Science Priorities Related to the Organic Contamination of Martian Landers

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1. Introduction

A current goal of the Mars Exploration Program is to achieve an understanding of the possible emergence and duration of life on that planet. This demands an increasing focus on the quality of measurements that address Astrobiology objectives. Continuing advances in instrument technology lead to the possibility of measurements of increasing sensitivity and selectivity. Thus the steps necessary to reduce the potential impacts of terrestrial contamination on *in situ* Mars measurements require increasing attention. The Mars Program Office at NASA Headquarters chartered the Organic Contamination Science Steering Group (OCSSG) to address this issue following the recommendation of the Mars Exploration Program Analysis Group (MEPAG) at its September 2003 meeting [MEPAG, 2003]. The charter of the group was to define the contamination problem and suggest plans and priorities for solution that could provide direction for the engineering teams responsible for the design, fabrication, assembly, and processing of Mars landed systems. The group consisted of scientists conversant with a range of *in situ* measurement techniques for organics and engineers familiar with Mars lander designs as well as spacecraft cleaning and contamination characterization techniques. This report is a summary of the analysis of the OCSSG.

The primary focus of the study was organic contamination introduced into those Mars samples that would be delivered to sensitive analytical instruments after processing by lander acquisition and sampling devices. It is recognized that requirements set by the Planetary Protection Policy in effect for any specific mission only indirectly address the larger question of the potential interference from terrestrial contaminants during *in situ* measurements. Furthermore, we considered certain non-organic molecular or particulate contaminants that might also impact Astrobiology-focused measurements. The contamination issues were considered most specifically in this report with reference to the 2009 Mars Science Laboratory (MSL) Mission, currently under definition. However, the relevance to other lander missions including the Mars Scout Phoenix Mission and a Next Decade Astrobiology Mission was also considered by the OCSSG. Phoenix is presently under development for a 2007 launch [Smith, 2003] and a possible Next Decade Astrobiology Mission has been described in very general terms by the Mars Program Science Synthesis Group [MPSSG, 2003] as a candidate Astrobiology focused mission that would employ the next generation of measurement tools. Although the primary focus of the analysis of the OCSSG was on the impact of terrestrial contamination, the issue of cross contamination of organic material between different Mars samples was also considered. Because strategies utilized by the Viking mission successfully reduced terrestrial contamination, they served as valuable reference points for the present study.

The OCSSG divided the issues highlighted in its Charter into four primary areas of focus:

1. Identify and quantify the contaminants of most concern with regard to their possible adverse impact on the goals of each lander mission,
2. Understand methods of quantifying residual contamination, its abundance and transport during all stages of lander development and operation,
3. Suggest possible contamination mitigation options, and
4. Examine the use of controls and facility-provided standards to be analyzed by lander instruments after arrival at Mars.

As detailed in Sections 2 and 3 of this report, the first two items can provide direction and contamination requirements for the engineering teams that design, fabricate, and test the landers. For example, a comprehensive contamination-monitoring plan during the development of MSL can provide not only an understanding of the level of organics that are transported to Mars in this mission, but also a documented reference for future missions. Items 3 and 4 are addressed in Sections 4 and 5. Section 4 of this report addresses strategies for contamination mitigation. Success in the area of contamination mitigation is important for Phoenix and is also likely to be key to achieving major goals of the MSL and future astrobiology landed missions. Section 5 addresses the possible use of standards and controls. Some residual contamination is likely to be observed by sensitive instruments on the surface of Mars, even with the best efforts at mitigation and the use of controls may then be important for achieving definitive scientific conclusions.

2. Organics of Interest and Contaminants of Concern

2.1 Sources of martian organic molecules: The search for reduced carbon species relevant to Astrobiology will be an important aspect of the missions considered by the OCSSG. However, organic compounds in near-surface materials on Mars may be derived not only from possible biotic or prebiotic processes, but also from various abiotic processes such as exogenous delivery from meteoritic or cometary material or synthesis in hydrothermal systems. Furthermore, reduced carbon species from any source will likely be transformed over time to some degree through chemical processes, including the transformation to more highly oxidized species. However, these mechanisms are presently not well understood. The identification of the source of organic compounds that might be discovered on or near the surface of Mars can be addressed by a variety of investigations. These include identification of specific molecules known to be associated with meteoritic sources, analysis of the distribution of organic molecules in different oxidation states, the determination of the molecular weight (mw) distribution in homologous series of these molecules, and a determination of the $^{13}C/^{12}C$ and D/H ratio in organic compounds (Kerridge, 1999, Cronin, 1993). For example, the amino acid α-aminoisobutyric acid (AIB) found in some meteorites, such as Murchison, is often used as a marker for extraterrestrial amino acids, since this molecule is not found in measurable amounts in sediments. The scientific objectives of MSL and follow-on missions are not only to search for specific biomarkers, but also to understand geochemical cycles that include reduced carbon compounds. Very little is presently known about the distribution, abundance, or chemical reaction products of reduced carbon-containing compounds in near-surface materials on Mars, although aromatic hydrocarbons, phenol, and benzonitrile have been detected by pyrolysis of small samples of the martian meteorites EET A79001 and Nakhla [Sephton et al., 2002]. Table 1 illustrates a range of molecular classes and compounds that are potential contaminants. Appendix A expands this list by giving estimates of contamination levels of concern and first order estimates of the possibility of migration of the contaminant to a sample delivered to an analytical instrument.

2.2 Transformations of organics on Mars: Although the Astrobiology objectives will place a high priority on characterization of reduced carbon compounds in samples collected for analysis, it is recognized that several chemical processes that potentially exist in the martian environment may transform these species. Models of such processes of organic degradation fall into several categories and it is likely that more than one mechanism operates. Each proposed mechanism has a potentially different consequence for the fate of organics.

For example, hydrogen peroxide would be expected to selectively oxidize organic compounds, resulting in the formation of species that may not have been detected by the Viking GCMS, such

as mellitic acid salts (Benner 2000). Solar ultraviolet radiation may cause photolysis of atmospheric species resulting in the formation of "odd-H" (H, OH, HO_2, and H_2O_2) compounds (e.g. Hunten, 1974, Barth et al. 1992). Subsequent recombination of these reaction products may produce oxidizing species that precipitate onto the surface.

Alternatively, superoxide radicals, which are more strongly oxidizing than hydrogen peroxide, are generally responsible for "deep oxidation" of organics, resulting in more complete oxidation (Yen et al., 1999; Haber, 1996) and, possibly, the complete removal of organic material from the surface of Mars (Chun et al. 1979). UV-silicate interactions may produce radical species (Yen et al., 2000) directly in the silicate matrices. The non-bridging oxygen defects resulting from broken Si-O bonds are mobile, and can migrate through silicate lattices. The soil and dust surfaces would then be strongly oxidizing, but the atmosphere itself need not be oxidizing.

Other mechanisms require both UV and atmospheric oxidants. The free radicals from radiation damage are highly reactive, and could easily form semi-permanent complexes, such as such as perchlorates from photolyzed, complexed halide compounds (Zent and McKay, 1994).

Table 1. Contaminants of concern for Mars landed missions (expanded in Appendix A)

Molecular class	Examples		Molecular class	Examples
C, H aromatics	benzene, toluene, higher molecular weight aromatics, PAH		**Carbonyl**	Esters, ketones, aldehydes and their mw distributions
S, N, O heterocyclic aromatics	furan, pyridine, pyramadine, benzothiophene		**Sulfonic, phosphonic acids**	Methanesulfonic acid
Carboxylic acids and their salts	Alkyl & aromatic acids, fatty acids		**Lipids and derivatives**	HC chains, fatty acids, fats, phospholipids. Hopanes, steranes
Non aromatic hydrocarbons	Alkanes, alkenes (i.e. isoprenoids such as pristane, phytane)		**Sugars and derivatives**	glucose
Nitrogen containing compounds	Amino acids, amines, amides, purines, pyrmidines, porphyrins		**Proteins**	Polar and non-polar
Alcohols	Methanol, higher molecular weight linear and branched chain alcohols		**Nucleic acids, nucleotides**	DNA fragment

2.3 Contamination issues driven by mission science goals: The OCSSG considered contamination most specifically in the context of three example missions.

(1) the recently selected Phoenix Scout Mission, is designed to land in what is predicted to be an ice-rich region and analyze near-surface and sub-surface samples. Organic contamination is of concern to this mission team, since a mass spectrometer is part of the payload. This instrument will search for organic molecules evolved from surface and near-surface samples and will also analyze atmospheric gases.

