Appendix III

THE FIRST MARS SURFACE-SAMPLE RETURN MISSION: REVISED SCIENCE CONSIDERATIONS IN LIGHT OF THE 2004 MER RESULTS

Mars Sample Return Science Steering Group II
(Glenn MacPherson, Chair)

February 16, 2005

This white paper is incorporated as an appendix within the following larger document:

MEPAG ND-SAG (2008). Science Priorities for Mars Sample Return, Unpublished white paper, 73 p, posted March 2008 by the Mars Exploration Program Analysis Group (MEPAG) at http://mepag.jpl.nasa.gov/reports/ndsag.html.

Recommended bibliographic citation:

MacPherson, Glenn, and the Mars Sample Return Science Steering Group II (2005). The first Mars surface-sample return mission: Revised science considerations in light of the 2004 MER results, Unpublished white paper, 68 p, Appendix III of Science Priorities for Mars Sample Return; posted March 2008 by the Mars Exploration Program Analysis Group (MEPAG) at http://mepag.jpl.nasa.gov/reports/ndsag.html.

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I. Executive Summary

The working concept for a first Mars surface-sample return mission, as defined in 2002 and named Groundbreaker, envisioned a static lander with simple sampling tools at the end of an extendable arm, and only an imaging camera for on-board science instrumentation. The experience during 2004 with the Opportunity Lander on Mars forced a rethinking of the Groundbreaker concept: had Groundbreaking Mars Sample Return (MSR) landed precisely where the Opportunity Lander did, the spectacular layered deposits within Eagle Crater would have been out of reach by the sampling arm and therefore inaccessible.

In order for the first MSR to be capable of taking maximum scientific advantage of the evaporite stratigraphy such as that exposed at Meridiani, the Groundbreaker MSR concept should be revised to accommodate small "Fetch" rovers equipped with small coring devices for sampling. On-board scientific instrumentation should still be kept to an absolute minimum, such as a color imaging camera.

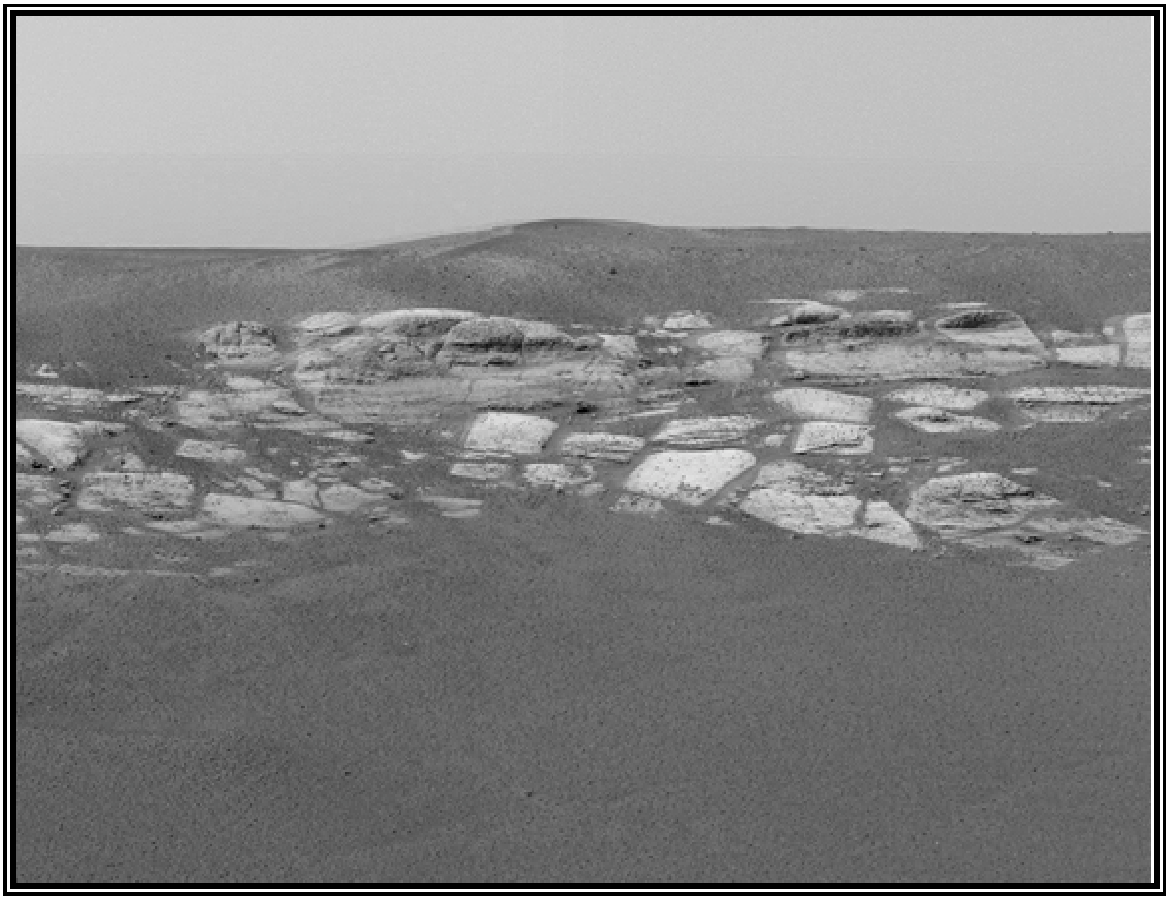
The potential for a previous mission (e.g., MSL 2009) to collect and physically cache samples for retrieval by MSR is an option that should be kept open and studied in more detail, but it should not be imposed as a requirement on MSR.

Cores of layered samples should, if at all possible, be separately stored and isolated. Active temperature control of the samples during the return mission would not be required. However, the discovery by Opportunity of abundant sulfur-bearing compounds on Mars makes it very important that passive controls be employed to retain the samples at < 20°C or below if at all possible, to prevent the dehydration of possible magnesium sulfate species that might in turn lead to degradation or even cross-contamination of samples.

II. Introduction

In 2002, NASA's Mars Exploration Program chartered a group of scientists to define the science floor for a Mars surface sample return mission: one that would be relatively simple and low cost (in comparison with industry proposals involving fully mobile rovers and robust on-board science packages), but still achieve important Mars science goals. This group, designated the Mars Sample Return Science Steering Group (MSR SSG), was formally a subcommittee of the Mars Exploration Program Analysis Group (MEPAG). The MSR SSG concluded that a static lander, having very simple sampling tools at the end of an extendable arm and no on-board science instrumentation other than an imaging camera, would achieve important Mars science objectives (as defined by the MEPAG) relating to both geology and astrobiology, provided that: (1) the lander went to a location within a geologic unit believed (on the basis of previous orbital or landed missions) to have biologic potential; and (2) the lander collected small pebbles in addition to local regolith. This concept, titled Groundbreaking MSR, served for two years as the reference at JPL for planning and budgeting a possible Mars sample return mission.

Early in 2004, the two Mars Exploration Rovers landed safely on the surface of Mars. The second to land, Opportunity, ended up inside a small impact crater. Exposed within the crater are finely laminated sedimentary rocks whose chemistry indicates them to be evaporitic in origin. This remarkable and unexpected finding was enabled by the ability of the rover to travel to the outcrops and analyze them. Had Opportunity instead been the Groundbreaker MSR mission, the layered deposits would have been out of reach of the extendable arm.



This event suggested that a rethinking of the Groundbreaker concept was in order, and in July of 2004 a second MSR SSG was created with the task of re-examining the science goals of a

Charter

We request that the MSR SSG II identify changes to these findings by answering the following questions:

- What degree of mobility (range, rate, slopes handled), if any, is now considered essential for the collection of returned samples?
- What are the science priorities for the functionality of the MSR sampling system?
- What does the science community consider the maximum acceptable levels of contamination in the returned samples? Please incorporate into your deliberations the findings of the 2003 MEPAG Organic Contaminants SSG, and consider the following potential contaminating materials:
  - Live Earth-sourced organisms (including viable microbial spores)
  - Dead Earth-sourced organisms and fragments of organisms
  - Earth-sourced molecular organic contaminants
  - Non-organic contaminants
- In order to select samples, what measurements must MSR conduct?
  - The MSR SSG I determined only a camera will be required.
- What are the science community's priorities for controlling the environment of returned samples?
- Would MSR benefit if samples cached for it by a prior mission, e.g. MSL?
  - Identify implications, both positive and negative, if MSR is designed to retrieve samples cached in a single container by MSL? It would be useful for the SSG to consider various issues, including:
    - Samples cached by MSL will have been collected from more widely distributed sites and with more extensive *in situ* measurements and context information than is likely to be possible from MSR alone.
    - MSR would likely be required to fund development and accommodation of a cache-container carried by MSL.
    - MSR would need to pinpoint land if it is to retrieve cached samples utilizing modest mobility.
  - What sampling capability must MSR have, as a backup, if a previously a sample cached previously is irretrievable?
  - The SSG need not delve into the issues of planetary protection requirements that may be imposed upon MSL if it caches samples for MSR.

first Mars sample return mission. Unlike the first MSR SSG, this second group was not tasked with costing out a revised mission. The active components of the charter for MSR SSG II are given below; the complete charter is given in Appendix B.

III. Process

The MSR SSG II met for the first time on August 25-26, 2004, at the Jet Propulsion Lab in Pasadena CA. At that meeting, four separate subgroups were established to consider the topics of (1) forward organic contamination; (2) forward inorganic contamination; (3) mobility and accessibility; and (4) sampling and sample handling. During September and the first half of October, each of the four subgroups held approximately weekly teleconferences to conduct their deliberations, supplemented by extensive e-mail communication. The MSR SSG II met for the second time on October 21-22, 2004, again at the Jet Propulsion Lab in Pasadena CA, at which time the four subgroup leads presented their preliminary findings. The subgroup leads delivered draft written reports to SSG Chair MacPherson by Mid-November. The four sub-group reports were bundled together and submitted to the MEPAG Executive Committee by the end of November. A complete draft document containing the SSG findings was be presented to the full MEPAG at its meeting on February 16-17, 2007 in Crystal City, Virginia. Comments received at that meeting will be incorporated into a final report.

The membership of the MSR SSG II and of the 4 subgroups is given in Appendix A.

IV. Philosophy of this Report

This report is intended to supplement rather than replace the original Groundbreaking Sample Return Report. It is predicated on the assumption that the results of the MER mission are so exciting and compelling that the agency support for a sample return mission be enhanced to the extent that the MSR concept itself would be financially enabled to allow for mobility. Thus none of the recommendations herein should be construed as requirements that financially threaten the very existence of a Mars sample return mission. The original Groundbreaking concept remains valid, but the MER experience indicates that taking maximum scientific advantage of anything like the Meridiani site would entail adding limited mobility back into the mission.

V. Scope and Structure of the Report

The diverse science issues taken up by the SSG were considered in far more detail than was possible in the original Groundbreaking MSR report. Therefore the tasks were divided into four parts and the committee divided into four subgroups. Owing to the limited size of the overall committee, most members belonged to two subgroups and thus there is significant overlap of subcommittee membership (Appendix A).

The subgroup leads each were responsible for preparing written reports resulting from their group deliberations. Those four reports are presented individually herein, largely verbatim. An additional section is added at the end that addresses the issue of how different potential landing sites might affect the desired spacecraft configuration. As the committee discussions evolved, it became very clear that desired mission enhancements beyond the Groundbreaker concept would vary depending on site location and other circumstances. One size will not fit all.

VI. Revised Science Considerations Pertaining to Mobility and Accessibility

The task for the mobility/accessibility subgroup was to examine to what degree of accessibility and mobility (range, rate, slopes handled), if any, should now be considered desirable for the collection and return of samples from the surface of Mars.

General approach

The subgroup proceeded in its examination by identifying sampling and science criteria that potentially dictate the degree of accessibility and mobility capabilities of MSR, defining accessibility and mobility parameters, evaluating these parameters within the context of increasing more complex MSR missions, and ranking these parameters within the framework of missions to specific Martian terrains. Based on these examinations and subsequent exercises the subgroup attempted to produce findings that would be applicable to a wide range of possible science goals defined by a future science definition team.

Identification of Sampling and Scientific Criteria

The subgroup identified numerous sampling criteria/tasks that influence the mobility and accessibility capabilities of MSR. The relative importance of these criteria is dependent on characteristics of landing site terrain, MSR science goals, and complexity of the MSR. As such, establishing these criteria was valuable for ranking of mobility capabilities and evaluating potential trade offs among capabilities within the framework of diverse missions with different degrees of complexity, costs, and goals.

The criteria identified by the subgroup are

(1) The ability to traverse and perform sampling upon rocky terrain, crater walls, and sloping hills at angles up to 30 degrees. This would allow access to boulders and bedrock where sampling has the best chance of avoiding surficial weathering products and finding organics.

(2) The ability to access samples that would be minimally contaminated by exhaust from the MSR lander.

(3) The ability to sample lithologic diversity within a terrain or across terrain boundaries.

(4) The ability to place samples within a well-defined geologic context.

(5) The ability to return to a previously explored site or terrain (i.e. MPF, MER A/B, MSL, V1,2).

(6) The degree of accessibility to different Martian terrains (i.e. high percentage of the Martian surface, Martian highlands).

Identification of Important Accessibility and Mobility Parameters

Numerous accessibility and mobility parameters were identified by the subgroup. These are listed in Table 1. These parameters are extremely different in terms of overall metrics (distance, time, slope, degree of autonomy). Their relative importance is dependent upon scientific goals of MSR and characteristics of landing site (rough or flat terrain, location). Many of these parameters are highly dependent upon one another. For example, access to higher altitudes may effect precision landing and distance capability of rover. Linkages between parameters dictate the efficiency of sampling. This is illustrated by the interaction between landing precision and roving capability that will dictate duration on the Martian surface and the number of samples collected. Trade off among these parameters will be eventually made based on science goals, cost, and risk.

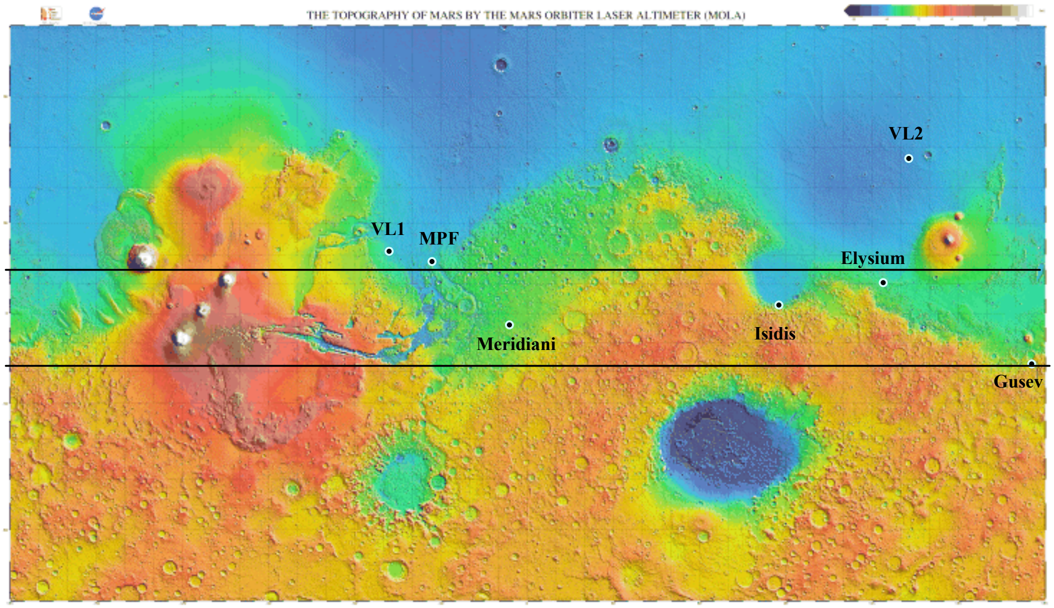
Table 1. Range of Accessibility and Mobility Parameters relevant to MSR.

Landing Precision	**100 meters to 10s of km**
Distance capability of rover	**10s of meters to multiple kms** **obstacle avoidance of 8 to 20 cm**
Time on Martian Surface	**< 1 month to 4 months**
Ability to traverse slopes	**0 to 30 °**
Communications	**Line-of-sight of lander, direct-to-Earth, orbiter relay. In order of increasing bandwidth.**
Degree of navigational autonomy	**None to high**
Altitude requirements	**<-1.5 km accesses 39.5 % of Mars** **<+2 km accesses 83.1% of Mars**
Latitude requirements	**Equator to +/- 60°**

Parameters that dictate the distance capability of MSR includes landing precision, distance capability of rover and time on the surface. The overall distance capability of the rover is related to a variety of other constraints such as radial distance from lander, traverse distance, obstacle avoidance, and sols/sampling site. Parameters that dictate the terrain capability of the MSR include the ability to traverse slopes, communications, degree of navigational autonomy, ability to navigate obstacles, and altitude and latitude of terrain. Many of the mobility parameters listed in Table 1 are potentially attainable with the rocker-bogie suspension system design that was incorporated in both Mars Pathfinder (MPF) and MER.

Evaluating the ability for MSR to access Martian surfaces at variable altitudes can be made using the topography derived from the Mars Orbiter Laser Altimeter (Figure 1).

Figure 1. Topography of Mars determined by the Mars Orbiter Laser Altimeter illustrating location of previous Mars landing sites and altitude of Mars highlands.



The percentage of Martian terrains within select elevations constructed from the laser altimeter data is illustrated in both Figure 2 and Table 2. Figure 1 illustrates that to return previous Mars landing sites or similar terrains would require the access to terrains at altitudes of < - 1km relative to the Mars geoid. This altitude requirement would provide access to approximately 45% of the Martian surface (Table 2) but would give no access to the older highlands. Gaining access to a substantial portion of the early Noachian environments in the highlands (a potential target for the Mars Science Lab (MSL)) is much more demanding and would require the ability to access Martian terrains between 1.5 to 2.5 km above the Mars geoid. This altitude requirement would provide access to approximately 89.5% of the Martian surface (Table 2).

Figure 2. Mars hypsometric curve.

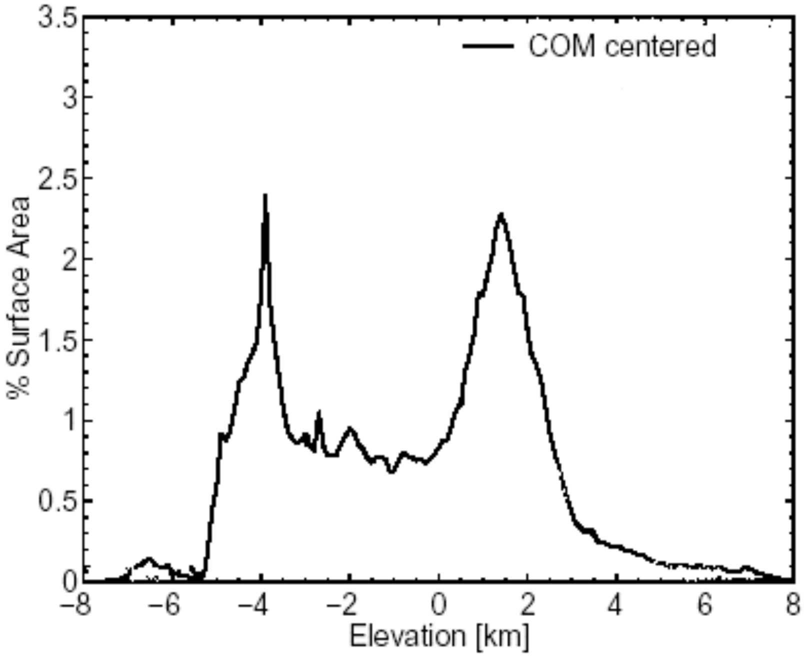


Table 2. Percentage of Martian terrains within select elevation ranges from <-1.5 to >2.5 relative to geoid. Data derived from Figure 2.

