stationary phase	2A, 2E, 2F		Detection down to below ~ 1 ng per compound	Detection limits are potentially lower if GC does not have significant non-specific absorption, or other issues. Lower detection limits possible by radio GC or LC using radiolabeled derivatizing agent.	
GC/MS using high temperature GC column, and ammonia chemical ionization				Probably similar detection limit to above (methanizer w/ flame ionization), depending upon MS capability. Back calculating the sensitivity dependent upon the background, detector noise, … kind of tough to say in general. Evolved compounds other than CO2	
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
Pyrolysis-MS, Pyrolysis-GC-MS		Destructive via pyrolysis. Typical amount of sample required per analysis: x mg		Does not indicate compounds present, only their fragments.	
Liquid extraction and derivatization followed by GC-MS	2A, 2D, 2E, 2F	Extraction, destructive	Detection limits are compound-specific, but as low as ~1 pmol; more like 100pmol for many hydrocarbons. Nominal mass accuracy in typical system.	Can use library mass spectra to suggest compound class. QqQ-MS can target specific compounds, ultrahigh resolution MS can deduce molecular formulae. Can target chirality (e.g. amino acids, amines, etc). Requires authentic standard for definitive identification.	
LC-MS	2A, 2D, 2E, 2F	Sample crushing followed by destructive solvent extraction, possibly hydrolysis, desalting, and more	Detection limits are compound-specific, but typically ~1 fmol 5 ppm to sub ppm mass accuracy possible	QqQ-MS can target specific compounds, ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APcI, APPI) can target different functionalities. Targets M+1 parent ion. Can target chirality (e.g. amino acids). nano-LC can improve sensitivity 10-100 fold. Can couple mass and optical (fluorescence, absorbance) detections. Requires authentic standard for definitive identification. Cannot use library spectra.	
high resolution MS (infusion or DART)		Sample crushing followed by destructive solvent extraction, possibly hydrolysis. Minimal other workup reqired	Semi-quantitaitve, wide range of sensitivites including sub-fmol, sub ppm mass accuracy possible	Ultrahigh resolution MS (e.g. ToF-MS, FT-MS) can deduce molecular formulae. Different ionization modes (ESI, APcI, APPI) can target different functionalities. Targets M+1 parent ion. DART required minimal preparation and has ~1 mm spot size. No chromatography, so no distinction of isomers or enantiomers.	
liquid ICPMS		destructive; sample oxidized to sulfate	5 nmol dissolved sulfate at 0.15‰ precision;	targets any sulfur in solution as sulfate; can be used for organic compound-class analysis	Paris G., Sessions A. L., Subhas A. V. and Adkins J. F. (2013) MC-ICP-MS measurement of δ34S and Δ33S in small amounts of dissolved sulfate. Chemical Geology 345, 1–12.
combustion EA-IRMS		destructive	25 nmol N, 41 nmol C, both at ±1.0‰precision;	relatively low sensitivity but high precision (0.1 permil)	Polissar P. J., Fulton J. M., Junium C. K., Turich C. C. and Freeman K. H. (2009) Measurement of 13C and 15N Isotopic Composition on Nanomolar Quantities of C and N. Analytical Chemistry 81, 755–763.
pyrolysis EA-IRMS		destructive	1 ug organic H or O	precision of 2-4 permil for H; O??	
Tunable Laser Spectroscopy	2B	Destructive via pyrolysis. Typical amount of sample required per analysis: x mg			
GC-combustion-IRMS	2B	Extraction, destructive	130 pmol CH4 at 0.1‰precision;	Requires excellent separation of compounds and prior identification of structure.	Merritt D., Hayes J. M. and Marais Des D. J. (1995) Carbon isotopic analysis of atmospheric methane by isotope-ratio-monitoring gas chromatography-mass spectrometry. Journal of Geophysical Research 100, 1317–1326.
GC-pyrolysis-IRMS	2B	Extraction, destructive	25 nmol H as heptadecanoic acid at 2.7‰ precision	compound must be GC-amenable	; Hilkert A., Douthitt C., Schluter H. and Brand W. A. (1999) Isotope ratio monitoring GCMS of D/H by high temperature conversion isotope ratio mass spectrometry. Rapid Commun. Mass Spectrom. 13, 1226–1230.
GC-ICPMS	2B	Extraction, destructive	20 pmol S as dimethylsulfide, at 0.3‰ precision;	compound must be GC-amenable	Amrani A., Sessions A. L. and Adkins J. F. (2009) Compound-Specific δ34S Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS. Analytical Chemistry 81, 9027–9034.
PCR	2F				
FISH -- Fluorescence imaging of fluorescently tagged compounds	2F			only useful in very specific conditions for terrestrial contaminants	
ELISA	2F			only useful in very specific conditions for terrestrial contaminants	