(2) The 2009 Mars Science Laboratory (MSL), presently under definition, is expected to carry out an ambitious search for organic molecules in a wide variety of locations that can be accessed by this lander. A powerful analytical laboratory is in the baseline for this mission with sample preparation using a facility acquisition and processing station. A concept for this station on the MSL is illustrated in Figure 1, taken from the Proposal Information Package [MSL PIP, 2003] for this mission.

(3) A Next Decade Astrobiology Mission was defined by the Mars Planning Science Synthesis Group as a candidate Astrobiology-focused mission with life detection experiments as likely elements of the payload. The MEPAG Astrobiology Field Lab Science Steering Group further defined (Steele et al., 2004) the objectives of this mission. It is assumed that this mission might carry advanced extinct or extant life detection experiments that would be sensitive to even lower abundances of complex organic materials, and that stringent control of the terrestrial bioload will be critical to the success of this mission.

The specific contamination thresholds described in this report are primarily directed toward MSL, although the Phoenix Mission Team may consider implementation of elements of this approach as resources allow. Contamination thresholds for future missions will need to be revisited as measurement capabilities and contamination mitigation technologies develop.

2.4 OCSSG definition of clean: Since analytical laboratory instruments are expected to play a key role in identifying and characterizing organic molecules, terrestrial contamination introduced during sample acquisition and processing is a significant concern. The instruments in the analytical laboratory of MSL will accept samples that not only have contacted sample acquisition tools, but also have been processed by crushing and grinding tools. However, contaminants on this lander will not be of concern if they are not incorporated into these samples above a certain threshold. Thus, the OCSSG adopted a system-level definition of "a clean sample" as a sample that is delivered to an instrument with LESS THAN a specific level of organic contamination.

2.5. Derivation of cleanliness thresholds for MSL: Example levels of cleanliness in samples delivered to analytical instruments as specified for the MSL rover are given in Appendix A. These levels are based on consideration of the science objectives for MSL and likely science objectives for astrobiology-focused follow-on lander missions.

Contamination levels of concern can be derived from estimates of the abundance of reduced organic material that is expected to be delivered by meteorites to the surface of Mars and mixed into the regolith. For depths of gardening from meters to a kilometer, reduced organic groups such as aromatics or their oxidation products at mixing ratios of hundreds of parts per billion to hundreds of parts per million are expected [Benner, 2000]. However, in order to understand the distribution of species within these groups and the effects of chemical transformation processes

on Mars, it is highly desirable to measure a range of species to parts per billion (mass mixing ratio to the matrix). Keeping terrestrial contamination to below 1-10 parts per billion in Mars samples should allow significant scientific conclusions to be reached concerning the fate of organic material delivered by meteorites. The total molecular carbon contamination allowed could be substantially higher (for example, 40 ppb) if the contamination by specific critical species or classes was maintained at dependably constant levels. Although extinct or extant life on Mars has the potential to leave signature organic material in either much higher abundance than the parts per billion levels discussed above, the OCSSG concluded that a definitive search for such signatures could be implemented on MSL by maintaining terrestrial contamination below levels of 1-10 ppb for relevant biomarkers.

The present state of the art for detection thresholds for analysis of volatile organic compounds in meteoritic materials in terrestrial laboratories can be as low as 10^{-13} mole/g using gas chromatograph mass spectrometers and on the order of 10^{-12} to 10^{-11} mole/g for a single liquid chromatography analysis of amino acids [Glavin et al., 1999,2003], although highly specific analysis techniques may detect even smaller quantities (i.e. sub 10^{-18} mole for immunochemical

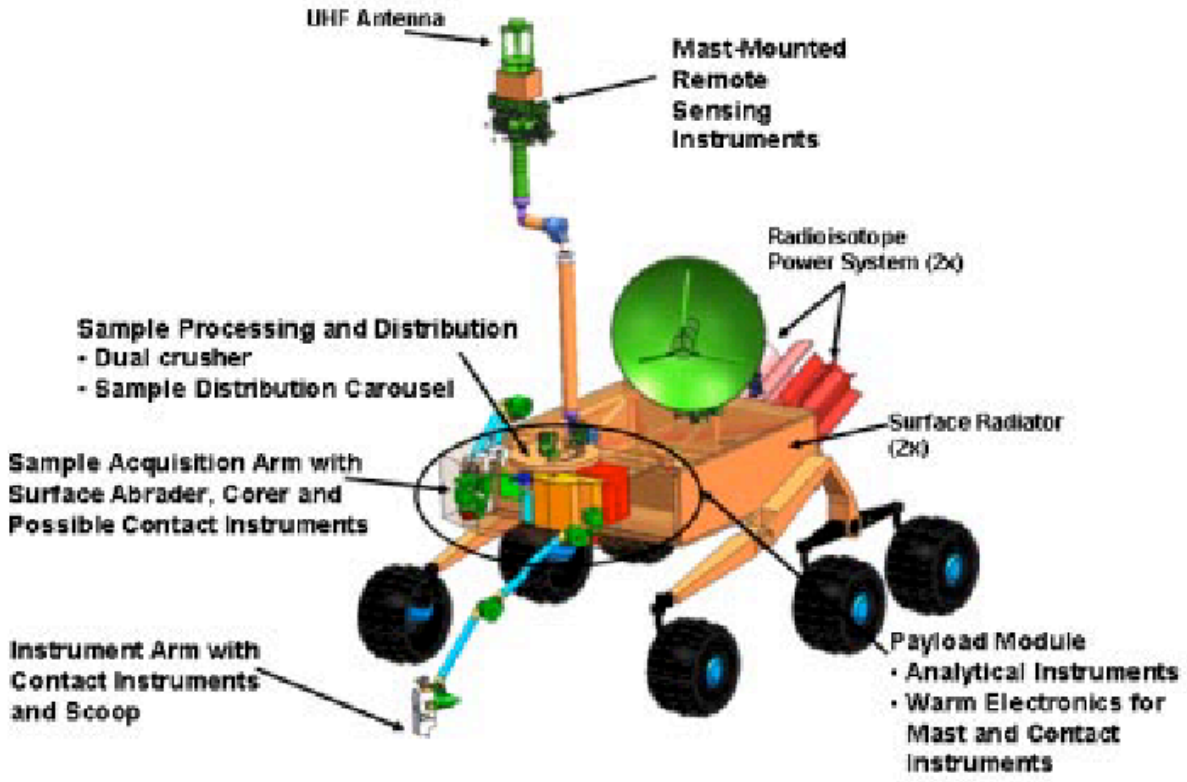

Figure 1. The location of the sample acquisition and processing elements of MSL is illustrated in the MSL Proposal Information Package.

reactions [Guomin et al., 2000]). These detection limits equate to sub parts per billion mixing ratios by mass. Miniaturized laser desorption mass spectrometers developed for space flight applications can detect several parts per billion by mass of polyaromatic hydrocarbons. The OCSSG concluded that the thresholds driven by the scientific goals of MSL were well within the capability of *in situ* instruments that were likely to be selected for this mission.

2.6 Sources of terrestrial organic contamination of Mars samples: Several potential sources of terrestrial contamination could adversely impact the *in situ* search for organic molecules and their sources and sinks on Mars. These include moderately volatile organic molecules that might be released from materials used in spacecraft fabrication, particulate material that might contain organic residues, and organic molecules produced from the residual terrestrial bioload. Even with careful cleaning of sample acquisition and processing systems, transport of contaminants to these systems in various phases of the missions may occur. These contaminants are of concern if they interfere with the measurement of organic molecules that are targets of payload instruments. Most terrestrial, reduced carbon containing species that might be incorporated into a martian sample are a potential source of interference with high quality *in situ* measurements.

2.6.1 Organic materials contained in spacecraft hardware: Organic compounds are utilized extensively in spacecraft hardware. Complex mixtures of branched and straight chain aliphatic hydrocarbons are the most common contaminants. Lubricants and pump oils found in many industrial environments are sources of these compounds. These can generally be removed with most common solvents (Freons, alcohol, acetone). Silicones are also very commonly employed as lubricants, materials, sealants and adhesives. Silicones can outgas or leach out of silicone based polymers. Like aliphatic hydrocarbons, silicones exhibit a broad range of molecular weights. The most common silicones are polydimethylsiloxane and polymethylphenylsiloxane. This class of organic contaminants is difficult to remove completely; although freon and toluene are at least partially effective as solvents.

Salts of organic acids are used in mold release agents, soaps, silicone polymer activators, and fluxes and are best removed by polar solvents such as alcohols. In thermal vacuum systems the copper cold-finger may react with hydrolyzed esters to form (green) organic copper salts.