Elevation Range	% of Mars surface	Cumulative % of Mars
< -1.5	39.5	39.5
-1.5 - 0	11.4	50.9
0 - 0.5	4.7	55.6
0.5 - 1	7.6	63.2
1-1.5	10.4	73.6
1.5-2	9.5	83.1
2-2.5	6.4	89.5
≥ 2.5	10.6	100.0

Sampling Models, Mission Complexity and Science Value

Five MSR sampling models were derived based on an increasing degree of complexity and scientific payoff from the original GMSR proposed by the MSRSSG #1 to a model that is essential MER plus sample return capabilities (Table 3). Intermediate sampling models include original GMSR with minor mobility capability (100 m roving capability), a highly mobile MSR (1 km roving capability) returning to a previously visited site to return a real or virtual sample cache, and a highly mobile MSR (1 km roving capability) to an interesting, unvisited sampling a site that was documented by orbital data. The cost, risk, and scientific advantages and disadvantages of each sampling model are presented in Table 3.

Table 3. Sampling Models and Scientific Value.

Original GMSR
Description of capabilities: ▪ The first MSR need not "follow" MSL or any other prior mission, but land in a scientifically interesting area, as determined by previous *in situ* or orbital missions. ▪ Mobility not required. ▪ Limited sample characterization package. Context camera for sample selection and collection. ▪ Grab samples of regolith and clasts adjacent to lander.
Advantages: ▪ Lowest cost MSR. ▪ Least complex of the MSR missions and therefore it has a higher probability of success. ▪ Duration of surface operations is short. ▪ Samples are put into a geologic context based on by previous *in situ* or orbital missions. ▪ Will return rock fragments, regolith, and atmosphere within reach of the lander.
Disadvantages: ▪ Cannot directly sample outcrops. ▪ Cannot reach samples out of reach of arm/scoop. ▪ No mobility to explore and sample local geology. ▪ Collection of only regolith and rock fragments has a lower probability of returning organic compounds. ▪ Higher likelihood of returning altered samples.
Original GMSR with minor mobility capability
Description of capabilities: ▪ Land in a scientifically interesting area, as determined by previous *in situ* or orbital missions. ▪ Mobility less than MER. ▪ Core large rocks. ▪ Limited sample characterization package. Context camera for sample selection and collection.
Advantages: ▪ Possibility of sampling unaltered lithologies. ▪ Lessen the possibility of sample contamination from lander. ▪ Duration of surface operations shorter than sampling models 2, 3 and MER.
Disadvantages: ▪ Cannot sample outcrops in crater walls. ▪ Limited mobility to explore and sample local geology significant distances from lander. ▪ Regolith samples will have a lower probability of sampling organic compounds ▪ Samples are put into a limited geologic context.
Mobil MSR to previous visited and documented site

Description of capabilities:

- Return to previously documented site.
- Access to outcrops in crater walls.
- Core large rocks and outcrops
- Limited sample characterization package. Context camera for sample selection and collection.
- Mobility equivalent to MER.

Advantages:

- Samples put into context of local geology defined by previous missions (i.e. MER, MSL).
- Return to previous site lowers cost resulting from smaller sample characterization package and known site specific engineering requirements.
- Cored outcrop samples may be unaltered.
- Duration of surface operations shorter than sampling models 3 and MER.
- Sample outcrops in crater walls.

Disadvantages:

- First sample return mission will not be a mission of exploration to a new Martian terrain.
- Contamination from previous mission.
- Return sites are limited in number and interest if MSL fails or does not provide adequate characterization of the surface.

Mobil MSR to interesting site documented by orbital data

Description of capabilities:

- Explore site unexplored by previously *in situ* missions.
- Access to outcrops in crater walls.
- Core large rocks and outcrops.
- Limited sample characterization package. Context camera for sample selection and collection.
- Mobility equivalent to MER.

Advantages:

- Sample outcrops in crater walls.
- Cored outcrop samples may be unaltered.
- Has the flexibility to explore new sites.

Disadvantages:

- Samples are placed within the context of orbital geology and not local geology.
- With a limited sample characterization package, samples are not well documented on surface.
- Higher costs resulting from unknown site specific engineering requirements.
- Duration of surface operations longer than sampling models 1 and 2.

MER with sampling capabilities

Description of capabilities:

- Sample characterization package similar to MER with the capability to document sampling site prior to sampling.
- Explore site unexplored by previously *in situ* missions.

- Access to outcrops in crater walls. - Core large rocks and outcrops. - Mobility equivalent to MER.
Advantages: - Sample outcrops. - Has the flexibility to return to documented sites or document new sites. - In situ documentation of samples prior to collection. - Further exploration could continue after sample collection and launch of MAV.
Disadvantages: - Estimated costs greater than $3 billion. - Duration of surface operations longer than sampling models 1-3 if sample collection-documentation-exploration occurs simultaneously. - Most complex of all the MSR missions.

Analysis of Mobility-Accessibility Requirements of Different Martian Terrains

Lacking a science definition team report establishing specific science goals for the first MSR we evaluated mobility and accessibility requirements necessary to sample both real and hypothetical sampling sites: (1) Meridiani-like site, (2) a Gusev-like site, (3) a high altitude MSL site, and (4) a previously unvisited site with a geologic contact. Each site would require some differences in mobility and accessibility requirements and necessitate some trade offs between requirements (Table 4).

Table 4. Accessibility and mobility requirements for example sites.

	Meridiani site	**Gusev crater**	**MSL site**	**Unvisited site with geologic contact**
accessibility to rock interiors	Go to outcrop; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring
accessibility to uncontaminated samples	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g., coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g., coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g., coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g., coring)
altitude	-1.3 km	-1.9 km	CRITICAL to match MSL's altitude capability (+2.5 km)	Higher altitude range (+0.5 or +1 km) would be desirable because it would provide access to high-quality science sites in the ancient Southern Highlands (possibly recording a warmer wetter climate on Mars)
landing precision	Accessibility to >20 m diam crater; ~ 200m precision? Note: Landing precision and roving distance are intertwined. It's probably more important to minimize the time the rover spends on the surface collecting samples. The terrain at Meridiani between craters is smooth, flat and barren of rocks, so it would take less time to	Within 500 m of the contact between the hills and the plains; closer is better. You would want accessibility to the terrain boundary between the plains and the hills, to sample both terrains away from the landing contamination	Within 500 m of any contact._ You would want accessibility to the terrain boundary between the two geologic units, to sample both units away from the landing contamination	Within 500 m of any contact._ You would want accessibility to the terrain boundary between the two geologic units, to sample both units away from the landing contamination

	drive.			
minimum roving distance	1 km	1 km	1 km	1 km
time on surface, autonomy to lessen the time	Time sufficient to sample stratigraphy by coring within single crater, and to also sample regolith, dust, and atmosphere	Time sufficient to sample plains regolith, plains rocks, a diversity of rock types in the hills, regolith in the hills, dust, and atmosphere	Time sufficient to sample the diversity of rock types by coring, and to also sample regolith, dust, and atmosphere	Time sufficient to sample the diversity of rock types and regolith in both geologic units; as well as dust and atmosphere samples
slopes/ terrain	Must be able to enter and exit crater	Must be able to drive up and down the side of the Columbia Hills and the rugged rocky plains	The more MSR matches its slope/terrain capability to that of MSL, the better able we would be to follow MSL	Need flexibility to respond to unknown terrain characteristics to maximize the diversity of rock types collected
rover communication	Rover must be able to communicate w/orbiter and/or directly to Earth. Rationale: rover entering/exiting craters may be out of range of direct lander com.	Orbiter and/or direct to Earth com is advantageous, but we could design a mission that would not require it.	Rover must be able to communicate w/orbiter and/or directly to Earth	Orbiter and/or direct to Earth com would be advantageous, but we could design a mission that would not require it.
latitude	2 degrees S	15 degrees S	CRITICAL: MSL latitude range (+/- 60 degrees?)	Opening the latitude range as far south as possible would improve the science by allowing access to more possible ancient highlands landing sites

Findings

These examinations by the M&A subgroup indicate that several of the mobility and access parameters will vary depending upon the scientific goals and surface terrain to be sampled. The most site sensitive mobility and accessibility parameters are latitude, altitude, and communications. In addition, changes in these MSR parameters may affect less sensitive parameters (i.e. a site at high latitudes and altitudes may affect roving capability, landing precision, and duration on Martian surface).

Access to uncontaminated samples would require rover mobility sufficient to escape exhaust pattern, lander debris, and organic contamination. Lander contamination which may extend 200-400 meters requires rover mobility of at least 1 km. With pinpoint landing the exhaust pattern may be more extensive and should be monitored. A potential trade off for requiring extensive mobility to escape lander contamination would be to sample the uncontaminated subsurface via coring of rock boulders and outcrop interiors and trenching regolith. It is important to better understand the dispersion of exhaust during landing and the extent exhaust permeates the subsurface. This is particularly important for the regolith.

Sampling that would be the least demanding on MSR would be coring large boulders or near-horizontal relatively smooth expanses of bedrock. Slopes that need to be navigated under this sampling scenario would not be substantial (<10˚). Direct communication to lander would likely be sufficient in this case. Much more demanding on MSR would be gaining access to outcrops that may be exposed along walls of a crater (i.e. Meridiani site) or inclined slope of hills (i.e. Columbia Hills). This more demanding sampling strategy would fulfill the desire to sample stratigraphy that may be exposed in outcrop and increases sample diversity. In addition, sampling of outcrops would allow the samples to be placed within a regional and perhaps planetary-scale context. To fulfill this more challenging sampling agenda, the rover would need to navigate and sample from slopes up to 30˚. The rocker-bogie suspension system of MPF and MER rovers has demonstrated some of these capabilities. It would also be advantageous to be able to communicate to an orbiter and/or directly to Earth. A rover that is entering and exiting a crater or hilly terrain may be out of range of direct lander communications. Navigating over rough and inclined terrain for the purpose of coring outcrop may require substantial residence time on the Martian surface (1-3 months). Some degree of rover autonomy and pinpoint landing may assist in lessening the time on the surface. There may be trade offs between time on the Martian surface and accessibility to higher latitudes since the solar power available to the rover is strongly coupled to latitude.

Reducing surface time, placing samples with a well-defined geologic context, collecting a diverse set of lithologies, and returning to a previously visited site (retrieving a sample cache) are closely coupled to the linkage between roving distance capability and precision of landing. Generally, the most efficient manner to use surface time to explore and sample would be to use precision landing to land close to the scientific target. In the simplest situation in which previously documented (orbit or in situ) geologic units having a lateral extents of > 10 to 100s km are targeted landing precision of up to 10 km would be adequate. In the scenario in which a geologic terrain boundary between two distinct lithologies is targeted (*i.e.* Gusev crater), so that both could be sampled, a landing precision of better than 500 meters is recommended. In the more demanding scenario in which accessibility to outcrops in a >20m diameter crater is required (i.e. Meridiani) an even greater landing precision may be required to minimize roving time. In all these sampling scenarios, roving capabilities still need to be at least 1 km.

Returning to a previously explored site that has a real or virtual sample cache would have several advantages. Duration on Martian surface would be less due to the retrieval of cached samples or sampling more efficiently due to the previous documentation of outcrops. Decreasing the time on the Martian surface may mitigate risk. Sending MSR to a documented terrain would increase sample diversity and better place samples within the context of local and regional geology. A documented terrain presents a more predictable environment for engineers. There are trade offs with returning to a site. These include eliminating exploration to a new Martian terrain, adding cost to preceding mission, and sampling a site contaminated by a previous mission.

Returning to sites previously explored by VL1,2, MPF, and MER would necessitate landing elevation requirements of less than -1.3 km relative to the Mars geoid. Returning to a previously explored site at high elevation and high latitude (i.e. possibly MSL) or gaining access to a substantial portion of the early Noachian environments in the highlands would be much more demanding and require the ability to access Martian terrains between 1.5 to 2.5 km above the

Mars geoid. This was considered problematic and potentially costly by the MSR SSG#1. Therefore, the MSR SSG #1 eliminated latitude and elevation requirements. In that early Noachian terrains may have preserved remnants of a possible warm and wet environment conducive for life and the possibility of real or virtual sample caching by MSL having the ability for MSR to sample terrains at elevations up to +1.5 km above the geoid would provide access to approximately 74% of the Martian surface and a portion of the early Noachian terrains. The capability to access this terrain for sample return will be demonstrated by the design (and possibly landing) of 2009 MSL. MSR SSG#2 does realize expanding the Martian surface available to sample return (by both latitude and altitude) does have its trade offs with regards to cost, the size and roving distance of the rover, the precision of landing and time on the Martian surface. We consider access to more of the Martian surface, especially the early Noachian terrains, more important than extensive roving distance (> 1 km). Returning to a MSL site at high altitudes may limit the effects of rover capability (size, roving distance, time on surface, limited sample documentation package) on the MSR science goals. Returning to such a site still requires pinpoint landing

Summary Findings on Mobility and Accessibility

- Terrain navigability is site dependent. Gaining access to outcrops that may be exposed along crater walls (i.e. Meridiani site) or inclined hillslopes (i.e. Columbia Hills) would require the ability to negotiate slopes of ~ 30º
- Landing Precision is site dependent; but the requirement would always be within 500 m
- Access to uncontaminated samples would require rover mobility sufficient to (1) escape exhaust pattern, lander debris, and organic contamination; (2) travel to and return from target. Round trip distance ~ 1 km regardless of landing precision.
- Access to elevations > 1.5 km is highly desirable but is recognized as possibly prohibitive.

VII. Revised Science Considerations Pertaining to Sampling and Sample handling

The Sampling Subgroup of the Mars Sample Return Science Steering Group (MSR SSG II) was convened to revisit sampling needs based on an evolution from the previous capability of "Groundbreaking Mars Sample Return". The sampling goal of GMSR was to return regolith and rock fragments from a site that was hypothesized to have relevance to following the water on Mars. The conceptual GMSR consisted of a stationary lander with a simple scoop-rake sampling system, and a single bin into which all samples would be placed. This mission also had the requirement to maintain the temperature of the samples below 50°C. The MSR SSG I concluded that the first samples to be returned from Mars probably wouldn't contain evidence of past or present life, because at the time that the previous MSR SSG report was written, we had little confidence that we could find the type of rocks capable of preserving this evidence. MER discoveries, especially at Meridiani, but possibly also at the Columbia Hills, have revealed likely outcrops of sedimentary rocks and low-temperature aqueous precipitates and alteration products, rendering this previous conclusion incorrect. It appears now that rocks that could preserve evidence of complex aqueous processes, organic geochemistry, and even life are accessible at the Martian surface. The SSG sampling subgroup was tasked to address the clear desire and scientific need to sample adequately these types of units. In short, we were asked: how do the MER results affect how we select, collect, store, and return samples?

In detail, the MSR SSG Sampling Subgroup Charter addressed the following questions for the *first* MSR:

1. *Sampling approach:* What are the science priorities for the functionality of the MSR sampling system?
2. *Sample packaging:* What are the science priorities for the functionality of the MSR handling and storage system?
3. *Assay techniques & Caching:* In order to select samples, what measurements must MSR conduct? Would MSR benefit if samples were cached for it by a prior mission, e.g. MSL?
4. *Sample Preservation:* What are the science community's priorities for controlling the environment of returned samples?

Note that the *italicized* titles for each question were added by the group – these are shorthand for the topics we discussed, and will be repeated throughout this document.

General approach and comments

Our approach to addressing these questions initially involved combining them into a holistic sample-related discussion, where the characteristics of a realistic but optimized first sample return were considered. This was followed by a "science value exercise" to consider the science value of increased capabilities more "quantitatively." We held discussions in person at our two SSG meetings, in four teleconferences, and via email.

Finding: **It was generally agreed that in the absence of a MSR Science Definition Team (SDT) and a list of science objectives for the MSR mission, the job of defining and prioritizing sampling strategies is very difficult**

Recommendation: **During or after convening an MSR SDT, the conclusions of this subcommittee should be re-examined to ensure consistency with the outcome of the SDT process**

Lacking an SDT report laying out the specific science goals of the first MSR, for most of our discussions, it was assumed that a site with exposed sedimentary rocks, preferably with accessible igneous rocks, would be a very likely target of the first MSR. Objectives would be related to (1) seeking the preservation and history of organics (possibly life), water, and other volatiles, (2) understanding the depositional history and environment of the samples and (3) determining their age if possible. The larger SSG considered application to other sites of the priorities we derived from this site and found virtually no differences in sampling needs if MSR visits a (1) Meridiani-like site, (2) a Gusev-like site, (3) the MSL site, or (4) a previously unvisited site with a geologic contact. Thus the results of this subgroup's discussion are considered to be fairly resilient to site selection details.

It is important to note that part of the reason for undertaking this evolution of MSR capabilities was the realization that the GMSR concept would likely not have fulfilled its goals at Meridiani (i.e., there would have been no small rocks within the reach of a stationary lander).

Thus the simplest evolution to GMSR would be a "mobile GMSR", capable of "fetching" the rock fragments. *Such a mission would have increased cost and complexity, but no real increase in science value over GMSR.* Increased science value comes from enhancing the stated goals and capabilities beyond those of a mobile GMSR mission.

Science Value Exercise

Introduction. In order to evaluate the *relative science value* of various types and levels of increased sampling and sample handling capabilities to the first MSR mission, we undertook a "science value exercise" to determine where the most science value would be gained by increasing capability. The exercise in its entirety is given in Appendix C, and is summarized only briefly here. Basically, the exercise consisted of defining the range of mission elements related to sampling approach possibilities, sample packaging options, assay techniques and caching, and sample preservation, then combining variations of each of these four elements into example missions, and finally having each panel member subjectively rate the science value of each mission on a scale of 1 — 1000 (where GMSR is defined = 1, and a MER-scale and capable MSR is defined = 1000). The entire purpose of this exercise was to find out which capabilities give the most "bang for the buck" in the minds of the committee. Of course, missions of higher capability will always have higher science value, but some components provide especially large gains in science value. This was not and did not pretend to be a quantitative exercise, but rather a qualitative way to articulate the more and less valued characteristics of the first MSR mission.

The conclusion from this exercise is that enhanced capabilities in the sampling system (specifically, a coring device for bedrock sampling) and sample isolation (to isolate regolith, windblown fines, and individual cores from each other) are strongly viewed as most important to greatly increasing the science value of the mission.

Each of the four major element categories – sampling approach possibilities, sample packaging options, assay techniques and caching, and sample preservation – are discussed individually below.

Element #1: Sampling Approach

As stated above, the group strongly prioritizes the ability to sample bedrock (either igneous or sedimentary), in stratigraphic context preserving weathering gradients into unaltered rock. We believe the most straightforward way to do this would be through coring. Sampling bedrock would provide the most direct record of geologic processes on Mars, and would provide the highest likelihood of being able to place the small amount of MSR samples in local, regional and even global context on Mars, thus maximizing the knowledge gained from MSR. Although rock fragments and soil would be extremely valuable, sampling a stratigraphic sequence would clearly be the priority if such a sequence is available. MER showed us that such sequences exist, and contain extraordinarily interesting rocks!

Obtaining a suite of samples from a single "site" where outcrop is available (e.g., Eagle or Endurance crater) is considered sufficient for the first MSR. Sampling strategy for a sedimentary site would need to optimize a mix of sample diversity (determined with whatever means available) and documentation of a stratigraphic time series by collecting samples along a defined rock sequence. This sampling strategy must integrate on-site knowledge and thus cannot be pre-determined before landing and viewing the site.

Coring into rocks would allow important textures as well as chemical and physical gradients to be preserved. These signatures would provide clues to evolving conditions as the rocks were deposited. Preserving the exposed surface on at least some of the samples would be critical to understanding atmospheric weathering effects (such as oxidation) after the rocks were deposited. Some of these effects may erase the biosignatures that we seek – recognizing them is therefore critically important.