There are at least three pathways by which contaminants can be transported into samples:
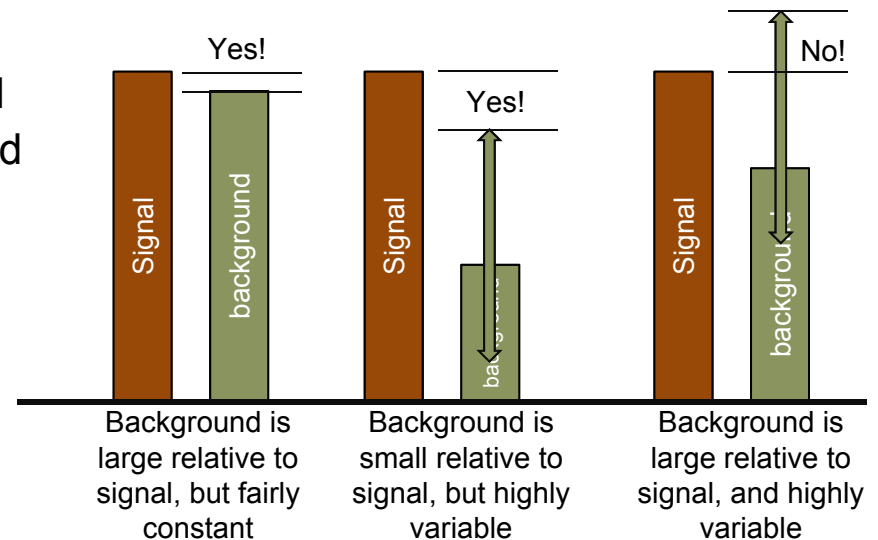
1. Direct contact – microbial and molecular contaminants are transferred from the hardware surfaces to samples by direct contact.

2. Particle transport – Microbes and molecular contaminant-containing particles are dislodged from spacecraft hardware surfaces by wind or by mechanical forces and are then carried by wind to the sampling ground or into the sample tube.

3. VOC transport – outgassed volatile organic compounds from nonmetallic parts will diffuse or be carried by wind to condense on the sampling ground, sample contacting hardware, and samples.

Levels of Signal and Background for a Successful Measurement

- A measurement involves subtracting the "background" signal from the total measurement. Two significant factors:
  - Average size of background versus signal
  - Uncertainty or variability in the background around this mean
    - Could be high either because it was not measured well, or because it is inherently variable

- If the background signal is large but exceptionally stable, then we can confidently resolve signals that are orders of magnitude smaller.

- If a background is highly variable, then it needs to be much smaller than the analyte concentration.

- Contamination levels are likely to be somewhat predictable
  - e.g., if the sample tubes are prepared together in the same way, they are likely to have similar levels of the same contaminants

Can We Confidently Detect A Signal Above Background Contamination?

Background is large relative to signal, but fairly constant

Background is small relative to signal, but highly variable

Background is large relative to signal, and highly variable

Finding #12: In addition to knowing the identity and concentration of organic contaminants, it is important to know their variability as a function of multiple measurements (from sample to sample or blank to blank) as well.

Mars 2020 Organic Contamination Study Panel
Preliminary results for planning/discussion and review purposes only