Esters are found in plasticizers, pump oils, adhesives, polymer degradation products and many other materials. Phthalates are common contaminants.. Phthalate esters such as Bis 2-ethylhexyl phthalate (DOP) are used to make vinyl plastics and in many other polymer formulations. DOP is a common catastrophic contaminant often discovered after a thermal vacuum processing. Acetone, methyl ethyl ketone (MEK), and alcohol solvents are often used to remove these phthalate esters.

Epoxy is frequently used in spacecraft construction and consists of a class of compounds with a range of molecular weights and chemical/physical properties. These may have complex formulations and can be a source of other compounds. Epoxy consists of a mixture of two compounds that requires “curing”, usually by adding a chemical catalyst and applying heat. Curing is not 100 percent complete and uncured components of epoxies can outgas or selectively leach a variety of compounds from the structural materials to which they are applied. These volatile products are generally amines and phenol ethers. The best strategy for removing uncured epoxy is to treat or wipe surfaces with solvents such as alcohol, acetone and aromatic solvents (e.g., toluene). Cured epoxy is difficult to remove by common solvents.

Inorganic particulates can also be released from the spacecraft. Metallic and device-shed particles can be released from the spacecraft hardware either from wear or machining debris. Carbonates are used as fillers in materials and are a major component of “water spots.” Carbonates are also encountered as a corrosion product from paints using potassium silicate binders (micas). Inorganic particulates may adsorb molecular contamination prior to their migration to other locations.

2.6.2 Personnel handling or exposure of instruments or spacecraft components: Manipulation of spacecraft elements often introduces a variety of contaminants into the instruments and spacecraft components. Fingerprints contain a complex mixture of compounds. These residues consist mainly of high molecular weight, long-chain alkyl esters of fatty acids while the more volatile fractions contain free fatty acids. Fingerprints also contain sodium chloride, protein, and urea. Organic acid salts can form when fingerprints react with some metallic surfaces. Fingerprints can be removed by wiping with most common solvents (Freon, alcohol, acetone, and MEK).

Some additional types of particulates can be introduced during handling and construction. Cloth fibers such as cotton, nylon, polyester, lycra, silk, cellulose etc. can be inadvertently introduced from a variety of sources including clothing and cleaning wipes.

Bio-organic materials of concern include dead skin, hair, spores, pollen, and organic wind-blown matter. These comprise the majority of "dust." The Planetary Protection group at JPL monitors a crucial subset of this vast class of materials with separate biological assays. The remainder of dust consists of silicates that are commonly fine components of soil. The composition is mainly fine quartz and mixed silicates. These are also found in construction materials such as wallboard, wood fibers, etc.

Exposure of spacecraft materials to smoke, smog and associated particles can introduce polycyclic aromatic hydrocarbons and tars. Ablation of the entry heat shield and propulsion chemicals may introduce additional levels of contamination to the spacecraft during landing.

2.6.3 Microorganisms (dead or alive): Microorganisms contain a complex mixture of organic compounds. Sterilization does not remove the organic contaminants and therefore dead terrestrial organisms could contribute to the analyzed organic material. A "typical" microbe weighs approximately 10^{-12} g per cell and is comprised of 55% protein, 20% RNA, 9% lipid and 3% DNA. Microbes, a small fraction of which are spores, detected by planetary protection NASA standard methods, are themselves only a fraction of the organic contamination on a spacecraft. The current allowable level for Planetary Protection Level IVA is 300 spores per square meter with the total available bioburden of the landing event to be less than 300,000 spores.

2.7 OCSSG proposals regarding identification of potential contaminants of concern and their thresholds:

1. The OCSSG proposes that each project adopt the "system" definition of clean given in Section 2.4 to assess the degree of terrestrial contamination in samples that are physically processed by sample handling mechanisms.
2. The OCSSG proposes that each project consider maintaining a list of contaminants and their thresholds of concern such as that found in Appendix A, as a guide for both members of the lander development teams and the instrument providers.

3. Quantification of Contamination

Appendix B gives an overview of the contaminants, including their functional groups that are often found on spacecraft surfaces prior to launch. Appendix C lists organic materials that were used in MER. In unusual cases, a spacecraft's payload includes instruments that can measure specific contaminants . More typically, contamination is assayed prior to launch and it is

mitigated only if it might substantially degrade the performance of the spacecraft or the key instruments.

3.1 Analytical techniques: Although a wide range of analytical techniques can be used to analyze spacecraft contamination, the primary methods for molecular contamination measurements use Fourier transform infrared spectroscopy (FTIR), gas chromatograph mass spectrometry, or ion chromatography. FTIR provides chemical functional group information for quantitative analysis and qualitative identification of materials. FTIR allows complex mixtures to be classified while still providing quantitative information on chemical and spectroscopic effects. Time of flight secondary ion mass spectrometry (TOF-SIMS) may be used to supplement the above approaches by providing spatial information on distribution of contamination allowing eluciation of outgassing or contact contamination.

3.2 Hardware sampling: Organic molecular contamination may be sampled using witness plates strategically positioned near in the spacecraft or by directly sampling the hardware with solvents and porous Teflon swabs. Solvents are carefully selected for compatibility with hardware materials. The solvents used include Freon TF, 2-propanol, ethanol, methanol, hexane, dichloromethane, acetone, and various azeotropic combinations. Proper use of solvents removes most residues that may have outgassed and collected on critical surfaces. Very high molecular weight, cross-linked materials are not readily removed by solvents; however, these materials tend to neither migrate nor outgas appreciably. The monomolecular contaminant layer may strongly bind to its host surface and is not easily removed in most cases. Here, the distinction between contamination and corrosion is blurred.

Contamination control methods on Earth can establish more quantitatively the transfer of molecular contamination from a source material or contaminated surface to a sensitive surface by testing the parent material at its assumed operational temperatures. The outgassing or off-gassing constituent flux (contaminant mass per unit collection area per time) can be measured with quartz crystal microbalances (QCM) operating at the assumed temperatures mimicking those of the sensitive hardware. The mass of molecular contamination that will collect on the sensitive surfaces can be estimated. A QCM that operates at 15 MHz (using the principle of beat frequency change between a reference crystal and the collection crystal) can detect 1.56 ng/cm^2 of collected material. Under optimal conditions, transferred molecular contamination can be quantified at this level.

3.3 Typical contamination levels: The amount of molecular contamination found on nominal spacecraft surfaces is generally in the range of 0.05 to 0.3 micrograms per square centimeter ($\mu g/cm^2$). A level of 1.0 $\mu g/cm^2$ equates to an average thickness of 10 nanometers (nm) for a residue having a density of 1.0 g/cm^3. A rule of thumb is that a monomolecular layer is about 1 nm (0.1 $\mu g/cm^2$). After system thermal vacuum testing, contaminants migrate, create a more uniform distribution on accessible surfaces, and, under optimal circumstances, lower the levels of contaminants in areas of critical importance.

Microbial contamination of space craft has been measured in several surveys most recently by Venkateswaran et al., (2001). This research has shown typical bioburdens of spores in the range of 10^6 m^{-2}. This would approximately indicate a contamination level in the range of ~0.1ppb of carbon from bacterial compounds which can be further divided into the relevant classes of molecules to be detected. This does not represent a significant problem to the levels of contamination restriction needed for the instrumentation suggested above, if contamination stays

at this level. It is only when these organisms find food and nutrients to grow that this will lead to problems. The most likely place for this to happen is in any place harboring liquid water and shielded from external radiation or upon landing on Mars. Further studies to understand the possible niches microbes may proliferate in on spacecraft hardware are a necessity. This need has been identified in several studies including the NRC Signs of Life Report [NRC, 2002], updated MEPAG documents, and the 1992 report of the National Research Council's (NRC's) Space Studies Board, *Biological Contamination of Mars: Issues and Recommendations*, [SSB, 1992] that rapid *in situ* methods for measurement of contamination be developed and implemented in replacement of the reliance on culturing methods. Such methods as rapid immunoassays, enzymes assays, ATP detection, RT-PCR etc., can give real time data on the bioload of a space craft assembly. This will allow faster more sensitive and efficient monitoring of bioloads, testing of the efficiency of sterilization procedures and secondary site specific sterilization of hotspots formed after any primary space craft sterilization.

3.4 Contamination Migration: Molecular cleanliness does have a time dependency due to migration of contaminants. Immediately after cleaning, the surface will begin to collect molecular and particulate contamination. Parts cleaned to a very high degree, such as the sample path on the Viking lander, were cleaned to the submonolayer level. At the other extreme, surfaces of any kind left exposed to Class 100,000 cleanroom air will collect particulates over time. This can be minimized by mitigation approaches such as conducting assembly in more stringent class cleanrooms and housing components and systems in particle and vapor barriers. In the extreme case of the Hubble Wide Field Planetary Camera, recontamination is limited to a rate of 47 nanogram/ cm^2/ month and the cameras undergo a monthly decontamination cycle that reduces the level to 1 nanogram/cm^2.