Although rocks are the highest science priority samples for the First MSR, locally-derived regolith and windblown fines are also considered extremely important samples to understand the role of water both locally and globally on Mars. Because of the fine-grained nature of these materials, they are extremely difficult to analyze remotely, and therefore they are uniquely suited for returned sample analysis on Earth.

A *separate* atmosphere sample on the first MSR is also considered very important. Returning an atmosphere sample, uncontaminated by degassing of or interaction with soil (in other words, in a separate container from soil) has been a high priority of Mars science for many years. The chemical composition and isotopic ratios in the atmosphere provide a unique snapshot of the current state of volatiles on Mars, as well as windows into volatile loss through time. If forced to prioritize among the sample types (rock, regolith, windblown fines, and atmosphere), a *separate* atmosphere sample would be considered less important than the other four sample types. However if a separate atmosphere sample could not be accommodated on the first sample return, every effort must be made to recover the “headspace gases” that would inevitably be returned in the rock, regolith, windblown fines containers.

The group discussed the nature of a contingency sample. A scoop/rake sample from the lander, below the effect of surface contamination, is considered an acceptable contingency sample.

The group did not close on most of the *sample size* issues – these need to be revisited FOR ALL SAMPLE TYPES (rocks of different types, regolith, windblown fines and atmosphere). For example, the group recognized that most prior constraints on rock sample sizes (~10-20 g per “sample” – where a sample is from a single outcrop location or subsample of a rock – equivalent to a “RAT hole” on MER) were driven by knowledge of analysis protocols on meteorites and/or lunar samples. This needs to be revisited for sedimentary rocks. To do so would require development of analysis protocols for such samples. These protocols are likely to differ from those for igneous rocks mainly in (1) the number of analyses that are performed in sequence on the same sample rather than splits of the sample and (2) the sub-sampling of fine-scale layers that might be necessary. In spite of these uncertainties, a preliminary finding is that 10-20 g per rock sample should be approximately sufficient and could be used as a placeholder until this matter can be taken up by a sample handling protocol group.

Regolith and wind-blown fines samples would be analyzed both in bulk and essentially grain-by-grain to investigate their components in more detail. Regolith samples of 20 - 50 g in size should be sufficient for replicate diverse analysis types and sample curation. It would be ideal to obtain a sample of regolith right at the surface (away from the lander to minimize contamination from descent), and from at least one depth below the surface as far as would be feasible without seriously driving requirements. Similarly, a 10 g sample of windblown fines should be sufficient for science purposes, but more sample than this may be desired for human spaceflight preparation purposes (this needs to be addressed through coordination with the other MEPAG SSG).

Atmospheric sampling is still very much an open issue, especially whether a small (say, 20-30 cc) ambient atmosphere sample would be sufficient to meet the science objectives of MSR. It is possible that a 30 cc sample at ambient Mars conditions would allow most all types of analysis to be done, but this needs to be revisited. In any case, leakage of gases from the container would result in some alteration of the abundances and isotopic compositions of gases during transport, and such changes need to be well understood. Monitoring leak rates, or having good constraints on them would be desired in an atmosphere sample. The container material needs to be considered carefully, as most materials will interact with the gas in some way over time.

Element #2: Sample Packaging

The highest priority in sample packaging would be to keep individual cores separate from one another and from regolith/fines contamination. Separate containers are also strongly desired for regolith and windblown fines samples. Each rock, regolith and fines sample records a unique history and set of processes by which it formed and evolved. Unraveling these processes is at the heart of the goals for sample return. A broad science community would apply the most sensitive analytical capabilities achievable toward deciphering the record in these materials. Mixing the samples would cause the records of these critical processes to be jumbled, and make them very difficult to interpret. Such an approach would significantly compromise the great promise of MSR to reveal a detailed history of rocks and soils on Mars. The prospects of making a great discovery and (more importantly) of properly interpreting it, would be maximized by isolating individual samples from one another.

The potential for migration of volatiles from one sample to another is a matter of some concern. Beyond simple cross-contamination of sample chemistries, there is the potential for release of substantial amounts of water from some samples (e.g., samples rich in hydrated magnesium sulfate salts). This water could significantly alter samples to which it migrates, whether it migrates as vapor or liquid. Container design elements that could potentially mitigate volatile migration include gas-tight seals, desiccants, and cryotemperature stabilization.

Element #3: Assay Techniques and Caching

The group discussed the idea of requiring MSR to visit only sites that have been previously explored by another landed mission (virtual caching)[1]. We discussed strengths and weaknesses of this approach. Because samples at the site will have been previously characterized, fewer on-board tools (and possibly less mobility) would be needed, decreasing cost and complexity of MSR – this would clearly be a strength. Also, if the terrain is well understood from a previous mission, spacecraft constraints perhaps could be more targeted to this site, simplifying the design. Clearly the main weakness of this approach would be the inability of MSR to explore new sites. This would be especially limiting if MSR has improved landing capabilities (e.g., pinpoint landing) over previous missions. Imagine that MRO discovers some very interesting units or features that are inaccessible except by pinpoint landing. Would we want to turn our back on such a site simply because we hadn't visited it before? It could be argued that such sites present more science risk, because their make up has not been confirmed or studied by an in situ mission. However, by the time of the first MSR we will have increasingly sophisticated orbital measurements and we will have visited at least 7 sites on the Martian surface. Surely our

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[1] This idea is alternatively known as The Golombek Manifesto, The Golombek Prophecy, The Golombek Miracle…

predicative capabilities will be reasonable enough to allow us to choose a compelling site even if it has not been visited previously. The group concluded that although returning to a previously visited site may be desirable in some cases, we believe it is not wise to commit exclusively to this strategy. In other words, in order to allow MSR to be as discovery driven as possible, we should not commit to sending the first MSR to a previously explored site.

The above discussion was useful because it forced us to consider how much we value on board instrumentation for sample "assaying" even in the event that a previous lander had not surveyed a site. Given the MER experience in Eagle and Endurance craters, the group concluded that simple on-board instrumentation (i.e., a reasonable quality imager capable of seeing layering and crude color differences) would probably be sufficient for this mission. Assuming we are capable of choosing a compelling landing location, this instrumentation would allow us to design a sampling strategy that would have a high probability of maximizing the diversity of samples from the site. For example, such a camera was the primary tool used to decide where to "sample" (with the RAT and the IDD tools) along the outcrop in Endurance Crater, and it could easily observe differences between the igneous rocks on the floor of Gusev Crater and the different rocks in the Columbia Hills. For the first MSR, sample documentation with imaging at the outcrop scale (resolution comparable to Pancam on MER) and the hand sample scale (resolution comparable to Microscopic Imager on MER) is considered important.

The group also discussed having MSR pick up a physical cache from MSL. The group felt that this idea has merit and should be studied, but we are (1) content with the conceptual MSR constraints we have laid out with or without the added capability MSL would provide, and (2) concerned that pursuit of MSL caching may divert attention and resources from MSR issues, and therefore could threaten mission success. This ambivalence was reflected in the Science Value Exercise in which the addition of the MSL cache to mission capabilities resulted only in a very slight increase in science value (see missions 14 and 18 in Table 2). *A critical point is that MSR must not be designed to be completely dependent on a cache; MSR must have independent sampling and storage systems in the case that the caching system fails or if another site is deemed of higher value for MSR than that visited and cached by MSL.*

Element #4: Sample Preservation

The group considered four types of sample preservation issues: packaging (discussed above), physical integrity, sterilization issues on Mars, and sample temperature history after leaving the Martian surface.

Physical integrity. Every effort must be made to preserve the physical integrity of the samples during all phases of the mission. Minor fracturing of cores would not significantly impair scientific study if the core pieces remain in their original orientation and only small amounts of powder are produced along the fracture planes. Preserving physical and chemical gradients in the samples is of high scientific value. Such information would be lost if the samples are pulverized. Put simply, the main value of coring would be lost if the samples are powdered. The group was satisfied that this constraint could be met without driving design significantly, and thus did not focus much attention on it after initial discussions. However, it is a high priority that rock samples be returned as close to intact as possible, and certainly without powdering.

Sterilization: Mechanisms for collecting "clean" samples, including sterilizing the surface chemically, or physically scraping surfaces off of rocks/soils were NOT considered acceptable. As discussed above, much important science would be lost if the surface materials are removed or chemically altered through sterilization. In addition, the science community represented on the SSG is skeptical of chemical or other sterilization approaches being reliable to the point of being acceptable for use. For example, a porous and permeable regolith could easily permit the penetration (to several mm depth) of terrestrial spores and/or microbes shed from a rover or lander. If an approach to sterilizing the surface were absolutely required to meet Planetary Protection requirements, physically scraping surface materials off is considered better than alteration of the samples by some in situ chemical sterilization method. From the perspective of *science* (not planetary protection), a slightly contaminated sample could still have value as long as the contaminants are well understood. These topics are taken up in more detail by the contamination subgroup.

Temperatures. The subgroup explored in great detail the ramifications of heating of the samples once they leave the Martian surface, primarily during Earth atmospheric entry and especially after landing on Earth. The original GMSR concept did not require active refrigeration, but did recommend sufficient insulation to ensure that the samples would not experience temperatures in excess of 50 °C; simple temperature monitoring during Earth landing would be required.

The present subgroup looked at the temperature effects on specific classes of compounds, organic and inorganic. The results at Meridiani seem to support the possibility that hydrated salts exist in abundance at interesting sites on Mars, and some of these salts (especially magnesium sulfates) could release water upon mild heating, possibly accelerating other breakdown reactions. Therefore, it is prudent to study the possibility of including some desiccant materials in the return capsule to trap any released water. Clearly, such material would need to be accessible to any gases being released, but physically isolated from the Martian samples.

Our study of temperature effects is given in complete form in Appendix D; excerpts from that study are given here.

The main finding is that significant science would be compromised even at 50 °C – especially volatile organics, which would be of high scientific interest, may be mobilized or altered.

From a science perspective, therefore, it is desired that sample temperatures should be kept below 50 °C; ideally, they should remain at or below Mars surface ambient temperatures (<0 ^{o}C). However, the group recognized that requirements for active refrigeration were unrealistic for the first MSR, and so this should be pursued through design optimization of the sample capsule and Earth entry vehicle (EEV) to the best extent possible, as well as mission plans to recover and cool the EEV as soon as possible after impact.

The potential alteration of inorganic phases centers on the fate of water: structural in certain minerals, interlayer in clays, brine ice or liquid brines in fractures and interstices, and chemisorbed and physisorbed on mineral surfaces. The main concern would be preventing hydrated magnesium sulfate salts from melting. Data from Viking 1 and 2 and from Pathfinder suggest that MgSO4 is present at roughly 10 wt % (anhydrous equiv.) in Martian soils (Vaniman et al., 2004; Wänke et al., 2001), and data from Spirit at Gusev crater are not inconsistent with this finding (Gellert et al., 204). These salts are likely to be present on Mars, in the minerals kieserite ($MgSO_4 \cdot 1\ H_2O$), epsomite ($MgSO_4 \cdot 7\ H_2O$), and $MgSO_4 \cdot 12\ H_2O$, as well as in amorphous phases with variable water contents (e.g., Vaniman et al., 2004). Hexahydrite

($MgSO_4 \cdot 6\ H_2O$) could be formed by hydration or dehydration reactions of these other phases if the sample storage temperature climbs above about 280K.

At temperatures above 270K, these phases are all near the point of partially dehydrating or melting to form a Mg++, SO4-- rich brine (Appendix D, Figures 2, 3). The phase changes appear to be rapid, for example the dehydration of hexihydrite at 298K, 580 torr, and relative humidity of 0.3-0.4% takes on the order of several hours (Appendix D, Figure 4). However, the kinetics of most of the phase changes have not been studied sufficiently well to understand what would happen in a sample return container as temperature and relative humidity rise in concert.

Table 5. Thermal Effects on Inorganic Phases During Storage and Return of Mars Surface Sample. *Worst case scenario: heating a Mars surface sample to 50°C for several hours.*

Possible major effects:

1) Dehydration and/or melting of hydrated magnesium sulfate salts (e.g., epsomite, hexahydrite).

Major issues if ice and/or hydrated magnesium sulfate salts are present in sample

1) Melting of ice or hydrated magnesium sulfate.
2) Minor dissolution of evaporitic minerals in the resultant aqueous solution.
3) Enhanced redistribution and reaction of organics if present.
4) Loss/exchange of some interlayer cations in clays minerals (if present).

Probable minor effects:

1) Volatilization of chemisorbed and physisorbed water (especially from clays & zeolites if present).
2) Slow dehydration of hydrated clay minerals (if present).
3) Loss (dehydration/decomposition) of minor abundance, delicate evaporitic minerals.
4) Reversible changes in fluid inclusion chemistry due to temp-dependent salt solubilities.
5) Reactivity and catalytic properties of mineral surfaces towards volatile/soluble organics.

Possible minor effects:

1) Recrystallization/hydration/oxidation of reactive iron minerals.

Probable non-issues for this scale of temperature/time history:

1) Decrepitation of fluid inclusions.
2) Thermal sensitivity of hydroxylation/dehydroxylation reactions.

Table 5 summarizes the expected effects of heating on inorganic phases in Martian surface samples. This summary assesses a worst case scenario in which samples would be kept below 0˚C from collection time until reentry into Earth's atmosphere; then following reentry and prior to retrieval the samples reach 50˚C for a maximum of a few hours due to heat soakback from the reentry vehicle's heat shield. This table takes into account the phases likely to be encountered in Martian regolith and in weathered and unweathered outcrops.

If these salts serve as a cement in regolith materials or sedimentary rocks, then dehydration or melting could result in physical disaggregation of samples and concomitant loss of structural features and chemical gradients. Phase stability fields are a function of relative humidity, and thus, desiccant functionality in the sample return capsule may prevent melting of these salts (Figure 2). Hydration and dehydration reactions appear to proceed more slowly than melting, so a rapid recovery of the returned sample would help significantly in minimizing disaggregation problems.

Temperature Effects on Organic Phases

Few published organic geochemical studies report molecular or stable isotopic data for fine-grained sediments or sedimentary rocks on Earth containing trace (< 0.05 wt%) amounts of organic carbon for two reasons. First, samples containing trace concentrations of organic carbon are almost always contaminated during sampling to a level where extraneous organic compounds pervasively overprint indigenous organic compounds. Second, organic compounds are tightly bound to mineral surfaces in fine-grained siliciclastic, calcareous, and evaporitic sedimentary materials containing trace amounts of organic matter. Increasing sample size is ineffective because extraction yields from these types of samples are proportionally lower than yields for similar sediments containing higher contents of organic carbon. For all of these reasons, it is difficult to predict the fate of organic molecules in a Mars return samples that are anticipated to contain only trace level organic carbon. In Table 6, we described the fate of organic molecules using generalized terms because most of the compound classes contain a wide range of structural configurations and molecular weights combined with substantial uncertainties regarding mineral composition and hydration state for near-surface Mars regolith and rocks. The term *mobilized* refers to molecules that are unaffected chemically but are capable of physical migration between absorbed or complexed phases. *Volatilized* refers to molecular classes that will be present primarily in a vapor state. Volatilization at the chosen temperatures is estimated based on standard laboratory evaporation procedures at controlled temperature using vacuum aspiration to about 20 millibars (Rotavap or equivalent apparatus). *Partial decomposition* refers to initial stages of chemical transformation including isotope exchange, dehydration, and isomerization. *Decomposition* refers to chemical transformations more severe than those listed for partial decomposition, typically involving structural breakdown and/or molecular reorganization.

It is clear from the table that at 50^{o}C a significant number of compounds experience decomposition, and even at 20^{o}C some compounds are decomposed. At -5^{o}C some compounds are mobilized or even volatilized.

Fate Of Indigenous Martian Organic Molecules During Sample Return

Information Compiled in 2004 by Lisa Pratt, Simon Brassell, Arndt Schimmelmann, Bernd Simoneit

Molecular Class	Examples	Scientific Interest	Susceptible to Photo - Decomposition	Susceptible to Hydrolysis or Water Solvation	organic matter sampled in an intact sedimentary matrix, sample canister sealed under oxidizing atmosphere at 6-10 millibars pressure, maximum temperature during re-entry not exceeding:		
					-5°C	20°C	50°C
Aromatic Hydrocarbons	benzene	M			Unm	Mob	Vol
Polyaromatic Hydrocarbons	anthracene, phenanthrene	H	√		LMW - Mob HMW-Unm	LMW - Vol HMW - Vol	LMW - Vol HMW - Vol
S, N, O Heteroatomic Aromatics	pyrimidine, furan, pyridine, purines, benzothiophene	M			LMW - Mob HMW-Unm	LMW - Vol HMW - Mob	LMW - Vol /PDec HMW - Vol /PDec
Aliphatic Hydrocarbons	alkanes, alkenes, pristane, phytane	H			Unm	LMW - Vol HMW -Unm/ Mob	LMW - Vol /PDec HMW - Vol /PDec
	Methane	VH			Vol	Vol	Vol
	ethane, propane, butane	VH			Vol	Vol	Vol
	hopanes, steranes	H			Unm	Unm	Mob
Saccharides	tetrose, glucose, cellulose	VH		√	Unm	Unm	Unm
Carboxylic Acids and their Salts	alkyl and aromatic acids, fatty acids	H		√	LMW- Mob HMW-Unm salt-Unm	LMW - Vol HMW - Mob salt-Unm	LMW - Vol HMW - Mob/Vol salt-Unm
Amino Acids	basic, neutral, acidic	VH		√	Unm	Unm	LMW - Unm HMW - Unm
Nitrogen-Containing Compounds	amines, amides	H			LMW- Vol HMW-Unm	LMW - Vol /PDec HMW -Unm/ Mob	LMW – Vol /PDec HMW – Vol /PDec
	tetrapyrroles, porphines, siderophores	VH	√	√	Unm	Unm	PDec
Peptides	polar and non-polar	H		√	Unm	Unm	Mob /PDec
Functionalized Lipids	glycerides, fats	VH		√	Unm	Unm- Mob /PDec	PDec
	ether lipids	VH			Unm	Unm	Unm
	esters, ketones, aldehydes	H	√	√	Unm	LMW - Mob HMW -Unm	LMW -PDec HMW -PDec
	alcohols	H		√	LMW- Mob HMW-Unm	LMW - Mob HMW - Mob	LMW -PDec HMW -PDec
Humic and Fulvic Acids		M	√	√	Unm	Mob /PDec	PDec/Dec
Unresolved Complex Molecules		H			Unm	Mob	Mob /PDec
Phospholipids		VH		√	Unm	Mob/PDec	Mob /PDec
Nucleic Acids, Nucleotides	DNA, RNA, TNA	VH	√	√	Unm	Unm	DNA -Unm RNA -PDec
Nitrogen-Containing Gases	NH_3, HCN, NO_2, N_2O, NO	H			Mob	Vol	Vol
Sulfur-Containing Gases	H_2S, $(CH_3)_2S$	H			Mob / Vol	Vol	Vol /PDec

Abbreviations and acronyms

VH = very high
H = high
M = moderate
L = low
Unm = unmobilized
Mob = mobilized
Vol = volatilized
PDec = partially decomposed
Dec = decomposed
LMW = low molecular weight
HMW = high molecular weight

The conclusions of the MSR SSG Sampling Subgroup can be summarized as follows::

For the first sample return mission, the highest priority would be to increase sampling capability such that bedrock could be sampled (probably with a coring device), and increase sample storage capability such that multiple “bins” would be used and individual rock samples could be stored separately from one another.

It is important that options be examined that would allow the samples to be maintained at < 50°C (< 20ºC highly recommended, ~-5°C desired).

Complex in situ instrumentation is not considered very important for the first MSR mission -- a reasonably capable color camera is considered sufficient to select and document interesting samples. A close-up monochrome imager for documenting rock and soil texture at the hand-sample scale is also highly desirable.