The transfer of particulate contamination occurs particularly through extensive vibration during the launch and landing operations. For this reason, the entire Viking payload was encased in a contamination barrier that was removed in space after launch. Sensitive volumes should be manufactured with non-debris producing materials in clean environments (ISO Class 5, Class 100) and maintained to specific clean levels (PCL 50) prior to enclosure.

Molecular contamination that has accumulated on tools that physically contact martian materials can be directly transferred during sample collection and manipulation. In order to better understand the fraction of contamination that might be transferred during the required sample manipulation, laboratory studies were implemented by OCSSG members at JPL to model these operations. The variables in these studies were the tool materials, the sample analogues, the contaminants, and the temperature. The results of these studies are fully described in Appendix D and provide a basis for estimates of sample/tool organic contamination exchange during collection and manipulation of samples such as will take place during the upcoming Phoenix mission.

3.5 Models of Chemical Migration: Contaminants will migrate at different rates in the 6 to 10 millibar pressure of the Martian atmosphere than in the high vacuum of space. Contamination models developed for space environments should be modified to account for the higher pressure regime of the martian surface and also the range of thermal environments encountered by the lander over the course of the mission.

3.6 OCSS proposals regarding quantification of contamination and its migration:

1. Contamination monitoring should be employed in lander missions that seek to measure reduced carbon compounds and their alteration products on Mars. An important focus of the analysis, during all phases of the development cycle, should be on molecular contamination and its transport.
2. Samples of organic-containing materials, such as plastics and epoxies, employed in spacecraft fabrication should be archived for possible use in studies after MSL organic detection studies are underway. This archive should include different batches of the same component when necessary.
3. Although the tools to monitor organic contamination are largely in place with a focus on quantification of molecular functional groups, these tools may need to be enhanced with more detailed molecular identification if contamination is determined to be above a desired threshold.
4. DNA assays should be carried out over the course of the development for selected critical elements of MSL.
5. Rapid *in situ* methods of bioload monitoring should be implemented and protocols established to ensure that these methods replace the older culture based criteria.
6. The relevance of existing contamination transport models to predict migration of contaminants during long-term MSL operations should be assessed. The feasibility of adapting these models to pressure and temperature conditions present on the surface of Mars should be evaluated.
7. The primary analysis of contamination levels on the surface of Mars will be derived from measurements made by the selected payload. After this selection, the MSL team should evaluate the cost/benefit trade of including simple sensors such as quartz microbalance devices for contamination monitoring during cruise and after landing.

4. Contamination Mitigation

The process of contamination mitigation involves many steps that start with the design of key isolation barriers and include fabrication material selection, spacecraft and instrumentation cleaning, identification of key contaminant levels throughout the development project, and monitoring a subset of the contaminant levels during the mission. The most critical areas are those that come into physical contact with Mars solid phase or atmospheric samples. These areas require higher standards of cleanliness and more attention to monitoring of contaminants. However, due to the possibility of contamination migration from other parts of the spacecraft over the course of development and implementation of a lander mission, great attention must also be paid to the cleanliness of all elements of a lander system and the assembly and test environments to which each lander is exposed.

4.1 Identification of sensitive areas: Surfaces of sample acquisition and processing mechanisms, or surfaces in close proximity to these surfaces, have the highest potential to compromise the scientific detection of organic material in the Martian soil by terrestrial contamination. It is important that the sensitive areas be identified early in the design of a lander such as MSL. These areas should then be isolated from terrestrial organic sources to the greatest extent possible during all on ground integration and test operations as well as during flight and

operation. Selected surfaces should be designed to operate at elevated temperatures to reduce their collection of terrestrial contaminants. **The spacecraft design should minimize, to the greatest extent possible, the total surface area, volume and geometric complexity of those regions where samples are processed.**

4.2 Materials selection: Consideration should be given in materials selection to reduction or elimination of materials that produce the molecular compounds identified in Table 1. Although this may not always be possible, attention should be paid to the quantity and location of these materials. Of particular importance, for example, are materials in the MSL Analytical Laboratory instruments and the MSL sample acquisition and processing mechanisms. The information on materials throughout the MSL system should be specified as accurately as possible as it will then be used to develop contamination models of the spacecraft. This consideration should extend not only to an examination of materials lubricants, epoxies, and resins, but also to selection of solvents used to clean and reduce the bioload of spacecraft materials. For example, if a solvent, such as isopropyl alcohol, or an oxidizing agent, such as hydrogen peroxide, is used to clean, sample, or reduce the bioload on spacecraft materials, consideration should be given to the residue from that material that might remain on the lander at Mars and migrate to a sample. Materials in sensitive areas should generally meet total mass loss (TML) and volatile condensable material (VCM_ levels of less than 1.0% and 0.1% respectively.

4.3 Cleaning procedure examples: Organic contamination comprises a significant fraction, usually over 50%, of both the volatile (film) and non-volatile (particulate) portion of the spacecraft hardware surface contamination. Spacecraft are typically cleaned to a non-volatile residue cleanliness level of 1 microgram/ cm^2 which is known as level A. Level A10 is 0.1 microgram/ cm^2, and is considered extremely clean for most missions. One of the most extreme cases of flight hardware surface cleanliness is the Viking sample handling hardware. The sample path hardware was cleaned to 1 nanogram/cm^2 and the sample path hardware was sealed and pressurized after cleaning to protect against recontamination. The following techniques serve to clean or reduce organic contamination:

- **Precision cleaning** is a general name for a process that is targeted at removing both particles and molecular films. It consists of a series of steps beginning with wiping gross contamination off the article, following by a series of rinses with organic solvents and aqueous rinses with or without ultra sonic treatment. The test article is then subjected to a Freon vapor degreasing process, followed by a final rinse. A final isopropyl alcohol rinse is performed and the rinse is analyzed for particles shed. This process commonly achieves level 100 cleanliness, which equates to1 particle /ft^2 of 100 micrometers diameter (IEST-STD-CC1246D). Other treatments that are less harsh to sensitive plastics and polymers are also being developed. These include chemical, gamma and beta sterilization and RF plasma or E-beam treatments that may provide for better removal of organics in some cases.
- **The "thermal bakeout"** is a process by which spacecraft components that are known to outgas organic vapor are treated by heat to reduce the subsequent outgassing rate of the process at room temperature. "Typical" bakeouts can range from 70^{o}C to 105^{o}C and can last from 72 to over 160 hours, depending on the material.
- **Repeated wipes** with clean room cloths saturated with isopropyl or ethyl alcohol remove molecular contamination during the course of spacecraft assembly. Both the flight

hardware and ground support equipment are subjected to this treatment. The isopropyl alcohol method is the only method that has been evaluated for its ability to remove bacterial spores from a surface. While there is considerable practical experience with cleaning spacecraft materials, none of the above methods has been systematically studied with regard to ability to remove the organics appearing on the reports list generated by the OCSSG.

- **The cleanroom** itself is a cross contamination mitigation tool. A "typical" aerospace cleanroom is class 100,000, i. e., contains 100,000 or fewer particles of 0.5 microns in diameter per cubic foot of air. In practice, a clean room classified at this level will for the majority of the time maintain particle counts at levels that are more than two orders of magnitude lower. The most extreme case of flight hardware assembly environment, sample collection hardware flown on Genesis was cleaned and assembled in a class 10 cleanroom that contained only one 10 0.5 micron size particles per cubic foot of air. This required that the personnel be isolated in clean suits during the assembly process.

4.4 Cleaning procedures and planetary protection requirements: Current planetary protection regulations specify residual levels of viable aerobic spores per square meter of spacecraft surface. Since procedures that address this requirement do not directly address removal of organic contamination produced from either synthetic materials or non-viable spores, these are not considered relevant by the OCSSG for the proposals of this study.

4.5 Primary system level cleaning requirements: The OCSSG proposes the primary system level requirements specified in Table 2. Solid phase samples delivered to analytical instruments for organic and molecular analysis should contain less than the specified amounts of example organic contaminants.

Table 2. Maximum amount of contamination in nanograms (ng) that can be transferred to organic and molecular analysis experiments prior to their delivery to the instruments.

	ng / g sample	Notes
Benzene or aromatic hydrocarbons	8	MSL will delivery approximately 5 g of sample to the processing system. Individual experiments may require only a few milligrams of sample for their analysis
Carbonyl and hydroxyl containing compounds	10	
Amino acids	1	
Amines, or amides	2	
Non-aromatic hydrocarbons	8	
DNA	1	
Total reduced carbon	40	
Assumptions: State of organic cleanliness can be assessed by analyzing specific representative molecules.		