Caching by MSL is considered desirable by the group because it adds science value, however, the group does not endorse requiring this. Many on the team expressed concern about placing burdensome requirements on MSL, and about expending excessive resources from the MSR project to make this happen.

VIII. Revised Science Considerations Pertaining to Forward Organic Contamination

Terrestrial Organic Contamination in Returned Samples:

Background: Identification and characterization of organic compounds on Mars is given high priority by the recent Mars Exploration Program Analysis Group (MEPAG) update (Taylor et al., 2004). This investigation of carbon compound sources and processing is considered to be an essential step to advance the understanding of the possibility of past or present life on Mars. The carbon investigation is intended to proceed in parallel with studies that lead to an increased understanding of the history of liquid water on the planet and the availability of other elements and energy sources necessary to sustain life. The ability demonstrated by the Mars Exploration Rover Opportunity to reach surface sites that show direct evidence of substantial aqueous alteration further motivates the search for organic compounds and the locations that might best preserve such compounds.

Although examination of patterns in complexity, oxidation state, and isotopic composition is expected to point toward sources and processing of organic compounds found on Mars, predictions regarding the abundances of organic compounds that might be found in near surface samples are presently highly uncertain. The most easily quantifiable source of organic compounds is exogenous delivery of meteoritic material that could, in principle lead to parts per million (ppm) of organics in the near surface (Benner et al., 1999). The degree of gardening of these materials into the regolith and the extent of subsequent chemical oxidation are highly uncertain. The recent reports of up to 30 ppb of methane in the Martian atmosphere (Formisano et al., 2004, Krasnopolsky, 2004) or even higher localized mixing ratios (Mumma et al., 2004) also has implications for the organic compounds present in the near surface of Mars. Methane that diffuses from the regolith into the atmosphere forms ethane and higher hydrocarbons by UV photolysis (Wong et al., 2003) and the subsequent condensation of these phases in surface ice and sorption on to mineral surfaces (for diffusion to the atmosphere at a rate of $\sim 2\text{-}6\times10^5\ \mathrm{cm^{-2}s^{-1}}$) should occur at a rate of ~7 ppb C $\mathrm{byr^{-1}}$ for a 10 cm thick layer. The degree of gardening of these materials into the regolith and the extent of subsequent chemical oxidation are highly uncertain. Other sources of organic compounds such as those that might be produced by abiotic synthesis are not quantified even to first order. Upper limits to the amount of biologically produced organic matter can be inferred from the austere environment in the Antarctica dry valleys (Wynn-Williams, 1990) where organic carbon concentrations are <200 ppm and the density of living bacteria are $\sim 10^5$ gm^{-1} (Cowan et al., 2002). Thus, a sensitive search for a wide range of organic compounds in returned samples by a variety of techniques would be of high priority. To avoid ambiguity in the interpretation of these measurements that seek to find and characterize organics it would be essential that terrestrial contamination introduced to the returned samples be limited and well characterized.

Organic Compounds of Interest in a Returned Sample: A wide range of possible organic compounds is of interest from the point of view of understanding the habitability of Mars – its potential for past or present life. Although distributions of organic compounds in classes directly participating in terrestrial biology such as amino acids, nucleobases, sugars, carboxylic acids, and more complex molecules such as proteins, enzymes, lipids or their fragments may provide the most direct potential biomarkers, a broad survey of organic molecules and molecular types would be necessary to develop an understanding of how a particular Martian chemical environment might transform exogenous or endogenous organic species. Thus, limits on total molecular carbon would be important as well as limits on individual species or classes of compounds.

Sources of Terrestrial Contamination in a Returned Mars Sample: Likely terrestrial contamination sources that might interfere with in situ measurements have been recently identified by the Report of the Organic Contamination Science Steering Group (OCSSG) (Mahaffy et al., 2003). These include materials used in spacecraft fabrication such as conformal coatings that outgas volatile organics, lubricants for moving parts, propulsion fluids and solids, and organics contained in particulate matter. Contaminants may accumulate during spacecraft assembly even in a typical clean room environment and are more rapidly distributed during events such as launch or entry, descent, and landing (EDL) where substantial levels of terrestrial material is both redistributed within the spacecraft and released into the Martian environment.

Many of the likely contaminants consist of or contain biologically produced or processed organic molecules of the type that would be of the highest interest if their Martian origin could clearly be established. These contaminants may migrate to the tools and surfaces that contact the sample at Mars or residual contamination on the landed system may migrate to the Mars surface prior to sample collection. While for an in situ experiment, it may be possible to make a measurement shortly after sample collection to minimize the amount of contamination transferred from the lander system, the extended time required to return a sample to Earth would provide an additional opportunity for contamination to mix with the collected sample prior to analysis.

The sample temperature history between collection and analysis in laboratories on Earth may be a critical parameter in determining the extent of mixing of both terrestrial organic contaminants and indigenous organics. The worst-case thermal environment may be during and shortly after Earth entry. Thermal transformation of the collected sample constitutes another type of sample contamination. Of particular concern is the chemical effect of thermally released water or water vapor on molecules of interest.

Storage and processing of the samples and their containers in the return sample facility again introduces an additional path for contamination. Subsequently, each analysis technique with the associated sample manipulation and physical and chemical processing, such as the use of solvents for organic extraction, has the potential to introduce additional contamination. The design of the sample curation facility must be an integral element of planning for the sample return mission.

Relationship to Planetary Protection Requirements: Agency planetary protection requirements for the first Mars sample return mission are expected to minimize the probability that a viable terrestrial organism that could be cultured with standard protocols would be returned with the collected sample. These mission requirements would not, however, address the contamination issues of non-viable terrestrial organisms and their molecular byproducts that might be contained in the return sample. Thresholds for these contaminants must be separately set during the mission science definition process.

Lessons from the Apollo experience: Considerable attention was paid to contamination issues during the Apollo program to maintain the integrity of returned lunar samples. Critical sample processing surfaces were cleaned to ~ 1 nano-gram/cm^2 of molecular material. The total organic content of the returned lunar samples was typically in the 0.1 to 100 ppb range. Several amino acids were present (Brinton and Bada, 1996) and in the worst case at an abundance of 70 parts per billion (ppb) by mass (ppbw). Amino acids such as free alanine and aspartic acid were identified as terrestrial contaminants. The lesson learned from the lunar organic contamination may be that additional measures beyond rigorous pre-launch cleaning of surfaces that contact samples may be necessary to obtain samples with terrestrial contamination below the several ppbw level.

Contamination Threshold Goals: The OCSSG report proposed thresholds of 1-10 ppbw for the maximum amount of terrestrial contamination that could be contained in a Mars sample on delivery to an instrument in a landed payload package for proxy compound classes of high scientific interest such as benzene or aromatic hydrocarbons, carbonyl and hydroxyl containing compounds, amino acids, amines, amides, or non-aromatic hydrocarbons. The OCSSG proposed a threshold for total reduced carbon contamination at 40 nanograms per gram sample delivered to an analytical instrument. In light of the great variety of state of the art analytical techniques that could be applied to organics analysis of returned samples, it would be desirable to realize even lower thresholds in a returned sample than these proposed thresholds for in situ analysis. For example, thresholds of less than 10 ppbw in total organic contamination and ppbw or below in the proxy compound classes listed above could enable robust conclusions to be drawn regarding the origin and processing of indigenous Martian organics found in the ppbw or higher abundances.

Significant scientific work in terrestrial organic geochemistry is carried out using sub parts per billion of certain species as discriminators. For example, phospholipid fatty acid analyses (PLFA) of deep subsurface rock cores provide the principle method of determining biomass and discriminating between contaminant and indigenous microorganisms (Onstott et al., 1998). In some cases the total PLFA is < 0.1 ppb C (Colwell et al., 1997) corresponding to ~10^4 cells gm^{-1}. The presence of 10me16:0 (a 16 carbon saturated hydrocarbon chain with a methyl group branching off a the C10 position) at < 0.01 ppb C was used to identify indigenous sulfate reducing bacteria existing in a rock sample collected at 3.3 km depth in which 95% of the bacterial biomass was contaminants (Onstott et al. 2004).

Sedimentary units on Earth contain widely varying contents of organic matter. Coal and oils shale are examples of sedimentary rocks containing more than 50 wt% organic carbon (C_{org}). At the other end the concentrations range, red sandstones, mudstones, and shales (collectively termed redbeds) are generally in the range 0.1 to 0.01 wt% C_{org}. Sedimentary units on Mars are anticipated to contain relatively small amounts of organic matter and, therefore, acceptable thresholds for contamination of Mars return samples logically are based on reported yields for specific classes of organic molecules in the lowest C_{org} sediments from Earth such as redbeds. The most widely studied classes of organic molecules in sedimentary rocks on Earth are aliphatic and aromatic hydrocarbons (see Table X).

Hydrocarbons in ancient sediments are extracted using nano-pure chlorinated organic solvents and are isolated using chromatographic separation preferably under clean-room conditions. Identification of individual molecules is performed using molecular mass spectrometers with sub-picogram sensitivity. The solvent-soluble fraction of a rock is called bitumen and the residual organic fraction is called kerogen. Bitumen yields from redbeds are generally less than 10 μg/g (weight bitumen/weight rock) and are often less than 1μg/g. Samples containing less than 1μg/g bitumen are challenging to study because substantial contamination occurs during sample collection and sample handling. For this reason, there are few published organic geochemical studies on any type of sedimentary rocks containing less than about 0.2 wt% C_{org} (Pratt, 1984). The major compound classes recovered from redbed samples are S-N-O-heteroatomic organic compounds, aliphatic hydrocarbons, aromatic hydrocarbons, and unresolved mixtures of high-molecular-weight organic compounds (asphaltenes). The proportion of aliphatic plus aromatic hydrocarbons can represent less than 1% of total bitumen. If we assume a yield of 1 μg/g bitumen and 0.01μg/g aliphatic plus aromatic hydrocarbons then the concentration of individual n-alkanes and hopanes (compounds of high scientific interest) would be in the range of 1 to 0.1 ng/g. Thus, contamination at a level of 1 ppb (ng/g) for an individual compound of interest would be equivalent to anticipated concentrations of indigenous Martian organic compounds and greater by a factor of 10^5 than current detection levels for mass spectrometers.

However, it is important to note that not all samples distributed for analysis would have organic measurements as a prime focus. If subsets of the returned sample that would be analyzed for organics are effectively isolated from transport of organic molecules contained in other samples, then the average contamination level in the returned sample could be larger than that in the isolated samples of interest without impacting the primary organics studies.

The OCSSG report also specified a 1 ppbw threshold for DNA as a proxy for very complex molecules that could only have a biological source. It is desirable for a returned sample to have the threshold for such complex molecules far below the thresholds desired for in situ exploration where the techniques for analysis of such materials are not present. A contamination threshold for DNA or complex molecules such as proteins could usefully be set at an abundance that would make any detection with current analytical technologies in analyses of a returned sample unlikely. Achieving this goal might require cleaning of the sampling containers and tools while on the surface of Mars, prior to sample collection and sealing.

Contamination mitigation: The OCSSG report describes a range of possible contamination mitigation steps including selection of low outgassing materials, cleaning of all spacecraft elements, and maintaining a clean environment during assembly and test operations. The microbial community in the assembly area and on the spacecraft would need to be fully and quantitatively characterized. Particular attention should be focused upon the removal of spore forming, phototrophic and autotrophic microorganisms (e.g. methane oxidizers) that have the ability to survive on Mars within the protective environment of the rover. In addition, a clear understanding of contamination pathways within the spacecraft systems must be developed. Special attention must be paid to sample processing and storage equipment both with regard to its cleaning and its effective molecular isolation from more contaminated areas of the spacecraft. In addition to these design and fabrication and assembly mitigation methods, surface operational sequences should be designed to minimize the amount of terrestrial contamination that would be mixed with the returned sample. For example, a landed system with mobility could remove itself sufficiently far from the landing site to minimize the collection of chemicals vented and released during the landing process. An approach to a sample of interest by a mobile collection system could be designed to minimize the time in close proximity to the sample to reduce accumulation of contamination from the collection platform. Monitoring of winds by the mobile landed system and approaching samples of interest from the down-wind side could minimize the amount terrestrial contamination transferred to the sample of interest.

Heat, UV, or plasma treatment of sample storage volumes and sampling tools shortly before sample collection could eliminate or minimize the contamination from large molecules that are effectively destroyed by high heat, plasma, or radiation. For example, even a short 500^{o}C treatment of sampling tools and containers is expected to rapidly destroy complex molecular species associated with dead organisms. Effective isolation of a sample immediately after collection could prevent contamination from either the landed system or other samples from migrating into the collected sample. In a subset of the sample containers, it might be useful to study the use of adsorbant traps such as synthetic zeolites that would remove water vapor as it was out gassed during the return to Earth in order to minimize its subsequent chemical interaction with the sample and retain it for analyses.

Blanks and Controls: Controls in the form of passive monitors that would collect contamination from the environment during the various mission phases from early in the assembly process to sample return are essential to build up a library that would enable the nature of the terrestrial contamination to be understood. Likewise, blanks, such as empty sample containers, that mimic sample processing operations and exposure could be valuable in validating organic measurements on returned samples. Use of organic free terrestrial blanks that would be exposed to the Martian environment and sealed for return might be useful, but should be approached with great caution to avoid any possibility of contamination of Martian samples with inorganic terrestrial materials. Post collection organic migration potentially could be studied by exposure of a small subset of Martian samples to the mobile lander environment for a variable time period prior to sealing. This would help to evaluate contamination transfer rates or heat devolitalization of a Mars sample prior to storage and isolation for return to Earth. Contamination monitors should not only be used in clean rooms and fabrication sites prior to launch, but could also be incorporated into the return system to collect contamination in the later mission phases. In spacecraft locations where contamination monitors cannot be collected for return, the use of active sensors such as quartz crystal microbalances should be considered to monitor the buildup of contamination.

Summary of Organic Contamination Issues and Findings

(1) **While OCSSG specified contamination levels for organic molecules would be adequate for a subset of the samples where organics analysis is not the primary objective, lower thresholds by a factor of 4 or more are desired for an isolated subset of the samples such as cores from sedimentary deposits or selected rocks where organics analysis would be a primary investigation.** Although modern instrumentation may be able to detect much lower levels of organics, achieving a significantly lower threshold may be impractical as may the realization of lower organic levels in blanks used during the sample analysis. The Apollo experience suggests that these thresholds can be realized.

(2) For large biomolecules that are the residue from terrestrial organisms (e.g. DNA, RNA, and large or medium sized proteins) the contamination threshold in returned samples should be sufficiently low that analyses of test samples have a high probability to produce a negative result. Technologies such as in situ heat, UV, or plasma treatment of sample containers and tools prior to collection activities should be explored as a means of breaking down these large biomolecules.

(3) Isolation of sample subsets after collection to prevent diffusion of organic contamination is recommended. Sample collection methods that lend themselves to effective sample isolation, such as leaving the sample contained in its coring device until return to Earth, should continue to be explored.

(4) Rigorous end-to-end contamination control and monitoring of contamination is required through use of witness plates. A library of spacecraft produced molecular contamination should be developed and maintained for use during the returned sample analysis period. A similar library should be developed for microbial contaminants where ever spacecraft instruments are assembled and in the final assembly area.

(5) Judicious use of blanks and controls is necessary to establish confidence in selected sample collection and processing protocols.

(6) Thermal perturbations of the sample to temperatures above its natural diurnal maximum for surface samples and mean annual temperature for cores from below the thermal skin depth have the potential to chemically transform organic species of interest. The possible release of water is of particular concern. Sample container designs that remove water vapor and other volatile species as they are produced after collection deserve study.

(7) Definition of the curation facility requirements and the protection of samples from contamination during analysis within this facility and during subsequent transport to and analysis in distributed laboratories should be carried out in parallel with definition of the space systems.

IX. Revised Science Considerations Pertaining to Forward Inorganic Contamination

General Considerations

Any spacecraft includes a semi-infinite multitude of components. Contaminants can be found in elemental form, alloys, and compounds and can have a variety of physical forms, including coatings, sealants and greases. While the distinction between organic and inorganic components may appear simple, it definitely gets blurred in practice. For this report we will emphasize inorganic contaminants.

The identification of contaminants is an ongoing process as mission design progresses. Since contaminants cannot be avoided for many mission components, emphasis must be placed on components that come into direct contact with samples or which can become attached or admixed with the samples of interest. For a sample return mission, the sensitivity of analytical techniques in laboratories on Earth, where the analyses would be performed provides stringent limits on contamination. However, there are also mechanical design considerations which may prevent elimination of certain contaminants. Of paramount importance is the recognition that space is a hostile environment and that experience with past successful missions is a key parameter for selecting materials for new missions. Heritage of use as well as technology developments and demonstrations are key considerations.

In considering components that may come into contact with samples, properties under use of these materials are important, such as:

a) components subject to wear and tear (drilling, abrasion, sliding, seals);

b) engine exhaust, including abraded particles coated with catalysts (e. g., Al_2O_3 spheres coated with Ir);

c) contributions pyro explosions, especially in tight spaces and near samples;

d) brazing/welding components;

e) lubricants and sealants

To minimize contamination, one needs to consider first-order design constraints:

a) prevention of contamination should be an intrinsic aspect of equipment design, from the start of the design;

b) the need to use tested materials, for reliability, with "heritage"; and

c) developments from identified technology tasks, which may allow use of alternative materials.

Relevant technology tasks may also address, the degree of abrasion and of release of contaminants; methods to clean surfaces, e.g., by processing duplicate (or multiple) identical samples through a sample collection and processing equipment (potentially removing or diluting surface contamination); and the degree of mobility of fine-grained contaminants, during sample collection for avoiding contamination. A specific example is provided by technology development needed on the design of drills. Materials used previously on the Moon and in the Lunar Curatorial Facility include: a) tungsten carbide cutters, brazed to stainless steel drill bits; b) diamonds imbedded in nickel or copper-based materials. Furthermore, the choice of cutting tool on Earth may depend on the specific scientific investigation. For example, a non-stainless steel chisel may be used if the study of platinum group elements is of interest. New potential materials may be identified by new technology developments, such as low-wear diamond bits for drilling, advanced diamond coating methods (e.g., chemical & physical vapor deposition). Drilling on Mars may also trade power level and drilling time, in order to reduce wear and contamination.

Of equal importance is record keeping for all materials used and for all cleaning components. This is especially important if we expect that contamination levels in the laboratory woulf improve during the many years it takes for a sample return mission to be designed, flown and to return to Earth. In particular, record keeping needs to include:

a) archive samples of all materials used (and identify all specific batches used);

b) tests of solutions used for chemical processing, such as for electro polishing, electroplating; anodizing

c) archiving of these solutions, used for plating, anodizing, etc.

d) archival materials processed through plating, anodizing etc.

e) keep sets of witness plates of materials ready to be flown.

In addition, it is important to require that new (not previously used) reagents and solvents be used for any chemical processing and cleaning, in order to prevent memory effects and contaminants introduced from previously processed items. It is recommended that reagent grade chemicals be used and that the processing tanks and equipment be made of acceptable materials (such as polypropylene, stainless steel cathodes for electro polishing, etc.).

Archiving of these many materials would require the existence or construction of a storage facility, with clean sections for archiving witness plates and provisions for venting from the materials being stored. Provisions need to be made for separate storage of inorganic and organic materials (e. g., solvents) in such a facility.

Acceptable Contamination Levels

It is important to emphasize that returned samples need to be subject to much less contamination than would be acceptable for in situ analyses on Mars because of the greater sensitivity of laboratory instrumentation as compared to instrumentation used in situ. **This suggests strongly that designs for sample handling and materials used for MSL may not be directly applicable to MSR.** In particular, an MSL corer and abrader may not be usable for MSR without modifications.