Table 3. Example of derived requirements on cleaning of lander surfaces			
Lander element	Cleanliness Requirement		
General surfaces of the spacecraft carrying organics detectors	Must meet or exceed Cleanliness Level 1		
General sample handling and processing facility surfaces	Must meet or exceed Cleanliness Level 2		
Specific sample handling elements coming in direct contact with samples	Must meet or exceed Cleanliness Level 3		
Cleanliness Level Definitions			
	1	2	3
Non-volatile residue (NVR) Contamination (nanograms/cm^2)	500	10	1
Particulate cleanliness level (PCL)	400	200	25
Outgassing Flux (ng/cm^2 hr)	100	10	1
Bio-organic proxy molecule(s)	TBD	TBD	TBD

4.6 Derived cleaning requirements: The primary requirements will lead to derived requirements for general cleaning of spacecraft surfaces. Although these may be modified as the fidelity of contamination migration models increases, example requirements are given in Table 3.

4.7 Designs that isolate sample acquisition and processing hardware: Contamination barrier technology involves cleaning selected spacecraft hardware to a specified degree and then encasing it in a lightweight barrier material for launch and transit to the martian surface. The contamination barrier is mechanically breached in a manner that allows the protected instrument to operate. Biobarriers have traditionally been envisioned as particle barriers, not vapor barriers because of the need to allow the pressure inside and out to equilibrate during launch and landing. One such approach incorporates a non-breathable Mylar film in conjunction with a HEPA filter to enable the structure to breath.

Another uses Tyvek, a woven fiber of polyethylene, which is a 99% effective barrier and is breathable. In general, the current biobarrier technology has not been characterized with respect to the specific compounds of concern. Issues to be addressed with contamination barriers to protect scientific investigations of organic molecules are the shedding of particles and outgassing of the materials from which the biobarrier is made as well as diffusion of volatile species through the barrier. These considerations may result in the adoption or development of more suitable materials than those mentioned above. Demonstration of the effectiveness of cleaning systems to remove compounds and of barriers to prevent their transport to sensitive instruments is needed.

4.8 *In situ* operations and processing: A number of operational and processing approaches may mitigate the impact of terrestrial contamination on the desired measurements. For MSL, dilution of samples by processing multiple samples through the acquisition, crushing, and grinding systems prior to delivery of samples to the experiments in the analytical laboratory could provide a substantial reduction in the level of contamination delivered to analytical laboratory instruments. The ability to bake sensitive areas of the sample crushing system might also be studied as a method of removing collected organic compounds.

Other operational mitigation strategies that should be studied during the MSL development phase include processing solid phase samples at night when various lander elements are colder and outgassing less or obtaining atmospheric samples in a lander orientation that places the inlet tubes upwind from most lander elements.

The cost vs. benefit should be established for such operational contamination mitigation strategies.

4.9 Summary of OCSSG proposals for contamination mitigation:

1. Success in contamination mitigation will require a multi-faceted approach. Attention must be paid to material selection, and cleaning procedures as well as fabrication and assembly procedures.
2. Contamination barriers for sensitive items should be studied early in the design of MSL.
3. The sample collection and analysis operating plan should take contamination mitigation concerns into account.
4. Contamination monitoring through the use of witness plates and other methods should be used in all phases of hardware development for MSL so that a comprehensive understanding of organic contaminants and their levels can be realized. A subset of the witness plates should be archived until the MSL mission is complete for possible analysis, in terrestrial laboratories, with different analytical techniques if warranted by the results of *in situ* measurements.
5. Additional technologies for sterilization and cleaning of space craft such as RF plasma and E-beam technologies should be studied.

5. Standards and Controls

Even with rigorous contamination control some level of organic contamination will be present in the samples delivered to the analytical instruments on a surface lander. The OCSSG considered the possibility of employing facility-provided standards for MSL as a method of quantifying residual contamination.

5.1 The use of terrestrial organic materials in standards: Two possibilities were considered for facility-provided standards: (1) employing blank standards free of organic contamination and (2) employing standards containing one or more selected organic molecules. The use of standards containing terrestrial organic material might enable the performance of the instruments of the Analytical Laboratory to be assessed over the duration of the mission. However, the OCSSG concluded that **the potential pitfalls of bringing facility standards containing organic molecules from Earth outweigh the benefits.** The potential for contamination of the spacecraft by organic standards might neutralize the ability of the mission to demonstrate conclusively that it has indeed detected organic carbon on Mars.

5.2 Organic-free blank standards: The potential benefits of employing an organic-free blank to assess the extent of migration of MSL molecular contamination into the sample acquisition and sampling systems could be substantial. In the operations dedicated to sampling the blanks, organic-free material from Earth would pass along all or much of the sample processing chain and be delivered to the organic detection instruments in the analytical laboratory. These measurements would then quantify the extent of molecular contamination migration into the sample acquisition and processing mechanisms. The blank material would subsequently be

purged from the sample processing elements by repeated processing of Mars samples through the system. The blank material would ideally be a material that in any case would itself be easily distinguishable from Martian samples. The primary objective of the analysis of the facility provided blank would be to assess the degree of molecular contamination of the elements of the sample acquisition and processing system. All other standards would be implemented as necessary by the individual instruments.

5.3 Summary of OCSSG proposals for use of standards and controls:

1. The MSL Mission should consider implementation of a facility level use of organic-free blank standards to assess the degree of residual organic contamination present on surfaces that come in contact with Mars samples delivered to instruments of its analytical laboratory. While this proposal is supported by a majority of the OCSSG, a minority view of the OCSSG is that the expense of this approach and the possibility of contamination of MSL instruments that do not focus on organic analysis make this implementation undesirable.
2. Any other standards desired for instrument calibration should be the responsibility of the individual investigations and should not be provided as a MSL facility.

6. Conclusions

Upcoming missions will directly address the nature of the source and processing of reduced carbon containing species on Mars through sensitive molecular analysis experiments not attempted since the Viking Mission in 1976. These measurements are expected to extend our understanding of the possibility for present or past life on that planet. Only careful attention to the reduction and quantification of terrestrial organic species brought to Mars on these lander systems will insure that definitive conclusions can be made regarding organic compounds indigenous to that planet.

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Appendix A. Example Potential Contaminants from Solid Phase Samples Including Soils, Rocks, or Samples with High Ice Content									
Molecular class	**Examples**	**Scientific interest**	**Exogenous or terrestrial source likely**	**Detection goal**	**Amount on lander**	**Migration concern**	**Concern level**	**Species to monitor**	**Notes**
C, H aromatics	Benzene	VH	E T	ppb	H	H	H	Y	Outgassing from coatings, laminates etc. even after cleaning
	PAH's	VH	E T	L	L	L	L		
S,N, O heterocyclic aromatics	furan, pyridine, pyramadine, benzothiophere	M	E T	L	L	L	L		Functional group screening may be adequate to test for these species during development
carboxylic acids and their salts	alkyl & aromatic acids, fatty acids	VH	E T	10 ppb	M +	L	M		Functional group screening
non aromatic hydrocarbons	alkanes, alkenes, atmospheric methane	H	E T	ppb	H	H	H	Y	Outgassing of more volatile members of this class likely. If significant contamination, MW distribution desired.
	hopanes, steranes	L	T	ppm	L	L	L		
nitrogen containing compounds	racemic amino acids, NH_3, HCN	VH	E	sub ppb	L	L	L	Y	Functional group screening will identify amines and amino acids if they are present over a threshold
	L or R enhanced amion acids	VH	T	ppb	M	L	M		Functional group screening will identify amines and amino acids if they are present over a threshold
	amines	VH	E T	ppb	M	L	M		
	amides	M	E T	ppm	M	L	M		
	purines, prymidines	H	E T	ppm	L	L	L		
	porphyrins	L	E T	ppm	L	L	L		
Proteins	Polar & non polar	M	T	ppm	M	L	M		Breakdown products of greatest concern

Appendix A (continued). Example Potential Contaminants									
Molecular class	**Examples**	**Scientific interest**	**Exogenous or terrestrial source likely**	**Ddetection goal**	**Amount on lander**	**Migration concern**	**Concern level**	**Species to monitor**	**Notes**
Lipids and derivatives	HC chains, fatty acids, fats, phospholipids	L	T	ppm	L	L	L		Molecules of this and related classes could become important for next decade mission
	pristine, phytane	M	T	ppb	H	H	H		
Sugars & derivatives		L	T	ppm	L	L	L		Molecules of this and related classes could become important for next decade mission
Carbonyl compounds	Esters, ketones, aldehydes etc.	H	E T	ppm	H	H	H	Y	These compounds could be particularly difficult to separate from terrestrial contamination
Alcohols		H	E T	ppm	L	H	M	Y	Knowledge of MW distribution of contamination alcohols would be useful
Sulfonic, phosphonic acids	Methanesulfonic acid	M	T	ppm	L	L	L		
Nucleic acids, nucleotides,or DNA fragments		M	T	ppm	M	L	M		DNA assay is standard method that will establish levels on spacecraft and sensitive areas

Notes:

MW = molecular weight, VH, H, M, L = very high, high, medium, and low respectively, Y = yes

E = exogenous, T = terrestrial

The list is intended to be illustrative and not comprehensive. Other molecular classes containing S and P will also be importance.