In addressing acceptable contamination levels, it is important to recognize that controls of inorganic and organic contamination are inexorably linked. In particular, competing and potentially contradictory requirements for prevention of inorganic and organic contamination need to be identified early and resolved. Contamination levels dictated for planetary protection may also present a challenge for inorganic and organic contamination. Examples include a) special surface coatings could compromise a suite of similar elements (e.g., Au and Platinum Group Elements, PGE); b) special cleaning procedures may adversely affect materials (e .g., excessive oxidation of Al); c) special cleaning procedures may introduce inorganic contamination. All these areas need to be addressed by a vigorous and detailed technology development program.

In addressing acceptable contamination levels it is important to consider the natural abundance of elements. It is harder to contaminate major elements in nature and easier to contaminate trace elements. By contrast, specific materials used as components for spacecraft and in specific areas of spacecraft may concentrate large amounts of minor and trace elements, due to specific chemical and physical processes. Generic categories of inorganic compounds which contribute major contaminants include:

a) Greases, lubricants;
b) Pyrotechnic devices;
c) Abrasives, as for drilling;

Specific compounds that are a potential serious source of contamination include: Mo and W disulfides, sulfates, nitrates and chlorates and perchlorates (from pyrotechnic devices); phosphates.

Significant attention must be exercised for any proposed use of separated isotope tracers. An integral part of control of inorganic contamination is the total avoidance of the use of separated isotope tracers for labeling of contaminants. Isotope tracers directly interfere with all key isotope geochemistry measurements, including those used for age determinations. Extensive experience shows that isotope tracers include cross-contamination for many elements with non normal isotopic compositions (in the tracers). An example helps clarify this issue. A ^{42}Ca tracer includes unacceptable levels of ^{84}Sr (collected in magnetic separators as ^{84}Sr^{2+}).

The use of isotope tracers is based on the isotope dilution technique. However, for the case of determining contamination in a complex process of construction and assembly the technique yields potentially uninterpretable results, because the calculations of contamination levels depend on when and how frequently contamination is introduced in time, relative to the introduction of the isotope tracer(s). In particular, contamination introduced after introduction of the tracer is not measurable, if no isotope exchange occurs with the tracer.

In deciding acceptable contamination levels we may consider that the chemical composition of Mars samples can be correlated to the chemical composition of SNC meteorites.

To first order, we may then accept contamination levels for major and minor elements at 0.1 percent of the contents of SNC meteorites.

For trace elements it is more reasonable to consider Shergottites and Nakhlites (at the exclusion of Chassigny, in which trace elements are highly deficient, due to the unique mineralogy of Chassigny). For trace elements at the ppm (parts per million, by weight) level, we may consider acceptable contamination at the ppb (parts per billion, by weight) level. For trace elements at the ppb level we may consider acceptable contamination levels at the ppb and sub-ppb level, on a best effort basis.

This general approach is not satisfactory because specific minor and trace elements have unique significance in geochemistry, in isotope geochemistry, and for dating techniques. Therefore, attention needs to be paid to specific elements. We attach a table of selected key minor and trace elements of interest to cosmochemistry and for the purpose of age dating. As a simplifying approach we have set acceptable levels by comparison with the abundances for SNC meteorites (the SN part) shown in the Table, down to sub-ppb levels of contamination. It is inevitable that some individual elements would be compromised by specific materials choices, so that careful choices would be needed, throughout the mission design and implementation. For halogens, we consider that low contamination for Cl and Br are desirable, but with due consideration of the apparent presence of evaporites on Mars, which contain substantial amounts of halogens. In any case it is recognized that control of halogen contamination may need to exclude restrictions on key lubricants and greases based on fluorocarbons and other chlorinated compounds, with strong heritage, unless alternates are identified through technology and research.

The Inorganic Contamination Subgroup has reached the following overall conclusions:

a) It is necessary to identify early, materials with sufficient heritage, expected to be used on *in situ* and sample return missions;

b) Sample return missions require much stricter constraints than *in situ* missions;

c) It is necessary to identify all materials in contact with the samples (sample acquisition and storage)

d) Technology development is needed for identifying alternates;

e) The cross-contamination between organic, inorganic and biologic materials needs to be identified;

f) Containment materials (e. g., for gaskets) need to exclude objectionable materials, as much as possible; and

g) The use of separated isotope tracers needs to be prevented.

Table 7. Recommended Limits on Inorganic Contaminants

Element	Units	Shergotty	Nakkla	Units	Contamination[1]	
C	ppm	620		ppm	1	
Na	%	1	0.4	ppm	4	
P	%	0.35	0.04	ppm	0.4	
S	ppm	1330		ppm	1	
Cl[2]	ppm	108		ppm	0.1	
K	%	0.14	0.14	ppm	2	
Cr	ppm	1389	1710	ppm	2	
Co	ppm	39	54	ppb	50	
Ni	ppm	83	90	ppb	100	
Cu	ppm	26	6.7	ppb	5	
Zn	ppm	83	55?	ppb	80	
Br[2]	ppm	0.9	4.6	ppb	1	
Rb	ppm	6.8	5	ppb	5	
Sr	ppm	51	51	ppb	50	
Mo	ppm	0.4	0.1	ppb	1	
Pt group (low mass)						
Pd	ppb	110	42	ppb	100	
REE						
Sm	ppm	1.4	0.8	ppb	1	
Nd	ppm	4.5	3	ppb	0.3	
Lu	ppm	0.25	0.06	ppb	0.3	
Hf	ppm	1.97	0.29	ppb	1	
Re	ppb		0.03	ppt	1	
Pt group (high mass)						
Ir	ppb	0.4	0.15	ppt	1	
Os	ppb		0.01	ppt	1	
Au	ppb	16	0.9	ppt	1	
Pb[3]	ppb	40	40			
U	ppb	0.12	50	ppt	1	
Th	ppb	0.4	200	ppt	1	
Reference: Mars Meteorite Compendium:						
	http://www-curator.jsc.nasa.gov/curator/antmet/mmc/mmc.htm					
[1] Desired contamination levels at 0.1% of Shergotty and Nakhla						
[2] Levels for halogens can be higher, based on MER results						
[3] Common Pb amount, based on 204Pb abundance						

X. Site Dependency of Mobility and Sampling Requirements

During the deliberations of both the mobility and sampling subgroups, it quickly became obvious that most of the parameters under consideration would be highly site dependent: e.g., what would be needed on the Meridiani plane would not necessarily work if the decision were made to follow MSL to pick up a cache, or to go to a previously unexplored site containing a major geologic contact.

In order to convey to NASA the need for flexibility in this regard, an exercise was set up in which each of the two subgroups was asked to consider the science needs for mobility and sampling under four very different landing site circumstances: (1) MSR returns to Meridiani; (2) MSR returns to Gusev Crater; (3) MSR follows MSL; (4) MSR goes to a previously unvisited site that contains a major geologic contact of interest.

The following table (Table 8) contains the results of this exercise. It must be emphasized: this table is for example only, and is intended to show in principle the kinds of flexibility that the SSG believes ought to be maintained in the program to the extent possible.

Table 8. Accessibility and mobility requirements for example sites.

Critereon	Meridiani site	Gusev crater	Go to MSL site	Previously unvisited site with geologic contact
MOBILITY AND LANDING REQUIREMENTS				
Accessibility to rock interiors	Go to outcrop; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring	Go to boulders and outcrops; rover mass sufficient for coring
Accessibility to uncontaminated samples	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g. coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g. coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g. coring)	Mobility sufficient to escape exhaust pattern (> 1/2 km?), lander debris, organic contam.; subsurface sampling ability (e.g. coring)
Altitude	-1.3 km	-1.9 km	CRITICAL to match MSL's altitude capability (+2.5 km)	Higher altitude range (+0.5 or or +1 km) would be desirable because it would provide access to high-quality science sites in the ancient Southern Highlands (possibly recording a warmer wetter climate on Mars)

Landing precision	Accessibility to >20 m diam crater; ~ 200m precision? Note: Landing precision and roving distance are intertwined. It's probably more important to minimize the time the rover spends on the surface collecting samples. The terrain at Meridiani between craters is smooth, flat and barren of rocks, so it would take less time to drive.	It would be good to land within 500 m of the contact between the hills and the plains, and closer would be better. You would want accessibility to the terrain boundary between the plains and the hills, to sample both terrains away from the landing contamination	If there is a geologic contact, it would be good to land within 500 m of the contact. You would want accessibility to the terrain boundary between the two geologic units, to sample both units away from the landing contamination	If there is a geologic contact, it would be good to land within 500 m of the contact._ You would want accessibility to the terrain boundary between the two geologic units, to sample both units away from the landing contamination
Minimum roving distance	1 km	1 km	1 km	1 km
Time on surface, autonomy to lessen the time	Time sufficient to sample stratigraphy by coring within single crater, and to also sample regolith, dust, and atmosphere	Time sufficient to sample plains regolith, plains rocks, a diversity of rock types in the hills, regolith in the hills, dust, and atmosphere	Time sufficient to sample the diversity of rock types by coring, and to also sample regolith, dust, and atmosphere	Time sufficient to sample the diversity of rock types and regolith in both geologic units; as well as dust and atmosphere samples
Slopes / terrain	Must be able to enter and exit crater	Must be able to drive up and down the side of the Columbia Hills and the rugged rocky plains	The more MSR matches its slope/terrain capability to that of MSL, the better able we will be to follow MSL	Need flexibility to respond to unknown terrain characteristics to maximize the diversity of rock types collected
Rover communication	Rover must be able to communicate w/orbiter and/or directly to Earth. Rationale: rover entering/exiting craters may be out of range of direct lander com.	Orbiter and/or direct to Earth com is advantageous, but we could design a mission that would not require it.	Rover must be able to communicate w/orbiter and/or directly to Earth	Orbiter and/or direct to Earth com is advantageous, but we could design a mission that would not require it.
Latitude	2 degrees S	15 degrees S	CRITICAL: MSL latitude range (+/- 60 degrees?)	Opening the latitude range as far south as possible would improve the science by allowing access to more possible ancient highlands landing sites (if altitude is also increased).
SAMPLING REQUIREMENTS				
Sample diversity	Sample identified units within single crater, based on imaging; regolith; dust; atmosphere. No req for finding non-sedimentary rocks. That means that the coring device could be designed for evaporite rock.	Samples of plains basalt lava, rocks in the hills that show variations in texture and degree of oxidation (red/blue reflectance ratio), regolith (from plains and from hills), dust, and atmosphere	Rock types as diverse as possible.	Rock types as diverse as possible.

Rover sampling arm (as opposed to body-mounted, 'under-rover' coring)	Desirable; much of the outcrop in the walls of Eagle & Endurance Crater could be driven on top of and sampled using a body-mounted corer. It would provide more flexibility to be able to sample diversity, e.g. if there were some impact ejecta blocks of a different rock type, sitting on the surface, that could not be driven over by the rover.	Highly desirable. Could not guarantee that some key diversity would be available as rocks under the body of the rover. This would help ensure maximum diversity.	Highly desirable. Could not guarantee that some key diversity would be available as rocks under the body of the rover. This would help ensure maximum diversity.	Highly desirable. Could not guarantee that some key diversity would be available as rocks under the body of the rover. This would help ensure maximum diversity.
Sample collection tool orientation	Corer with flexible orientation to respond to layering geometry	Corer with flexible orientation to respond to geometry of layers (or foliation) seen in the hills	Corer with flexible orientation to respond to the possible geometry of sedimentary rock fabric.	Corer with flexible orientation to respond to the possible geometry of sedimentary rock fabric.
Capability to do close-up imaging of rock interiors (1 possibility would be to spit out cores onto the ground that you would not return to earth)	Desirable, but not critical, because we know that we could sample the stratigraphic section without having to expose rock interiors	Desirable, but not critical, because the rock interiors are not diagnostic of diversity of rocks in the hills. Imaging of outer rock surfaces could discern the plains basalt lava rock from altered rocks in the hills.	If the rocks are highly dust covered or you cannot distinguish the diversity based on color camera images, then this would be desirable.	If the rocks are highly dust covered or you cannot distinguish the diversity based on color camera images, then this would be desirable.
Sample containers	Sample isolation critical. First in importance would be separation of regolith from rock from dust. Second would be isolation of individual rock cores from each other. This sample isolation would be especially important to prevent the migration of water vapor and organic volatiles in the event that hydrous minerals and/or organic volatile-rich samples are collected.	Sample isolation critical. First in importance would be separation of regolith from rock from dust. Second would be isolation of individual rock cores from each other. This sample isolation would be especially important to prevent the migration of water vapor and organic volatiles in the event that hydrous minerals and/or organic volatile-rich samples are collected.	Sample isolation critical. First in importance would be separation of regolith from rock from dust. Second would be isolation of individual rock cores from each other. This sample isolation would be especially important to prevent the migration of water vapor and organic volatiles in the event that hydrous minerals and/or organic volatile-rich samples are collected.	Sample isolation critical. First in importance would be separation of regolith from rock from dust. Second would be isolation of individual rock cores from each other. This sample isolation would be especially important to prevent the migration of water vapor and organic volatiles in the event that hydrous minerals and/or organic volatile-rich samples are collected.
Sample temperature reqs	Lower is better; desire Mars ambient T.; not active refrig.	Lower is better; desire Mars ambient T.; not active refrig.	Lower is better; desire Mars ambient T.; not active refrig.	Lower is better; desire Mars ambient T.; not active refrig.

On-board instrumentation	Color imager to see the outcrop would be CRITICAL. Desirable to see the hand samples at sub mm resolution.	Color imager to see the outcrop would be CRITICAL. Desirable to see the hand samples at sub mm resolution.	Color imager to see the outcrop would be CRITICAL. Desirable to see the hand samples at sub mm resolution. Could partly rely on MSL to provide a correlation between sample diversity and textures/colors/features seen in images	Color imager to see the outcrop would be CRITICAL. Desirable to also see the hand samples at sub mm resolution. Lower down in priority would be a remote sensing instrument on the lander (to cross-correlate orbital remote sensing textures/colors/features seen in color camera images) or on the rover, a brush or grinding tool on the rover to expose rock interiors to the close-up imager (if rock dust & coatings hide the diversity). For a site that has never been previously visited, some kind of diagnostic mineral analyzer would be helpful.
Sample surface layer	Desirable	Desirable	Desirable	Desirable
A "reasonable coring workvolume" (access to a large % of rock faces) for rocks as hard as dense basalt	Important at any site. A t this site, it would be less important, because the rover might not encounter any rocks as hard as dense basalt.	Ability to core into basalt boulders on the plains would be CRITICAL	Important at any site	Important at any site
TRADE-OFF POSSIBILITIES				
			Access to higher altitude would more important than large roving distances	Access to higher altitude would more important than large roving distances
	Outcrop accessibility and core sampling, and sample isolation, would be most important	Outcrop accessibility and core sampling, and sample isolation, would be most important	Outcrop accessibility and core sampling, and sample isolation, would be most important	Outcrop accessibility and core sampling, and sample isolation, would be most important
	A smaller number of carefully collected and stored samples would be more valuable than larger number of less carefully collected and stored samples	A smaller number of carefully collected and stored samples would be more valuable than larger number of less carefully collected and stored samples	A smaller number of carefully collected and stored samples would be more valuable than larger number of less carefully collected and stored samples	A smaller number of carefully collected and stored samples would be more valuable than larger number of less carefully collected and stored samples
	If samples are "hermetically" separated from one another to prevent water movement between samples, the stringent temperature desirements (as low as possible) could be relaxed somewhat.	If samples are "hermetically" separated from one another to prevent water movement between samples, the stringent temperature desirements (as low as possible) could be relaxed somewhat.	If samples are "hermetically" separated from one another to prevent water movement between samples, the stringent temperature desirements (as low as possible) could be relaxed somewhat.	If samples are "hermetically" separated from one another to prevent water movement between samples, the stringent temperature desirements (as low as possible) could be relaxed somewhat.

XI. Summary Findings of MSR SSG II

The finding by the 2004 Opportunity rover of layered evaporite deposits on the surface of Mars during 2004 necessitated a reexamination of the science priorities for a first Mars surface sample return mission. If additional resources would be made available relative to the ongoing planning for a static Groundbreaking MSR, it is highly desirable to add limited mobility back into that mission. Other science findings by the MSR SSG II, again contingent on necessary resources being available, include:

- Access to uncontaminated samples requires rover mobility should be sufficient to (1) escape exhaust pattern, lander debris, and organic contamination; and, (2) travel to and return from target. Round trip distance ~ 1 km regardless of landing precision.
- Desired landing precision is site dependent; but would always be within 500 m
- Rover navigability is site dependent, but the Opportunity experience suggests that gaining access to outcrops that may be exposed along crater walls or inclined hillslopes would require ability to negotiate slopes of ~ 30°
- Access to elevations > 1.5 km is highly desirable but is recognized as possibly prohibitive.
- The ability to sample bedrock, preferably with a coring device, is very important
- Particularly for cores, it is highly desirable to store individual rock samples separately from one another
- Samples should be kept as far below 50°C as possible during Earth atmosphere entry and sample retrieval; ≤ 20°C is highly recommended
- Complex in situ instrumentation would not be considered important for the first MSR mission -- high quality and high-resolution imaging would be considered sufficient to select and document interesting samples
- Caching by MSL is an interesting and potentially beneficial option that should be kept open, but it should not be a requirement for MSL or MSR.
- While OCSSG specified contamination levels for organic molecules would be adequate for a subset of the samples where organics analysis would not be the primary objective, lower thresholds by a factor of 4 or more are desired for an isolated subset of the samples such as cores from sedimentary deposits or selected rocks where organics analysis would be a primary investigation.
- To first order, the acceptable inorganic contamination levels for major and minor elements would be 0.1 percent of the contents of SNC meteorites.

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Appendix A

MARS SAMPLE RETURN SCIENCE STEERING GROUP II

Committee Members

Don Bogard
NASA / JSC
Donald.D.Bogard@jsc.nasa.gov

Max Coleman
NASA / JPL
Max.Coleman@jpl.nasa.gov

Albert Colman
Carnegie Inst. Of Washington
A.Colman@gl.ciw.edu

Joy Crisp
NASA / JPL
Joy.Crisp@jpl.nasa.gov

John Eiler
Caltech
Eiler@gps.caltech.edu

Matt Golombek
NASA / JPL
Mgolombek@jpl.nasa.gov

Albert Haldemann
NASA / JPL
Albert.Haldeman@jpl.nasa.gov

Bruce Jakosky
Univ. Colorado / Boulder
Bruce.Jakosky@lasp.colorado.edu

Laurie Leshin
Arizona State University
Laurie.Leshin@asu.edu

Tim Lowenstein
SUNY / Binghamton
Lowenst@binghamton.edu

Glenn MacPherson [Chair]
Smithsonian Institution
Glenn@volcano.si.edu

Paul Mahaffy
NASA / Goddard SFC
Paul.R.Mahaffy@gsfc.nasa.gov

Suparna Mukherjee
NASA / JPL

Tullis Onstott
Princeton Univ.
Tullis@Princeton.edu

Dimitri Papanastassiou
NASA / JPL
DAP@mail1.jpl.nasa.gov

Lisa Pratt
Indiana Univ.
Prattl@indiana.edu

Charles (Chip) Shearer
Univ. New Mexico
cshearer@unm.edu

Dawn Sumner
University of California, Davis
Sumner@geology.ucdavis.edu

Ashwin Vasavada
NASA / JPL
Ashwin.R.Vasavada@jpl.nasa.gov

Aaron Zent
NASA / Ames
Azent@mail.arc.nasa.gov

JPL

Dave Beaty
David.Beaty@jpl.nasa.gov

Carol Hansen
Carol.A.Hanson@jpl.nasa.gov

Frank Jordan
Jjordan@mail1.jpl.nasa.gov

Richard Mattingly
Richard.L.Mattingly@jpl.nasa.gov

Dan McCleese
Daniel.J.McCleese@jpl.nasa.gov

Andy Morrison
Andrew.D.Morrison@jpl.nasa.gov

Marguerite Syvertson
Marguerite.Syvertson @jpl.nasa.gov

NASA HQ

Dave Lindstrom
David.Lindstrom@nasa.gov

John Rummell
Jrummel@hq.nasa.gov

Subgroup Memberships

Accessibility / Mobility

J. Bibring
M. Coleman
J. Crisp
M. Golombek
A. Haldemann
B. Jakosky
F. Jordan
T. Lowenstein
D. McKay
D. Papanastssiou
C. Shearer *[group lead]*
A. Vasavada

On-Board Sampling and Analytical Instruments

J. Bibring
D. Bogard
A. Colman
J. Crisp
J. Eiler
M. Golombek
J. Jones
L. Leshin *[Group Lead]*
T. Lowenstein
P. Mahaffy
R. Mattingly
T. Onstott
L. Pratt
D. Sumner
A. Zent

Forward Organic Contamination

D. Beaty
A. Colman
B. Jakosky
P. Mahaffy *[Group Lead]*
R. Mattingly
D. McKay
T. Onstott
L. Pratt
D. Sumner
A. Zent

Forward Inorganic Contamination

D. Bogard
M. Coleman
J. Eiler
A. Haldemann
J. Jones
F. Jordan
L. Leshin
D. Papanastassiou *[Group Lead]*
C. Shearer
A. Vasavada

"Floaters"

D. McCleese
G. MacPherson
Suparna Mukherjee

Appendix B

Mars Sample Return Science Steering Group II

Charter

Early results from the Mars Exploration Rovers have revealed several discoveries that will influence strongly the future exploration of Mars. MER has also clearly established that access to distributed targets can be essential to surface science. In light of these findings, we believe that it is appropriate for the Mars science community to take a fresh look at the surface functionality required for the first Mars Sample Return mission.