The relative importance of molecular classes and specific species may change after the MSL investigations are selected. However, this method of assessing the importance of which contaminant species to monitor may still be followed.

Functional group screening may determine that an entire molecular class is present below a desired threshold. If contamination levels for a class are found to be above a threshold, then more detailed identification of individual species by different techniques may be desired.

Appendix B. Common Contaminates and their Chemical Functional Group	
Aliphatic Hydrocarbons (AHC)	AHC's are the most common contamination encountered. This is generally a saturated (branched and straight chain) mixture of hydrocarbons. It has typically a broad molecular weight range. Its source is mainly from lubricants and pump oils. It is found in many industrial environments. AHC's can generally be removed with most common solvents (Freon, alcohol, acetone).
Silicones	Silicones are very common contaminates and originate from lubricants, materials, sealants and adhesives. Silicones can outgas or leach out of silicone based polymers (RTV). Like AHC's, silicones are found with a distribution of molecular weights. The most common silicones are Polydimethylsiloxane and Polymethylphenylsiloxane. Silicones are difficult to remove. Freon and toluene are the best to try first.
Fingerprints	Fingerprints contain a complex mixture of compounds. The residue consists mainly of high molecular weight, long-chain alkyl esters of fatty acids. The more volatile fractions contain free fatty acids. Fingerprints also contain sodium chloride and protein. Fingerprints can be removed by wiping with most common solvents (Freon, alcohol, acetone, MEK).
Organic Acid Salts (OAS)	OAS's are used in mold release agents, soaps, silicone polymer activators, and fluxes. OAS's are also formed when of fingerprints react with some metallic surfaces. Polar solvents such as alcohols best remove OAS's. In thermal vacuum systems the copper cold finger may react with hydrolyzed esters to form organic copper salts. This gives the copper a green discoloration.
Phthalates and other Esters	Esters are found in plasticiziers, pump oils, adhesives, polymer degradation products and many other materials. A commonly found class of esters is phthalates. Phthalate esters such as Bis 2-ethylhexyl phthalate (aka DOP) is used to plasticize vinyl plastics and in many other polymer formulations. DOP is a common catastrophic contaminate and is typically discovered after a thermal vacuum processing. Acetone, MEK and alcohol are the best solvents to try first.
Epoxy	The uncured components of Epoxies can outgas or leach out a variety of components. These are generally amines (from the "B" component) and phenol ethers. The best solvent for these are alcohol, acetone and aromatic solvents. Cured epoxy is difficult to remove by common solvents. Epoxy compounds may have complex formulations and can be a source of other compounds.

Particles and Fibers	The particles and fibers are usually analyzed separately from molecular contamination. They can contribute the molecular contamination by physical transport, solvent extraction and outgassing molecular residue. Particles are readily identified by FTIR microscopy (non-metals) and Laser Ablation-ICP (metallic particles). *Silicate Dust:* Common fine component of soil. The composition is mainly fine quartz and mixed silicates. This is also found in construction materials. *Cloth Fibers:* Cotton, Nylon, polyester, Lycra, Silk etcetera. *Bio-Organic*: This includes dead skin, hair, spores, pollen, and organic wind blown matter. This is a very large class of materials. The *Planetary Protection* group monitors a crucial subset of this material with separate biological assays. *Construction Materials*: Wallboard, Wood fibers etcetera. *Metallic and Device Shed Particles*: These are particles from the spacecraft hardware. They can be from wear or machining debris. *Carbonates:* Carbonates are used as fillers in materials and are a major component of "water spots". Carbonates are also encountered as a corrosion product from paints using potassium silicate binders.
Ionic Contamination	The ionic contaminates of the greatest concern are chlorides, fluorides and sulfates. The main effect of this residue is to increase the corrosion rate of sensitive materials before launch when surfaces are exposed to humidity. Ionic contamination is not generally an outgassing concern and the acceptable levels of ionic contamination are not usually established in spacecraft specifications. If ionic contamination is monitored it is usually at the component level. The use of strongly activated solder fluxes (spiked with chlorides or fluorides) is probably the most common source of detrimental ionic contamination. The main background sources of ionic contamination are fingerprints and metal processing residues. Generally ionic contamination is removed by deionized water and to a lesser extent alcohols. Ion Chromatography readily analyzes ionic contamination with excellent sensitivity.

Appendix C: Organic Materials Inventory. Organic materials used on each MER spacecraft in amounts of one kg or more. Materials used in amounts of 25 kg or more are marked with an * symbol.

Material	Use
FM 73 Epoxy Film Adhesive	Bonding of aluminum core to composite facesheets for RED, WEB, and Lander
FM 300 Epoxy Film Adhesive	Bonding of heaters for Cruise Stage Shunt Radiators
EA 9309 Epoxy Paste Adhesive	Bonding of fittings for RED, WEB and Aeroshell
EA 9394 Epoxy Paste Adhesive	Bonding of fittings for RED, WEB and Aeroshell
EX 1541 Polycyanate Paste Adhesive	Filling aluminum honeycomb core for RED and WEB panels and Aeroshell
HT 424 Epoxy Paste Adhesive	Core splice adhesive for aluminum honeycomb core for RED and WEB panels.
Eccobond 56C Conductive Epoxy Adhesive	Bonding of Cruise Stage Shunt Radiators
Eccobond 57C Conductive Epoxy Adhesive	Bonding of Cruise Stage Shunt Radiators
BTCY-1 Polycyanate Resin *	Used as the matrix resin for carbon fiber and glass fiber reinforced panels for WEB, RED and Aeroshell
RTV 560 Silicone Adhesive	Bonding of SIRCA to the BIP
Uralane 5750 Polyurethane Resin	Potting and Conformal Coating for Lander, Rover
Teflon Polytetrafluoroethylene	Spacers and Standoffs for Lander, Rover
G-10 fiberglass epoxy	Standoffs, Insulators, PWBs for Lander, Rover
Y966 Pressure Sensitive Acrylic Adhesiv	Used in tape on Rover, WEB and RED
Kapton Polyimide Film	Thermal Blankets for Cruise Stage
Mylar Polyethylene Terphalate film	Thermal Blankets for Cruise Stage

Appendix C: Organic Materials Inventory. Organic materials used on each MER spacecraft in amounts of one kg or more. Materials used in amounts of 25 kg or more are marked with an * symbol.

Material	Use
Vespel Polyimide	Standoffs, spacers and antenna components for the rover and lander
Polyester*	Parachute
Vectran*	Airbag
Kevlar Tape/Webbing*	Parachute, Airbags, Bridle, DRL
S13 Silicone Paint	Painting of solar array substrates for Cruise Stage and Rover
M55J Graphite Fibers	Fiber reinforcement for composites used in RED, WEB, and Aeroshell
FlamemasterS1023 Silicone Paint	Exterior paint on Backshell
SLA-561V*	Thermal Protection System on Heat Shield
SLA-561S*	Thermal Protection System on Backshell
2216 epoxy adhesive	Potting and staking on Rover and Cruise Stage
Xylon (polybenzoxazole)	Straps for the Lander Bridle System
Torlon polyamide-imide	Bearings and standoffs for Rover and Lander
Solithane Polyurethane Resin	Conformal coating for printed circuit boards for Lander and Rover

Appendix D. Physical Transfer of Organic Contaminants from Hardware Surfaces to Simulated Mars Soil

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Summary

This work addresses the concern that nominal spacecraft surfaces may contaminate Mars soil prior to chemical analysis. Transfer of surface residue could compromise the science return particularly for trace organic experiments. This study was intended to bound the problem by determining the fraction of molecular contaminants physically-transferred from external spacecraft surfaces. Contamination transferred from typical spacecraft surfaces was studied. In addition, the JPL rock crusher tool was analyzed.

In general we measure 1.3% to 7.6% of the surface contamination is physically transferred to the soil analogs under conditions of moderate abrasion. In the case of passive transfer without abrasion, levels ranging from 0.10 –1.3% were measured. The high abrasion surfaces of the JPL rock crusher were found to transfer ~60% of surface molecular contamination. These measurements are based on a variety of organic compounds, soil analogs and metal surfaces. This work covers room temperature and low temperature (-40 ^{o}C) tests. Experimental procedures have been developed to address organic transfer for more specific operational conditions in terms of mechanical stress, temperature, contamination type and level of hardware contamination.

Introduction

A general method was developed to study the physical transfer of organic films to powders from metals surfaces. This is intended to simulate the pressing and translation of Mars soil across a nominally contaminated hardware surface. Methods were developed for the uniform deposition of the contamination analogs. Several soil analogs were used and this was dependent on the analytical methods for detecting the transferred contamination analog. This was not intended to simulate the high stress conditions of a cutting edge or the grinding surfaces of a rock crusher.

Three simulates of Mars soil were initially chosen for study: Potassium Bromide (KBr) based on its compatibility with FTIR analysis; Basalt (USGS, BHVO-2, http://minerals.cr.usgs.gov), a widely uses Mars soil stimulant; and chromatography grade quartz sand. The contamination analogs were Dioctyl Phthalate (DOP), adenosine triphosphate (ATP) and the amino acid lysine. The metal surfaces studied were common spacecraft alloys of aluminum and titanium. One of the soil analogs evaluated, the clay montmorillonite, was found to “irreversibly” bind the contaminant molecules making it difficult to directly extract for the soil analysis. This issue of the chemical binding of organic analytes and background residue to clays requires a separate evaluation. In addition, The JPL rock crusher was tested using the DOP contamination analog and a Andesite rock sample.

Experimental

Hardware Contamination Preparation: The contamination-analogs are deposited on circular metal plates using a spin coating process. The contamination-analog is dissolved in solvent and syringed on to the spinning plate in a uniform coating. This used a standard spin coater device (Headway Research, Garland, Tx) for deposition uniform polymer films. The rock crusher back plate was similarly spin coated at a level of 0.4 micrograms per square centimeter with DOP. The absolute amount deposited, while uniform, is not consistently the same level of residue from plate to plate. Therefore the results are reported for the

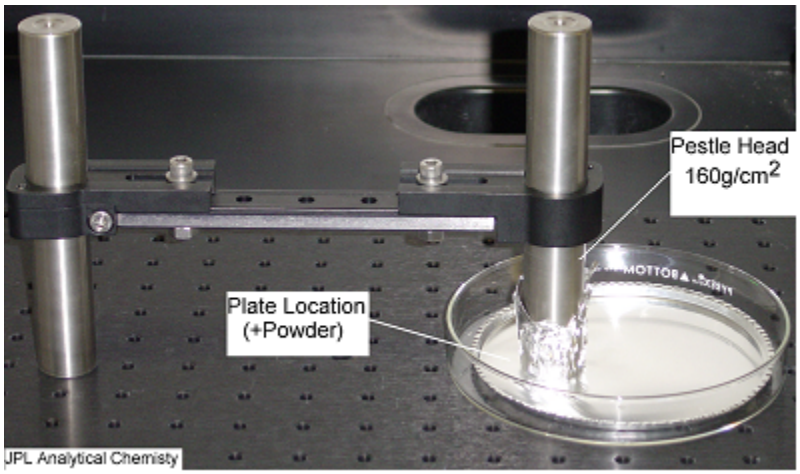
average percent contamination transferred for plates in a range of contamination levels.

Contamination Transfer Process

Passive Transfer: The amount of contamination transferred with no abrasion was evaluated at 25 ^{o}C and –40 ^{o}C. The weighed analogs (0.5 grams) were evenly applied to the surface and after 1 hour were poured off. The amount of residue was then analyzed. There was little or no mechanical action was applied other than the particles sliding over the surface.

Abrasion Transfer: The abrasive transfer experiment uses a known weight of a cleaned, flat-head stainless steel pestle. Weighed powder (0.5-0.75 grams) is placed between the pestle head and the circular plate surface (100cm^2) and the "mechanical transfer" is accomplished by moving the pestle radically outward and inward from the center of the plate using only the pestle weight and covering the entire contamination plate surface. This is done for a prescribed number of passes. The powder is then lightly brushed off the surface and collected into a vial and mixed. This powder is either analyzed directly or it is extracted and evaporated onto potassium bromide (KBr) for DRIFT analysis as describe below. The residue remaining on the plate is then rinsed with dichloromethane (DCM) and similarly analyzed. The fraction of the material transferred to the soil analog from the plate is reported as "% transferred". Blanks are run on solvents and all hardware that contacts the powder along surfaces. The error in the measurements is mainly a function of the grinding process that transfers oil from the surface to the powder.

Below is the apparatus for physical transfer of molecular films. This provides uniform pressure on a pestle to the powder-plate interface



FTIR Analysis

The contamination-analog on the plate and transferred to the soil-analog are both measured using Diffuse Reflectance/ Fourier Transform Infrared (DRIFT) spectroscopy. The samples are extracted using dichloromethane. FTIR provides chemical functional group information for sensitive quantitative analysis and qualitative identification of materials. The analysis followed the ACL-120 procedure that complies with Mil-STD-1246C Notice 3 and is sensitive to the most stringent level (A/100). A paper (1) co-authored and written under the direction of Mark Anderson details the quantitative methodology. The method has high precision and accuracy. The linear correlation coefficient (r2) is 0.980 for bis-ethyl hexyl phthalate (DOP), 0.982 for Silicone and 0.987 for hydrocarbon pump oil. This is valid for the range of concentrations used in this study.

Gas Chromatography- Mass Spectroscopy

The sample of crushed rock from the rock crusher (with the DOP coated back plate) was analyzed for DOP using a dichloromethane extraction, evaporative concentration and analysis using GC/MS. GC/MS provides separation using gas chromatography and mass analysis using mass spectroscopy.

RESULTS

Rock Crusher:

The back plate of the rock crusher was spin coated with 0.4 micrograms per square centimeter of DOP. A 32-gram Andesite rock was ground to completion (overnight). The crusher surfaces under high stress have fine powdered rock marking the surface. This area (~10 cm^2) was used to estimate the contact area. The crushed rock had 5.9 micrograms of DOP as determined by dichlormethane extraction and GC/MS analysis. This is ~ 60% of the residue on the abraded surface area. The resulting crushed rock sample had 185 parts per billion DOP.

The transfer fractions for the various plate-analog combinations are based on the average of 3 or 4 measurements (unless otherwise indicated).

Table #1 Abrasion: DOP Transferred to Soil Analog at 22°C

2 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate/ Analog	DOP Level on Plate Micrograms per cm^2	Fraction Transferred to Powder (f)	Standard Deviation	**Average % Transferred to Powder**
Al/KBr	0.07	0.063	0.033	**6.3%**
Al/KBr	0.7	0.055	0.011	**5.5%**
Ti/KBr	0.06	0.066	0.021	**6.6%**
Ti/KBr	0.36	0.023	0.0072	**2.3%**
Ti/Sand	0.21	0.023	0.013	**2.3%**

Table #2 Abrasion: DOP Transferred to Soil Analog at -40°C

2 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate/ Analog	DOP Level on Plate Micrograms per cm^2	Fraction Transferred to Powder (f)	Standard Deviation	**% Transferred to Powder**
Ti/KBr	0.09	0.072	*	**7.2%**
Ti/Sand	0.20	0.025	*	**2.5%**

Table #3 Passive Transfer: DOP Transferred to Soil Analog at 22°C

Plate/ Analog	DOP Level on Plate Micrograms per cm^2	Fraction Transferred to Powder (f)	Standard Deviation	**% Transferred to Powder**
Al/Sand	0.07	0.01	*	**1.3%**
Al/Sand	0.9	0.03	*	**2.7%**
Al/KBr	0.10	0.04	*	**3.9%**
Al/KBr	0.9	0.05	*	**4.6%**

Table # 4 Passive Transfer: DOP Transferred to Soil Analog at -40°C

Plate/ Analog	DOP Level on Plate Micrograms per cm^2	Fraction Transferred to Powder (f)	Standard Deviation	**% Transferred to Powder**
Al/Basalt	1.06	0.013	0.0047	**1.3%**
Al/Basalt	0.175	0.0085	0.0033	**0.85%**
Al/Sand	0.073	0.0043	0.00074	**0.43%**
Al/Sand	1.2	0.0013	0.00014	**0.13%**

* This is based on a single point measurement.