Current planning for a future MSR is based, in large part, upon the report of the MSR Science Steering Group, "Groundbreaking Mars Surface-Sample Return: Science Requirements and Cost Estimates for a First Mission" (MacPherson et al., 2002). We wish to form a MSR SSG II, chartered to re-examine aspects of the 2002 report in light of new discoveries and operations experience from MER. This new SSG will amend the earlier work by preparing an addendum to the 2002 report. The addendum will be reported back to MEPAG and, after acceptance, be delivered to the Mars Exploration Program no later than November 19, 2004. The terms of reference for the MSR SSG II follow.

The report of MSR SSG I included the following Executive Summary:

> Final Report of the Mars Sample Return Science Steering Group
>
> *EXECUTIVE SUMMARY*
>
> The first surface-sample return mission from Mars, termed Groundbreaking Mars Surface-sample Return, should consist of a simple lander whose only tools are an extendable arm with very simple sampling devices (e.g. combination of scoop + sieve), and a context camera (in addition to the navigation camera). Given that the mission will visit a site that has been previously characterized as interesting by other landed or orbital missions, the samples collected (minimum of 500g of fines + rock fragments + atmosphere) will provide critical fundamental knowledge about the evolution of Mars' crust and climate and thereby enable the selective targeting of more sophisticated sample return missions in the future.

We request that the MSR SSG II identify changes to these findings by answering the following questions:

- What degree of mobility (range, rate, slopes handled), if any, is now considered essential for the collection of returned samples?
- What are the science priorities for the functionality of the MSR sampling system?
- What does the science community consider the maximum acceptable levels of contamination in the returned samples? Please incorporate into your deliberations the findings of the 2003 MEPAG Organic Contaminants SSG, and consider the following potential contaminating materials:
  - Live Earth-sourced organisms (including viable microbial spores)
  - Dead Earth-sourced organisms and fragments of organisms
  - Earth-sourced molecular organic contaminants
  - Non-organic contaminants
- In order to select samples, what measurements must MSR conduct?
  - The MSR SSG I determined only a camera will be required.
- What are the science community's priorities for controlling the environment of returned samples?

- Would MSR benefit if samples cached for it by a prior mission, e.g. MSL?
    - Identify implications, both positive and negative, if MSR is designed to retrieve samples cached in a single container by MSL? It would be useful for the SSG to consider various issues, including:
        - Samples cached by MSL will have been collected from more widely distributed sites and with more extensive *in situ* measurements and context information than is likely to be possible from MSR alone.
        - MSR would likely be required to fund development and accommodation of a cache-container carried by MSL.
        - MSR will need to pinpoint land if it is to retrieve cached samples utilizing modest mobility.
    - What sampling capability must MSR have, as a backup, if a previously a sample cached previously is irretrievable?
    - The SSG need not delve into the issues of planetary protection requirements that may be imposed upon MSL if it caches samples for MSR.

It is our desire that the MSR SSG II interact closely with the mission development team at JPL. Like the MSR SSG I, which worked extremely well with JPL, the current group will be the source of detailed preliminary requirements for MSR while receiving feedback from engineering.

Jim Garvin, the Lead Scientist for MEP NASA, and Dan McCleese, Chief Scientist for MEP JPL, are available to address questions from the SSG. MEP JPL will facilitate the work of the MSR SSG II by assisting its Chairperson with logistical support and through coordination with JPL's mission development team. We look forward to your report.

July 24, 2004

Appendix C

An Exercise To Determine The Relative Science Payoff Of Different Sampling And Storage Options On An Enhanced MSR

Science Value Exercise (Sampling Subgroup)

Introduction. As stated above, our initial approach to reaching consensus was to examine in a holistic way the various components of the sampling approach. During these discussions, it became clear that we were trying to anticipate what would be difficult to implement and avoid concluding such capabilities were "required" for fear that the suggested mission would be too risky or expensive. However, this distracted us from our task, which was to provide well-considered science advice to NASA on the *relative science value* of various types and levels of increased capability to the first MSR mission. Thus, after general discussions about possible evolutionary paths for the various components of MSR, we undertook a "science value exercise" to determine where the most science value was gained by increasing capability. The Chair of the Subgroup created example missions with different characteristics. She took the capabilities of GMSR and assigned them a science value of 1, and a super-capable MSR was arbitrarily given a science value of 1000 (there is no implication that the super-capable mission has 1000 times better science value than GMSR). Missions with different levels of capability between these two end-members were then rated by individual members of the subgroup. The mission capabilities were broken down along the lines of the four questions in the subgroup charter, taking into consideration the priorities for deliberation that emerged from group discussions (e.g., only sample temperature was considered, rather than other "environmental controls" as this was considered the most important part of question 3).

Example Missions. What follows are the descriptions of the **mission elements** (Table 1) and the **example missions** (Table 2) that were rated by the group. Note that these 18 missions do not represent every conceivable combination of the various mission capabilities, but they were chosen to be reasonable combinations of these and spanning a reasonable range in overall MSR sampling capability. Specifically, some of the higher-end missions, which would clearly be "out of the box" for the first MSR were not included, thus there is a large jump in science value from the highest rated combination (#16) and the super-capable MSR, worth 1000 points on the science value scale.

Table 1. Mission Elements in the Science Value Exercise

A: Sampling Approach	**B: Sample Packaging**	**C: Assay Techniques**	**D: Peak Temperature of samples (assume this is for some time like an hour…)**
A1: ***Scoop/rake in a single location*** -- this does NOT mean 1 scoop/rake-full -- it means we would sit in one place and scoop/ rake anything in reach -- capable of collecting dust, regolith and small rocks of varying shapes and sizes	B1: ***One container***: All samples (dust, regolith, rocks, atm) would be put into a single "bucket", which is sealed	C1: ***Color Imaging*** (some reasonable number of filters, like 3 or more)	D1: ***50 deg C***
A2: ***Multi-site scoop/rake*** -- samples of dust/soil/rock collected from a mobile platform but, rocks must be loose fragments in order to be able to collect them	B2: ***Multiple containers***, probably separate ones for dust and soil and atm, but all rocks in a single "bucket" perhaps packed in soil, OR multiple containers with rocks and soil/dust from different sampling sites (e.g., at surface, slightly below surface, etc.), including a separate atm sample	C2: ***C1 + "remote sensing"*** like raman or IR spectroscopy	D2: ***20 deg C***
A3: ***Bedrock sampling:*** in situ sampling of bedrock, for example by use of a small coring device (say ~1 cm diam, 2-5 cm in length)	B3: ***Separate containers*** for atm, dust, regolith (perhaps 2 containers --one surface sample one subsurface) and rocks, with the ***rocks individually packaged*** to prevent cross contamination and minimize damage from Earth return forces	C3: ***C2 + MER-like contact instruments***	D3: ***-5 deg C***
A4: ***Super drilling:*** in situ sampling of bedrock through substantial continuous coring into both bedrocks and regolith	B4: ***B3 + multiple containers for different regolith samples***	C4: ***C3 + in situ lab instruments*** like MSL	

Table 2. Example Missions and ratings in the Science Value Exercise

Mission Number	Mission Capability				Sci. Value Rating**
1	A1	B1	C1	D1	1
2	A4	B4	C4	D3	1000
3	A2	B1	C1	D1	139
4	A2	B2	C1	D1	202
5	A2	B2	C1	D3	292
6	A2	B2	C2	D3	353
7	A2	B2	C3	D3	392
8	A3	B2	C1	D1	382
9	A3	B2	C1	D3	495
10	A3	B2	C2	D3	569
11	A3	B2	C3	D3	615
12	A3	B3	C1	D1	584
13	A3	B3	C1	D2	643
14	A3	B3	C1	D3	701
15	A3	B3	C2	D2	710
16	A3	B3	C3	D2	750
17	A3	B3	C3	D3	776
18	A3	B3	C1 (plus MSL Cache)	D3	735

** the science value for the first two missions were assigned, the values below these are the averages of the 9 individual respondents

Results. The results of the Science Value Exercise are given in the right-hand column of Table 2, in Figs. 1-3, and Table 3. Nine people on the team responded to the Science Value Exercise. Although these numbers are small, the group is broadly representative of the science community at large, so the qualitative results of the exercise are probably reasonable. In addition, the priorities expressed numerically in this exercise are in agreement with those obtained in general discussions with this subgroup, and the larger MSR SSG.

Figure 1 shows the raw "data" – the Science Value responses of the SSG subgroup members plotted against mission number. The black lines are individual responses, and the large dots connect the average values for each example mission. It is easy to see that there were a wide range of values for each mission within the group, but the trends are similar within each set of ratings, with missions generally increasing in science value from left to right across the diagram. From here forward we will use the average science value for each example mission.

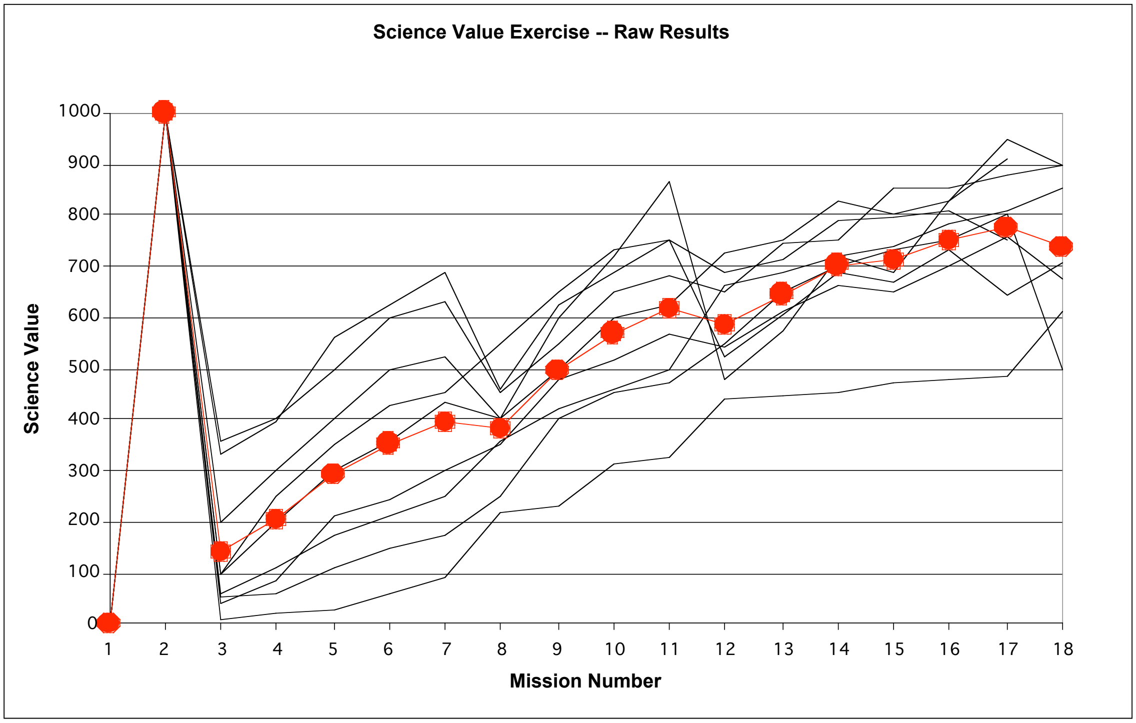


Fig. 1. Results of the Science Value Exercise. Lines are individual responses and large dots connect the average of the group. Recall that missions 1 (GMSR) and 2 (a super-capable MSR) had values of 1 and 1000, respectively, assigned to them.

Figures 2 and 3 show the average science values for each mission, this time arranged from left to right in increasing order of science value. These two figures are exactly the same, except Fig. 3 shows some superimposed trend lines demonstrating a break in slope in the science value as capability increases. The entire purpose of this exercise is to seek out such changes in slope, as they represent natural points where more "bang for the buck" can be achieved. In other words, it is not surprising that missions of higher capability would always have higher science value, the point is to see where especially large gains in science value could be achieved. The science value ratings level out significantly once the two highest priorities of the SSG subgroup, bedrock sampling capability and multiple bins/individual sample storage are included in the mission capabilities.

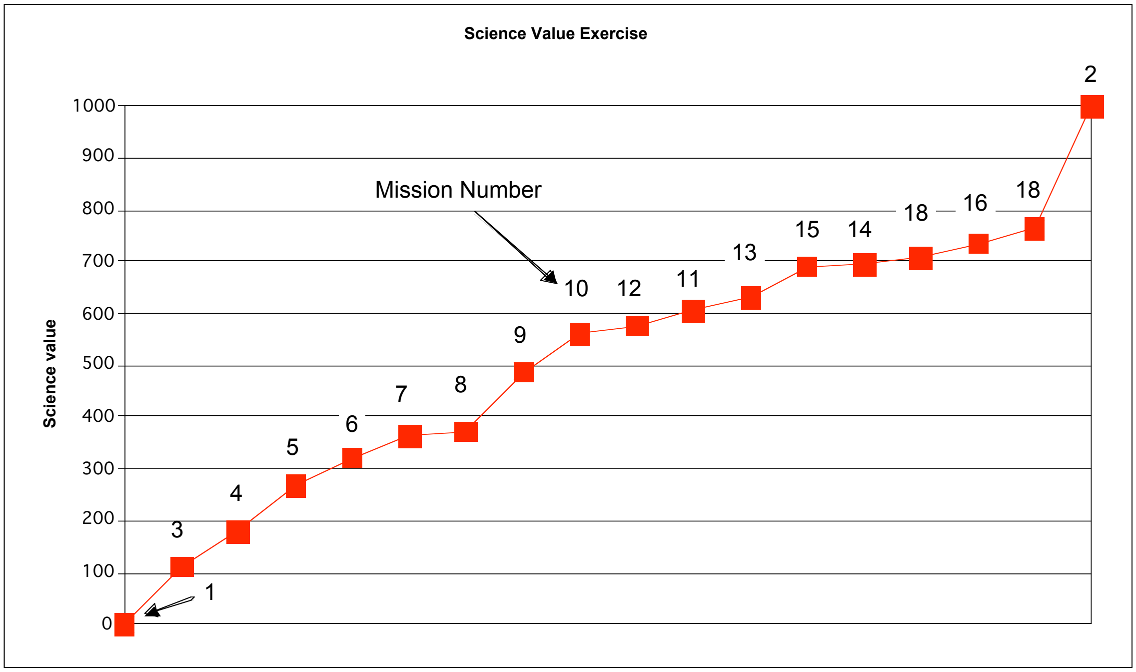


Fig. 2. Science Value of Example Missions in order of increasing Value. Each mission number is shown.

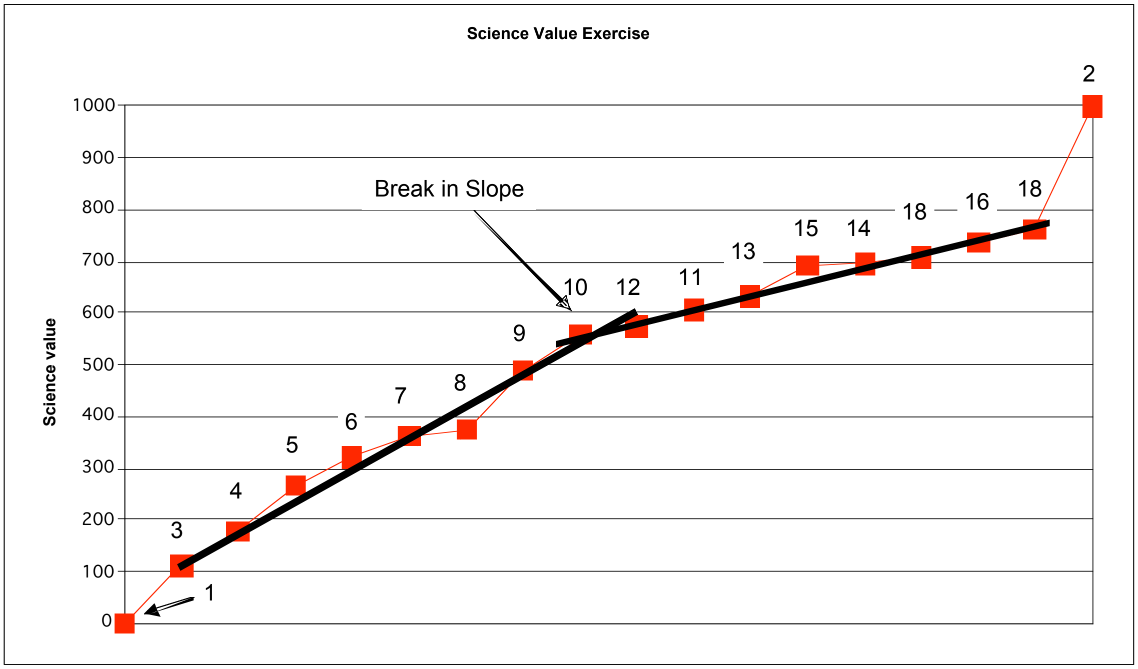


Fig. 3. Same as Fig. 2, but with trend-lines indicating a change in slope in the Science Value curve..

Another way to examine these results is to take the mission ratings and deconvolve the science value of each mission element. The results of this are shown in Table 3, and they confirm the conclusions of the science value exercise. Specifically, they show that increasing capability in the sampling approach, preferably with a coring device, and that providing the capability to isolate regolith, windblown fines, and individual cores from each other are of the highest science value.

Table 3. Science Value of MSR Sampling Mission Capabilities.

Refer to Table 1 for definitions of A1, B2, etc.

A: Sampling Approach		***B: Sample Packaging***		***C: Assay Techniques***		***D: Peak Temperature***	
element #	value	element #	value	element #	value	element #	value
A1→A2	138	B1→B2	63	C1→C2	67	D1→D2	59
A2→A3	206	B2→B3	170	C2→C3	43	D2→D3	48
A1→A3	**344**	**B1→B3**	**233**	**C1→C3**	**110**	**D1→D3**	**107**

Finally, it is important to caution that this is NOT a quantitative exercise, but rather a qualitative way to articulate the more and less valued characteristics of the first MSR mission. Clearly improvements to the sample acquisition system and the sample storage system are most highly valued.