Bio-Molecular Contamination Experimental

ATP (adenosine triphosphate) Determination:

In this study ATP serves as a surrogate for nucleic acids as it contains a purine, phosphoric acid and has a negative charge at neutral pH. The contamination-analog on the plate and that transferred to the soil are both measured using a bioluminescence-based assay. The bioluminescence reagent contains firefly luciferin and luciferase. Luciferase specifically reacts with ATP and the amount of luminescence produced by the reaction is in direct proportion to the amount of ATP in the sample. Specifically Kikkoman CheckLite HS plus reagent kit is used as specified by the manufacturer and the signal is detected with a Kikkoman Lumitester model K-210 spectrofluorimeter. The instrument has a linear response over a five decade rang and a lower limit of detection sensitivity of 10-14 M.

Amino Acid Determination: In this study Lysine served as a representative amino acid as it is the most easily detected since it has two primary amines. The contamination-analog on the plate and transferred to the soil were both measured using a fluorescence assay based on the dye fluorescamine. Upon reaction with primary amines the product shows absorbance/emission peaks at 381nm and 470nm respectively. The reaction is detected with a Gemini XS microplate spectrofluorometer with a detection range from 5 to 2500 ng/ml.

Compatibility of Assays and Materials: Like the DRIFT/FTIR both the ATP and amino acid assays were unable to detect signal from the Mars soil simulant montmorillonite. It is presumed to "irreversibly" bind the contaminant molecules making it difficult to directly extract for the soil analysis. In addition the KBr used is the DRIFT/ FTIR studies was found to significantly inhibit the biochemistries used in the detection of ATP and amino acids. Therefore, studies of transfer by this material were not conducted for this soil simulant This issue of the chemical binding of organic analytes and background residue to clays requires a separate evaluation as it may impact operation of some strategies for chemical detection on the surface of Mars.

Contaminated Plate Preparation: The water-based solutions of the bioorganic contaminants were not suitable for spin coating. The contamination-analogs, ATP and Lysine were deposited on circular metal plates (aluminum or titanium) using with micropipter in a 10x10 array of 2 microliter drops and allowed to dry. The contamination-analog was dissolved in sterile de-ionized water. This is a standard method for deposition aqueous solutions. The absolute amount deposited is determined from the known volume and concentration is consistently the same level of residue from plate to plate although not present as a contiguous film on the plate. The results are reported for the average percent contamination transferred for plates from three replicate experiments. Each experiment also has replicate positive and negative controls for the presence and absence of the analog contaminant.

Contamination Transfer Process: The transfer experiment uses a known weight of a cleaned, flat-head stainless steel pestle. Weighed sand (0.75g of SiO_2) is placed between the pestle head and the plate surface and the "mechanical transfer" is accomplished by moving the pestle across the surface of the plate using only

the pestle weight and covering the entire contaminated plate surface. This is done for a prescribed number of passes. The sand is then poured off the surface and collected into a vial. This sand is extracted with 1ml of water and the supernatant used directly for ATP and amino acid. The residue remaining on the plate is then rinsed with water and similarly analyzed. The fraction of the material transferred to the soil analog from the plate is reported as " % transferred". Blanks are run on solvents and all hardware that contacts the sand along surfaces. The error in the measurements is mainly a function of the grinding process that transfers bioorganic molecules from the surface to the sand.

RESULTS

The percent transferred to the soil for the various plate-analog combinations are based on the average of 3 or 4 measurements (unless otherwise indicated).

Table # 6 Abrasion: Lysine Transferred to Sand at 22°C

3 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate Type	Total Lysine on Plate Nanograms	Lysine transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	5,000	167.5	48.8	**3.4%**
Titanium	5,000	125.5	23.7	**2.5%**

Table # 5 Abrasion: ATP Transferred to Sand at 22°C

3 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate Type	Total ATP on Plate Nanograms	ATP transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	0.1	0.0013	.0045	**1.3%**
Titanium	0.1	0.0034	0.013	**3.4%**

Table #7 Abrasion: Lysine Transferred to Sand at -40°C

3 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate Type	Total Lysine on Plate Nanograms	Lysine transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	5,000	75.2	31.4	**1.5%**
Titanium	5,000	378.0	128.7	**7.6%**

Table #6 Abrasion: ATP Transferred to Sand at -40°C

3 Passes over 100 cm^2 with a Force of 160g/cm^2

Plate Type	Total ATP on Plate Nanograms	ATP transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	0.1	0.00088	0.0015	**0.9%**
Titanium	0.1	0.0019	0.0013	**1.9%**

Table #7 Passive Transfer: ATP Transferred to Sand at 22°C

Static transfer for one hour of direct contact

Plate Type	Total Lysine on Plate Nanograms	Lysine transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	0.1	0.00011	0.00012	**0.1%**
Titanium	0.1	0.00013	0.00017	**0.1%**

Table #7 Passive Transfer: Lysine Transferred to Sand at 22°C

Static transfer for one hour of direct contact

Plate Type	Total Lysine on Plate Nanograms	Lysine transferred to sand, Nanograms	Standard Deviation	**% Transferred to Sand**
Aluminum	5,000	46.5	24.3	**0.93%**
Titanium	5,000	121.22	50.0	**0.24%**

Estimation of Molecular Contamination Transferred to Soil

The following is a calculation to estimate mechanically transferred contamination from spacecraft hardware to a soil sample. The resulting concentration in the soil sample (Cppb) is given as parts per billion (ppb) by weight (nanograms per gram). The initial surface contamination, Cs, is given in nanograms per cm^2. This may be from direct hardware measurements or contamination modeling. The fraction of the surface contamination transferred from surface into the soil is given as f. This transfer fraction is reported in the tables above for various residues, substrates, temperatures and abrasion conditions. The soil sample weight, S is express in grams and the area, A is given in cm^2. The calculation is Cppb = f x Cs x A / S.

Example: Clean hardware (level A/10) with passive contact at –40°C:

f = 0.0085 Transferred fraction (Table 3, Basalt, -40^{o}C, passive transfer)

S = 100 g, Grams of Soil

A = 200cm^2 Contact Area (scoop area + external funnel)

Cs = 100 nanograms/square centimeter (Level A/10, IEST-STD-CC1246D)

Cppb = f x Cs x A / S = (0.0085) (100ng/cm^2) (200cm^2)/100g = 1.7 ppb

This is an optimistic estimate and is at a level that could be detected by the Phoenix TEGA mass spectrometer. Note TEGA has some further chemical discrimination between synthetics (silicones and fluoropolymers) and the hydrocarbons of scientific interest. This needs to be considered when organic detection is being estimated.

Example: General spacecraft hardware and light abrasion:

A more pessimistic estimate would assume standard spacecraft limit at level A cleanliness of 1ug/cm^2 (1000ng/cm^2) and a transfer of 7.2 percent (table 2 sand). This gives:

Cppb = f x Cs x A / S = (0.072) (1000ng/cm^2) (200cm) /100 = 144 ppb

Discussion and Recommendations

The range given above is near the detection limit of Phoenix-TEGA mass spectrometer (low to sub-ppb) up to 2 orders of magnitude higher. The lower end is manageable using good blank protocols and relying on the ability of the mass spectrometer to discriminate certain synthetic contaminates from organic compounds. The higher end could reduce the analytical sensitivity and requires greater resources devoted to blank measurement.

During the course of this study the Phoenix project had the need for an evaluation of the susceptibility of the TEGA mass spectrometer. This provides a context and the limitations of this study. The main drawback is the uncertainty of actual spacecraft contamination levels particularly for particles. This study does not include particle transfer estimates and this is of equal importance as the molecular contamination effects.

Lastly this work underscores the need for flight experiments to have end-to-end blanks and perhaps self-cleaning of critical surfaces. Given the uncertainties of spacecraft contamination this may be the only way to make convincing measurements for the detection organic compounds on Mars.

Rock Crusher Implications

The crushed rock collected 5.9 micrograms of DOP contamination analog in a 32-gram rock sample. This is ~ 60% of the analog residue removed from the abrasion surface area. The resulting crushed rock sample has 185 parts per billion DOP. The implications are that the high stress surfaces of the crusher need to be kept very clean. The amount of residue on the crusher plate was a “high nominal” surface (0.4 micrograms per square centimeter). Rigorous cleaning and protection of the critical rock crusher surfaces will greatly improve the levels of transferred residue.

References

1) M. S. Anderson and J. J. Herrick et al "Analysis of Semi-Volatile Residues Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy" in Optical System Contamination: Effects, Measurements, and Control VII; July 2002, edited by Phillip T. C. Chen and O. Manuel Lee; Proceedings of the SPIE, Vol. 4774, pp. 251-261, (2002).