Appendix D

Temperature Effects on Samples from Collection through Return

Introduction

The Martian surface is a thermally dynamic environment, which makes it difficult to define optimal temperature conditions for cached and returned samples. The surface temperature of Mars can fluctuate diurnally by roughly 100°C at the equator and may reach daily highs close to or slightly in excess of 0°C. These temperature fluctuations are damped with depth in the regolith and in exposed bedrock. In the context of cored, scooped, or grappled sample return, a single sample will have experienced within itself a range of temperature histories (in terms of the fluctuations and mean temperatures on daily and seasonal timescales). Multiple collected samples, even within a small radius at a single landing site, will differ from one another in temperature histories as a function of sun exposure, albedo, thermal conductivity, permeability (i.e., ventilation by Martian atmosphere), etc.

Deviations from in situ temperatures would begin once a sample has been removed from the Martian surface and placed in a sample return container. This would likely result in minor scale redistribution and alteration of hydrous, aqueous, and soluble inorganic phases as well as soluble or volatile organic phases. Keeping sample temperature low would slow the kinetics of these transformations. Temperature control (passive or active) of the samples would require balancing financial/technical constraints against sample quality degradation.

For the purposes of MSR planning, we are primarily concerned with transient temperature excursions during a return vehicles reentry to Earth's atmosphere and resultant soakback of heat from the vehicle's heatshield after "landing" and prior to transfer of the samples into a temperature controlled environment on Earth. We assume that sample temperatures would remain below the daily maximum summertime atmospheric surface temperature at the Mars sampling site from collection through transit from Mars to Earth. We assume this would be technically feasible using passive temperature controls, and that it would impart minimal changes in the chemical integrity of the samples relative to the period of brief heating during reentry. We have not addressed explicitly the effects of peripheral sample heating during coring. However, the concerns expressed below apply equally to such heating to the extent that it would be similar in magnitude and duration..

Here we have divided our scientific assessment of the potential for thermally induced sample degradation into two parts: (a) inorganic phases and (b) organic phases. These two are linked; many of the issues that arise with organics result from changes in the quantity and chemical activity of thin films and/or interstitial water and brine.

Temperature Effects on Inorganic Phases

Water on Mars

Table 1 summarizes the expected effects of heating on inorganic phases in Martian surface samples. This summary assesses a worst case scenario in which samples are kept below 0˚C from collection time until reentry into Earth's atmosphere; then following reentry and prior to retrieval the samples reach 50˚C for a maximum of a few hours due to heat soakback from the reentry vehicle's heat shield. This table takes into account the phases likely to be encountered in Martian regolith and in weathered and unweathered outcrops.

The potential alteration of inorganic phases centers on the fate of water: structural in certain minerals, interlayer in clays, brine ice or liquid brines in fractures and interstices, and chemisorbed and physisorbed on mineral surfaces. Figure 1 shows the concentration of water-equivalent hydrogen in near surface Martian regolith. These data correspond to 2-10 wt % water over the latitudes within 60˚ of the equator. However, these data represent areal averages over the 300km radius footprint of the Mars Odyssey Neutron Spectrometer. In all likelihood, heterogeneities exist in water content of the Martian regolith such that returned samples could be richer in hydrogen than these maps suggest. On the other hand, the temperature cycling of the surficial regolith likely promotes sublimation of water from ice, brine, mineral surfaces, and possibly interlayer positions in clay minerals and much of the adsorbed water in microporous zeolite minerals such that 2% appears to be a reasonable limit on the water-equivalent hydrogen content in the top few cm of the Martian regolith (Feldman, 2004).

$MgSO_4 \cdot n\ H_2O$ salts

If we assume that we could avoid ice and brine solutions in collected samples, then the main concern would be preventing hydrated magnesium sulfate salts from melting. Data from Viking 1 and 2 and from Pathfinder suggest that $MgSO_4$ is present at roughly 10 wt % (anhydrous equiv.) in Martian soils (Vaniman *et al.*, 2004; Wänke *et al.*, 2001), and data from Spirit at Gusev crater are not inconsistent with this finding (Gellert *et al.*, 204). These salts are likely to be present on Mars, in the minerals kieserite ($MgSO_4 \cdot 1\ H_2O$), epsomite ($MgSO_4 \cdot 7\ H_2O$), and $MgSO_4 \cdot 12\ H_2O$, as well as in amorphous phases with variable water contents (*e.g.*, Vaniman *et al.*, 2004). Hexahydrite ($MgSO_4 \cdot 6\ H_2O$) could be formed by hydration or dehydration reactions of these other phases if the sample storage temperature climbs above about 280K.

At temperatures above 270K, these phases are all near the point of partially dehydrating or melting to form a Mg^{++}, SO_4^{--} rich brine (Figure 2, Figure 3). The phase changes appear to be rapid, for example the dehydration of hexihydrite at 298K, 580 torr, and relative humidity of 0.3-0.4% takes on the order of several hours (Figure 4). However, the kinetics of most of the phase changes have not been studied sufficiently well to understand what would happen in a sample return container as temperature and relative humidity rise in concert.

Table 1. Thermal Effects on Inorganic Phases During Storage and Return of Mars Surface Sample. *Worst case scenario: heating a Mars surface sample to 50°C for several hours.*

Possible major effects:

1. Dehydration and/or melting of hydrated magnesium sulfate salts (e.g., epsomite, hexahydrite).

Major issues if ice and/or hydrated magnesium sulfate salts are present in sample

2. Melting of ice or hydrated magnesium sulfate.
3. Minor dissolution of evaporitic minerals in the resultant aqueous solution.
4. Enhanced redistribution and reaction of organics if present.
5. Loss/exchange of some interlayer cations in clays minerals (if present).

Probable minor effects:

6. Volatilization of chemisorbed and physisorbed water (especially from clays & zeolites if present).
7. Slow dehydration of hydrated clay minerals (if present).
8. Loss (dehydration/decomposition) of minor abundance, delicate evaporitic minerals.
9. Reversible changes in fluid inclusion chemistry due to temp-dependent salt solubilities.
10. Reactivity and catalytic properties of mineral surfaces towards volatile/soluble organics.

Possible minor effects:

11. Recrystallization/hydration/oxidation of reactive iron minerals.

Probable non-issues for this scale of temperature/time history:

12. Decrepitation of fluid inclusions.
13. Thermal sensitivity of hydroxylation/dehydroxylation reactions.

If these salts serve as a cement in regolith materials or sedimentary rocks, then dehydration or melting could result in physical disaggregation of samples and concomitant loss of structural features and chemical gradients. Phase stability fields are a function of relative humidity, and thus, desiccant functionality in the sample return capsule may prevent melting of these salts (Figure 2). Hydration and dehydration reactions appear to proceed more slowly than melting, so a rapid recovery of the returned sample would help significantly in minimizing disaggregation problems.

Table 2 illustrates more vividly the potential for water release that we face from hydrated magnesium sulfate salts. It is difficult to predict which $MgSO_4 \cdot n\ H_2O$ salts would be encountered in Martian soils given the wide diurnal and seasonal fluctuations in temperature and relative humidity. Nevertheless, at present we could not rule out the release of on the order of 1 g of H_2O (as an $MgSO_4$ rich brine) if temperatures are permitted to rise significantly above 0˚C and/or sample container relative humidity approaches 100%.

Table 2. Water release due to dehydration or melting of hydrated $MgSO_4$ salt. *This example considers water released in a 10g sample core that is 10% $MgSO_4$ by mass on an anhydrous basis. The table considers different initial and final salt compositions. Currently available experimental data suggest that at least some of these phase transitions are possible outcomes of taking near surface samples from Mars and heating them to 50˚C. Other transitions may or may not be possible depending on the reaction kinetics and persistence of metastable minerals.*

Waters of hydration in $MgSO_4$ salt		**Mass H_2O**
Initial n H_2O	Final n H_2O	**released**
12	7	0.75 g
7	6	0.15 g
12	6	0.90 g
12	aqueous sol'n	1.80 g
7	aqueous sol'n	1.05 g
6	aqueous sol'n	0.90 g

Clearly the potential for sample degradation caused by dehydration and/or melting of hydrated magnesium sulfate salts merits further experimental study. The presence of an aqueous solution bathing a sample would certainly compromise a wide range of organic and inorganic chemical measurements and could lead to the physical disaggregation of samples that are cemented by soluble salts.

Clays and Zeolites

Clay and zeolite minerals have both been invoked as possible hydrous phases in the Martian regolith. Clays have stacked sheet-like layers of silica tetrahedra and alumina octahedra; interlayer sites possess various cations to balance layer charges. The interlayer regions also can retain significant amounts of structurally bound water. Zeolites have high adsorption enthalpies for water and high specific surface areas. Both mineral classes are likely to be present in the Martian regolith, however, specific mineral identification awaits future lander missions and/or sample return. Nevertheless, the water carrying capacity and the kinetics of hydration and dehydration reactions have been examined experimentally and theoretically for a few candidate minerals.

These studies suggest that zeolites and possibly clays, if present in Mars soil samples, may contain 10-20 wt % water. Figure 5 illustrates the capacity for Na-clinoptilolite, a common zeolite on Earth, to release significant quantities of water as temperature is increased from representative Mars subsurface temperatures to 50˚C. This release is a continuum process; the warmer the temperature, the more water will be expelled from the clinoptilolite crystal structure if relative humidity is kept low.

Clay minerals probably have a reduced potential to release water because they would be likely less hydrated under Mars surface conditions than zeolite minerals (Bish *et al.* 2003, Zent *et al.* 2001). However, Mg-smectites retain water more strongly than do Ca- and Na- smectites and have not been studied as thoroughly under Mars-like conditions (Bish *et al.* 2003). Thus, it is still possible that Mg-smectites might retain water at Mars surface conditions and release it upon heating in the range proposed for the reentry and recovery phase of MSR. The kinetics of smectite hydration-dehydration reactions have an e-folding time on the order of an hour to a few hours (Figure 6; also Zent *et al.* 2001, Bish *et al.* 2003) -- rapid enough to redistribute water within a sample during even transient heating associated with soakback of heat from the heat shield following sample return to Earth.

Other Inorganic Phases Susceptible to Indirect Effects from Heating

Most minerals at Mars surface temperatures will adsorb one to a few mono-layer thicknesses of water (*e.g.*, Möhlmann, 2004). This water behaves like a 2-D liquid. The thickness of this water layer is a function of mineral, temperature, and relative humidity. The activity of the water and organic and inorganic species that are “dissolved” in this layer will be a function of temperature. Therefore, the catalytic properties of mineral surfaces even in an essentially dry sample will change as samples experience heating during sample return. It is unclear if this will have a significant impact on, for example, the composition and concentrations of trace organic species. It is possible that thin films of water, replenished by minerals undergoing dehydration upon heating, could result in alteration of mineral assemblages. One such example given in Vaniman *et al.* (2004) is the oxidation of lawrencite [$FeCl_2$] to goethite [$FeO(OH)$] in lunar samples despite short transit times and dry nitrogen storage. Some other possible minor effects of transient heating on inorganic phases are listed in Table 1.

Figure 1. *(Figure 4 from Feldman et al., 2004)*

A Robinson projection of the water-equivalent hydrogen content of the semi-infinite layer of water-bearing soils derived from epithermal-neutron counting rates measured by the Neutron Spectrometer on the 2001 Mars Odyssey. Hydrogen content data are draped over a global elevation map from the Mars Orbiter Laser Altimeter. The semi-infinite layer comprises the regolith below the relatively desiccated surface layer. The existence of a desiccated surface layer with roughly 2 wt % water content is supported by both theoretical and observational constraints. This surface layer is likely of variable thickness, however, it is considered to be 10g/cm^2 for the modeling of the neutron data to produce this map. Assuming the regolith has an average porosity of 30-70% and density of 2.5-3.5g/cm^3, then this surface layer is on the order of 4-14cm thick.

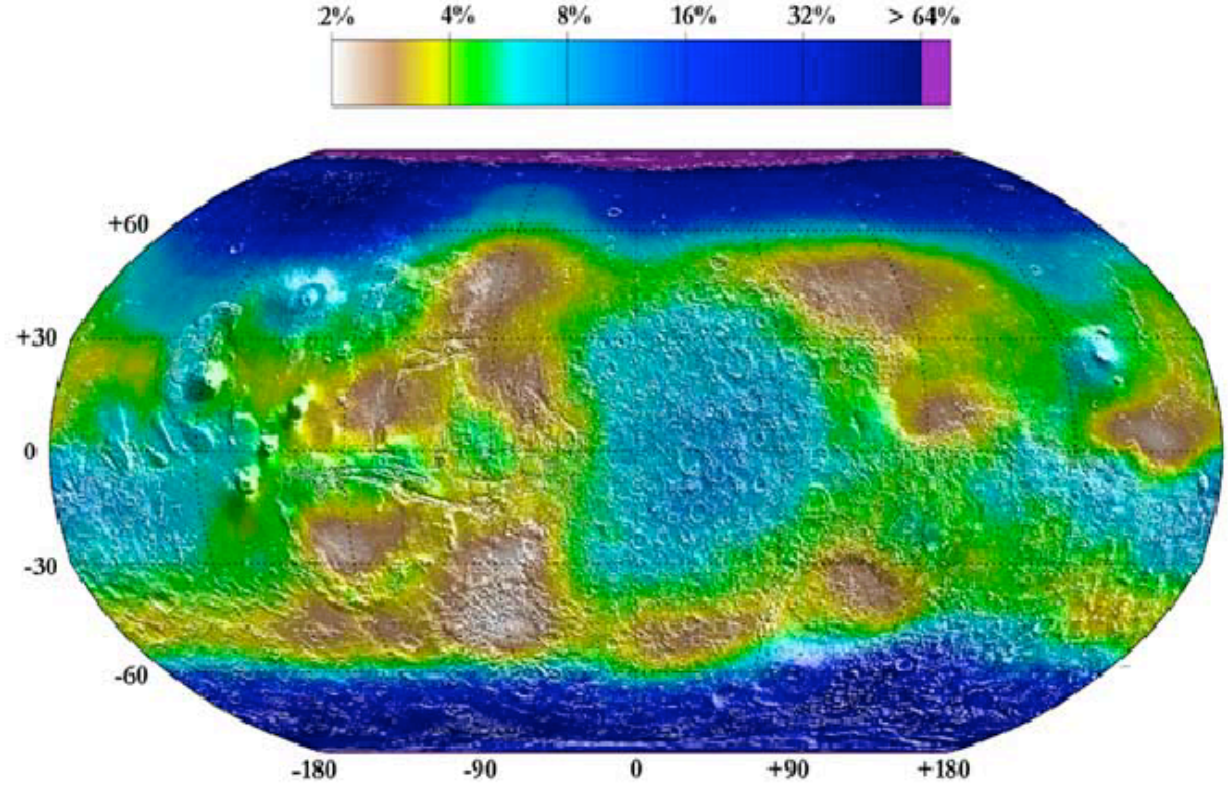


Figure 2. (*Figure 3 from Vaniman et al., 2004*)

Results of controlled-humidity XRD experiments at 298 K plotted against stability fields for epsomite, hexahydrite and kieserite, modified from Chou and Seal (2003). Their study provides accurate constraints on the epsomite to hexahydrite transition (curve 1); their estimate of the hexahydrite to kieserite transition (curve 2) is based on thermodynamic data extrapolated from the experimentally determined solution equilibrium; an alternative estimate of this transition is based solely on thermodynamic data (curve 3). Estimated stability of hexahydrite under Martian conditions depends on extrapolation of curves 2 or 3. Stability of the MgSO4·12H2O phase is poorly constrained. Our experiments show that at RH of 0.5%, hexahydrite forms from solution but becomes amorphous. Hexahydrite forms and persists at RH values from 55% down to at least 7%. Amorphous MgSO4·nH2O formed at RH of 0.5%, and subsequently exposed to RH of 7–55% crystallizes to various hydrates (n = 1.25 to 6) dependent on RH; ongoing long-term experiments suggest that crystalline end products vary with RH within the upper shaded region. Above RH of 55%, both amorphous MgSO4·nH2O and kieserite transform to hexahydrite and then epsomite. At Martian conditions below 280 K, the rates and ranges for comparable reactions are not yet determined. The diurnal temperature–RH range shown (lower shaded region) for the Mars surface in summer at the Viking 1 site is from Savijarvi (1995, *Icarus, 117*, 120). The average diurnal surface temperature of 220 K near the equator varies little despite changes in obliquity (Mellon & Jakosky, 1995, *JGR, 100*, 11781).

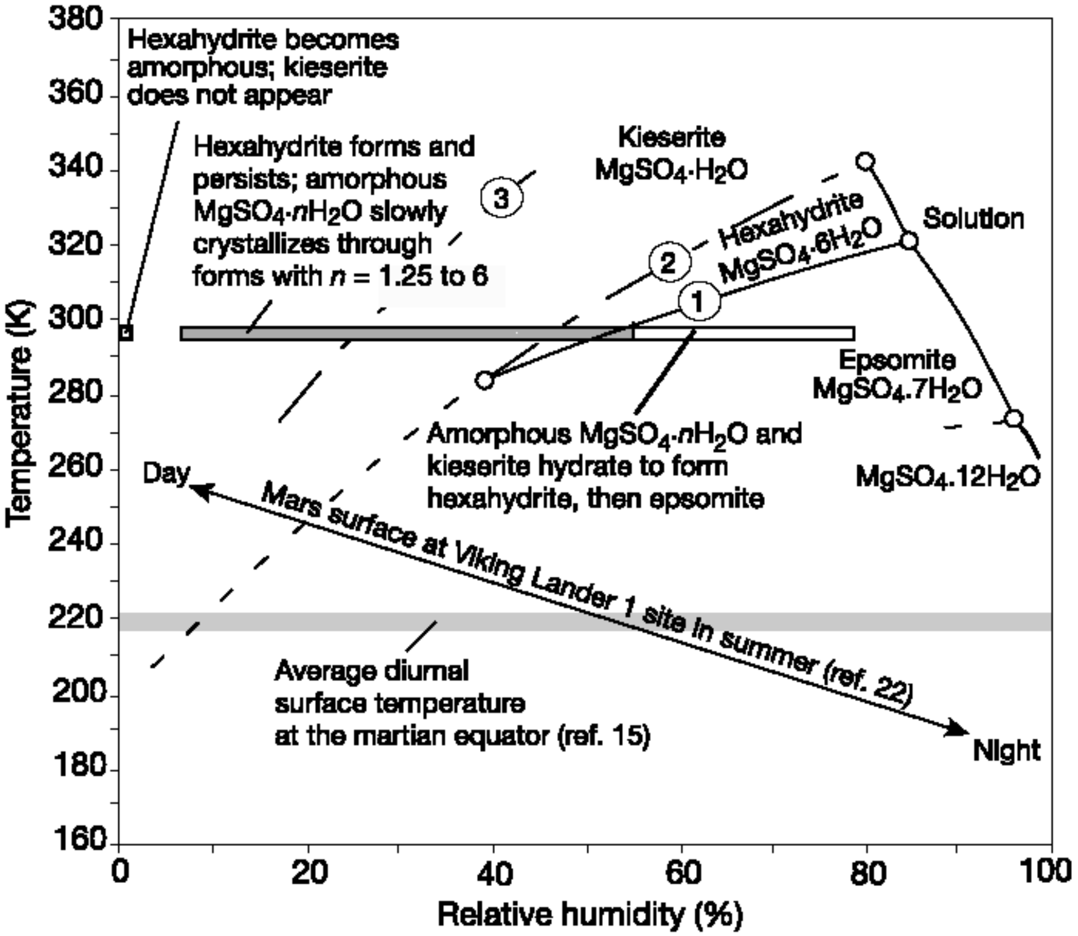


Figure 3. *(Figure 6 from Hogenboom et al., 1995)*

Phase diagram of the system $H_2O \bullet MgSO_4$ at 0.1 MPa. MS1, MS6, MS7, and MS12 stand for, respectively, $MgSO_4 \bullet 1\ H_2O$, $MgSO_4 \bullet 6\ H_2O$, $MgSO_4 \bullet 7\ H_2O$, and $MgSO_4 \bullet 12\ H_2O$. **E** is the eutectic; **P1, P2,** and **P3** are peritectics. Also shown are the metastable extensions of the liquidus branches of water ice and $MgSO_4 \bullet 7\ H_2O$ and the intersection of these branches (representing the metastable eutectic, **E'**).

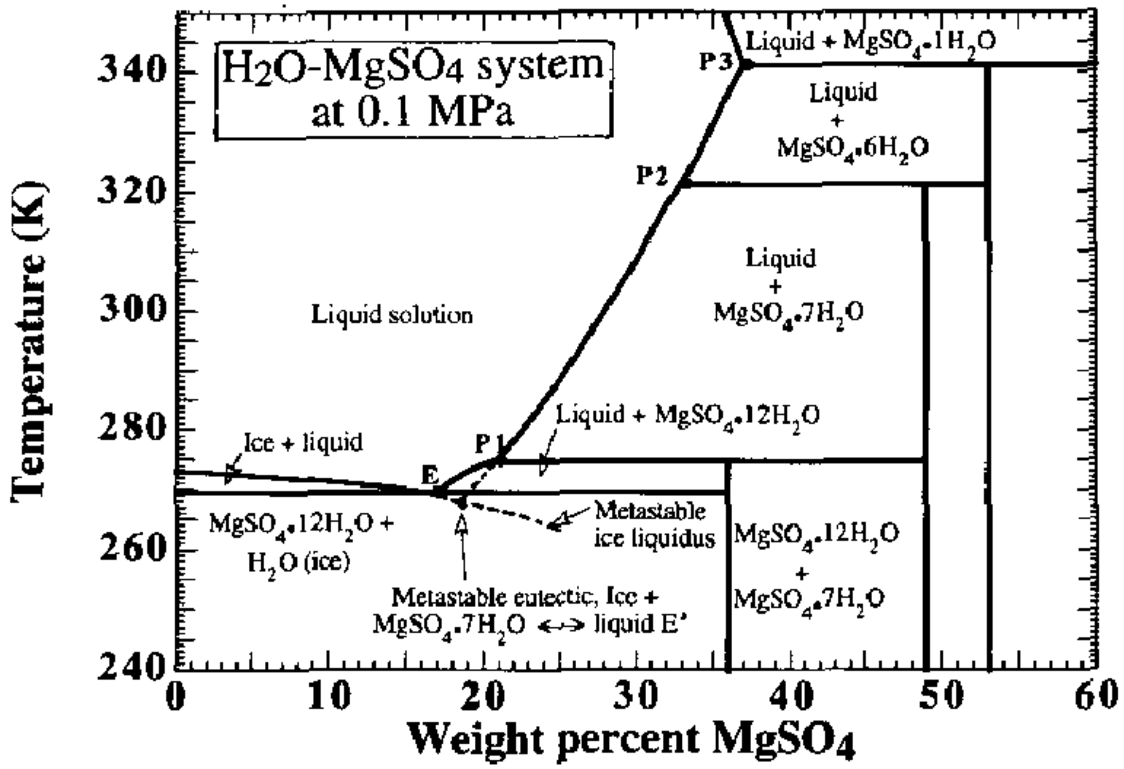


Figure 4. *(Figure 1 from Vaniman et al., 2004)*

Dehydration experiment in an environmental cell. Ten sequential X-ray diffraction (XRD) patterns of hexahydrite desiccated at 298 K and 0.3–0.4% RH to produce amorphous MgSO4·nH2O. The ten XRD patterns represent desiccation over a period of 40 h. b, The XRD pattern of the hexahydrite starting material. In Figs 1 and 2, XRD was performed using CuKa radiation.

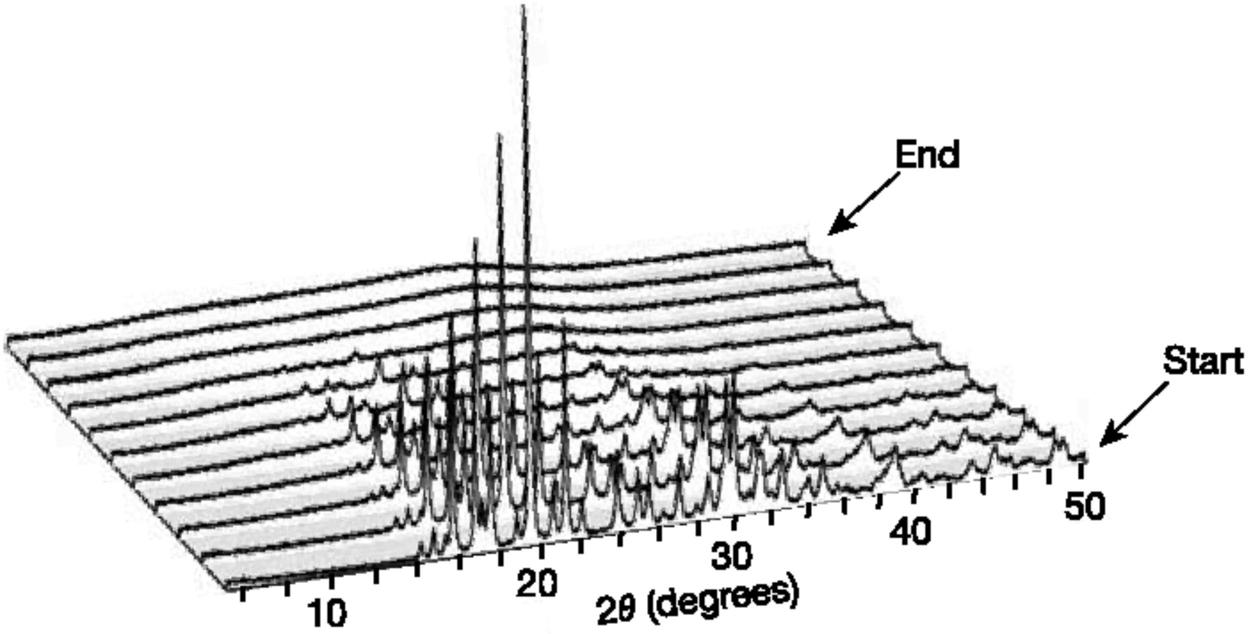


Figure 5. *(Figure 4 from Bish et al., 2003)*

Thermodynamic modeling of hydration state of smectites (example clay minerals) and clinoptilolite (an example zeolite). The modeled equilibrium water content as a function of temperature is plotted for Na- and Ca-smectites on the left axis and for Na-clinoptilolite on the right axis. $P(H_2O)$ is set to 1.5 x 10^{-6} bars in the model as an approximation of the average vapor pressure of H_2O at the surface of Mars.

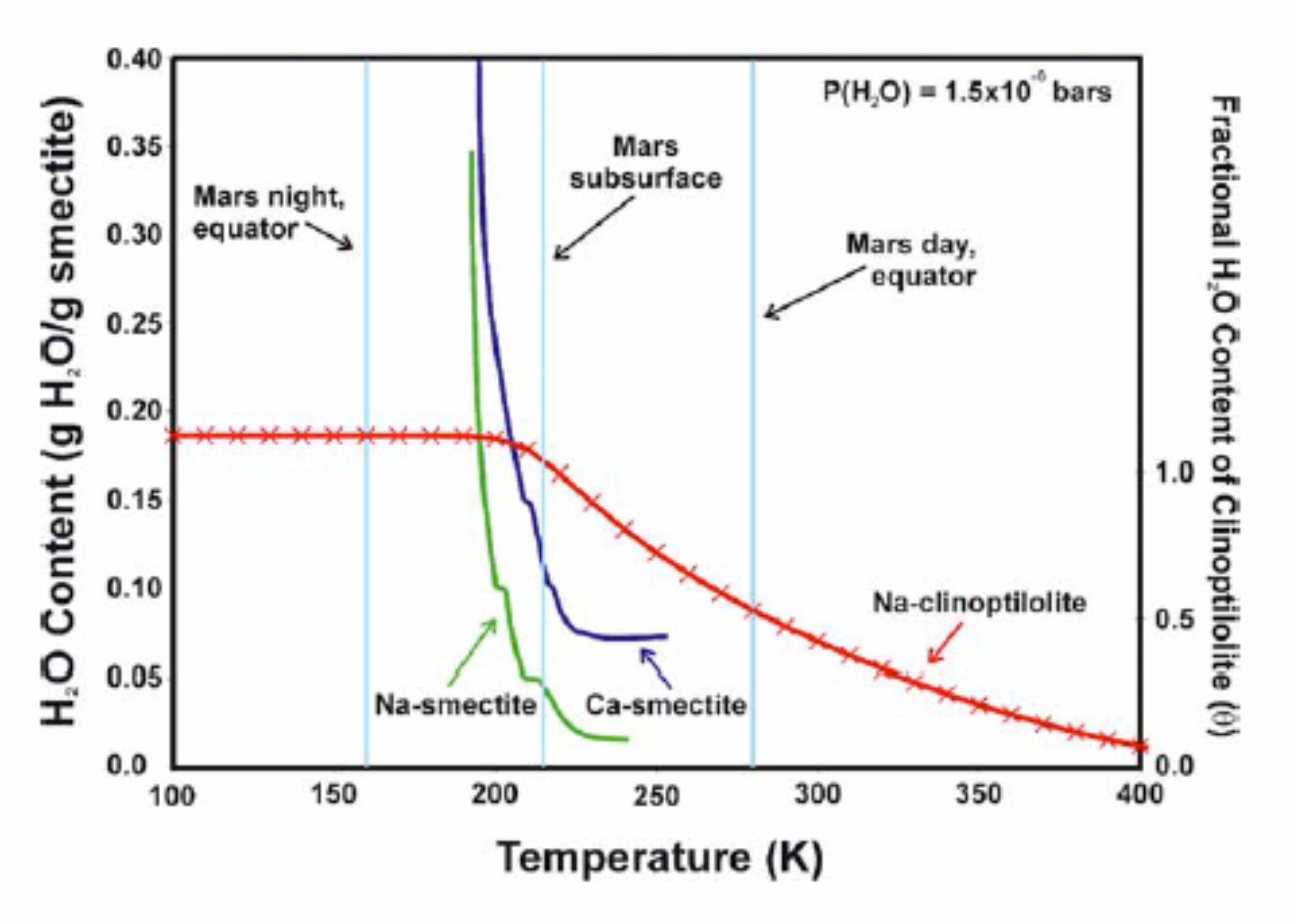
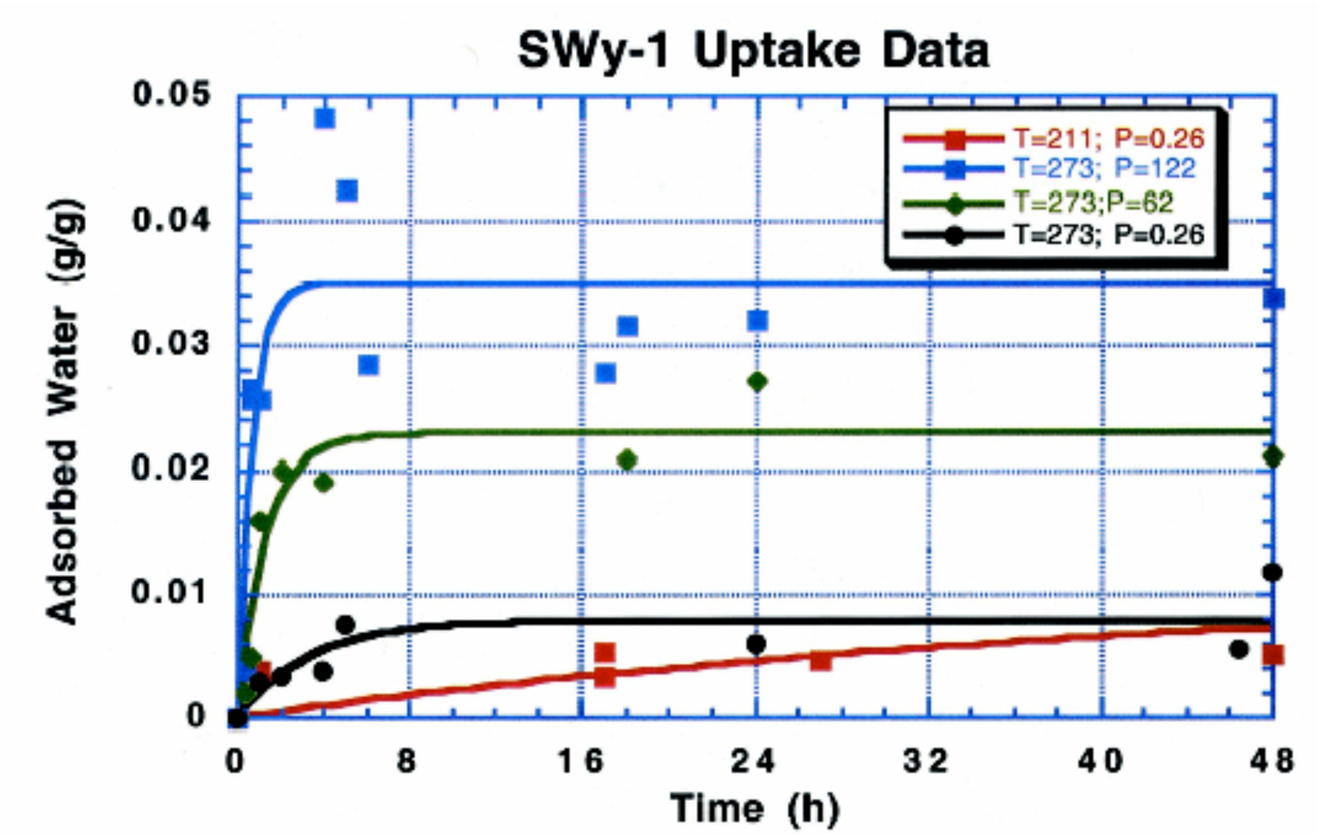


Figure 6. *(Plate 1 in Zent et al., 2001)*

The uptake curve of H_2O on SWy-1, a sodium-rich montmorillonite. The adsorbate is substantially loaded in only a few hours. The clay samples were preconditioned by baking under vacuum at 110°C to remove essentially all water while avoiding disruption of interlayer cations. The experimental temperature and $P(H_2O)$ conditions are listed in the inset legend.



Temperature Effects on Organic Phases

Few published organic geochemical studies report molecular or stable isotopic data for fine-grained sediments or sedimentary rocks on Earth containing trace (< 0.05 wt%) amounts of organic carbon for two reasons. First, samples containing trace concentrations of organic carbon are almost always contaminated during sampling to a to a level where extraneous organic compounds pervasively overprint indigenous organic compounds. Second, organic compounds are tightly bound to mineral surfaces in fine-grained siliciclastic, calcareous, and evaporitic sedimentary materials containing trace amounts of organic matter. Increasing sample size is ineffective because extraction yields from these types of samples are proportionally lower than yields for similar sediments containing higher contents of organic carbon. For all of these reasons, it is difficult to predict the fate of organic molecules in a Mars return samples that are anticipated to contain only trace level organic carbon. Above we described the fate of organic molecules using generalized terms because most of the compound classes contain a wide range of structural configurations and molecular weights combined with substantial uncertainties regarding mineral composition and hydration state for near-surface Mars regolith and rocks. The term *mobilized* refers to molecules that are unaffected chemically but are capable of physical migration between absorbed or complexed phases. *Volatilized* refers to molecular classes that will be present primarily in a vapor state. Volatilization at the chosen temperatures is estimated based on standard laboratory evaporation procedures at controlled temperature using vacuum aspiration to about 20 millibars (Rotavap or equivalent apparatus). *Partial decomposition* refers to initial stages of chemical transformation including isotope exchange, dehydration, and isomerization. *Decomposition* refers to chemical transformations more severe than those listed for partial decomposition, typically involving structural breakdown and/or molecular reorganization.

It is clear from the table that at 50ºC a significant number of compounds experience decomposition, and even at 20ºC some compounds are decomposed. At -5ºC some compounds are mobilized or even volatilized.

Fate Of Indigenous Martian Organic Molecules During Sample Return

Information Compiled in 2004 by Lisa Pratt, Simon Brassell, Arndt Schimmelmann, Bernd Simoneit

Molecular Class	Examples	Scientific Interest	Susceptible to Photo - Decomposition	Susceptible to Hydrolysis or Water Solvation	organic matter sampled in an intact sedimentary matrix, sample canister sealed under oxidizing atmosphere at 6-10 millibars pressure, maximum temperature during re-entry not exceeding:		
					-5°C	**20°C**	**50°C**
Aromatic Hydrocarbons	benzene	M			Unm	Mob	Vol
Polyaromatic Hydrocarbons	anthracene, phenanthrene	H	√		LMW - Mob HMW-Unm	LMW - Vol HMW - Vol	LMW - Vol HMW - Vol
S, N, O Heteroatomic Aromatics	pyrimidine, furan, pyridine, purines, benzothiophene	M			LMW - Mob HMW-Unm	LMW - Vol HMW - Mob	LMW - Vol /PDec HMW - Vol /PDec
Aliphatic Hydrocarbons	alkanes, alkenes, pristane, phytane	H			Unm	LMW - Vol HMW -Unm/ Mob	LMW - Vol /PDec HMW - Vol /PDec
	Methane	VH			Vol	Vol	Vol
	ethane, propane, butane	VH			Vol	Vol	Vol
	hopanes, steranes	H			Unm	Unm	Mob
Saccharides	tetrose, glucose, cellulose	VH		√	Unm	Unm	Unm
Carboxylic Acids and their Salts	alkyl and aromatic acids, fatty acids	H		√	LMW- Mob HMW-Unm salt-Unm	LMW - Vol HMW - Mob salt-Unm	LMW - Vol HMW - Mob/Vol salt-Unm
Amino Acids	basic, neutral, acidic	VH		√	Unm	Unm	LMW - Unm HMW - Unm
Nitrogen-Containing Compounds	amines, amides	H			LMW- Vol HMW-Unm	LMW - Vol /PDec HMW -Unm/ Mob	LMW – Vol /PDec HMW – Vol /PDec
	tetrapyrroles, porphines, siderophores	VH	√	√	Unm	Unm	PDec
Peptides	polar and non-polar	H		√	Unm	Unm	Mob /PDec
Functionalized Lipids	glycerides, fats	VH		√	Unm	Unm- Mob /PDec	PDec
	ether lipids	VH			Unm	Unm	Unm
	esters, ketones, aldehydes	H	√	√	Unm	LMW - Mob HMW -Unm	LMW -PDec HMW -PDec
	alcohols	H		√	LMW- Mob HMW-Unm	LMW - Mob HMW - Mob	LMW -PDec HMW -PDec
Humic and Fulvic Acids		M	√	√	Unm	Mob /PDec	PDec/Dec
Unresolved Complex Molecules		H			Unm	Mob	Mob /PDec
Phospholipids		VH		√	Unm	Mob/PDec	Mob /PDec
Nucleic Acids, Nucleotides	DNA, RNA, TNA	VH	√	√	Unm	Unm	DNA -Unm RNA -PDec
Nitrogen-Containing Gases	NH_3, HCN, NO_2, N_2O, NO	H			Mob	Vol	Vol
Sulfur-Containing Gases	H_2S, $(CH_3)_2S$	H			Mob / Vol	Vol	Vol /PDec

Abbreviations and acronyms

VH = very high
H = high
M = moderate
L = low
Unm = unmobilized
Mob = mobilized
Vol = volatilized
PDec = partially decomposed
Dec = decomposed
LMW = low molecular weight
HMW = high molecular weight