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Preservation of Martian Organic and Environmental Records: Final Report of the Mars Biosignature Working Group

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Abstract

The Mars Science Laboratory (MSL) has an instrument package capable of making measurements of past and present environmental conditions. The data generated may tell us if Mars is, or ever was, able to support life. However, the knowledge of Mars' past history and the geological processes most likely to preserve a record of that history remain sparse and, in some instances, ambiguous. Physical, chemical and geological processes relevant to biosignature preservation on Earth, especially under conditions early in its history when microbial life predominated, are also imperfectly known. Here we present the report of a working group chartered by the Co-Chairs of NASA's MSL Project Science Group, John P Grotzinger and Michael A Meyer, to review and evaluate potential for biosignature formation and preservation on Mars.

Orbital images confirm that layered rocks achieved kilometer-scale thicknesses in some regions of ancient Mars. Clearly, interplays of sedimentation and erosional processes govern present-day exposures, and our understanding of these processes is incomplete. MSL can document and evaluate patterns of stratigraphic development as well as the sources of layered materials and their subsequent diagenesis. It can also document other potential biosignature repositories such as hydrothermal environments. These capabilities offer an unprecedented opportunity to decipher key aspects of the environmental evolution of Mars' early surface and aspects of the diagenetic processes that have operated since that time.

Considering the MSL instrument payload package, we identified the following classes of biosignatures as within the MSL detection window: organism morphologies (cells, body fossils, casts), biofabrics (including microbial mats), diagnostic organic molecules, isotopic signatures, evidence of biomineralization and bioalteration, spatial patterns in chemistry and biogenic gases. Of these, biogenic organic molecules and biogenic atmospheric gases are considered the most definitive and most readily detectable by MSL.

Introduction

In the first decade of the twenty-first century, our understanding of Mars and its environmental history has increased dramatically. Orbital measurements provide unprecedented resolution of both physical and chemical features of the Martian surface. The Mars Exploration Rovers Opportunity and Spirit have contributed our first-ever geologist's-eye views of stratigraphic successions on Mars (e.g. Christensen et al., 2004; Squyres et al., 2004, 2006, 2009; Grotzinger et al., 2005; Haskin et al., 2005). Building on this success, the extraordinary instrument package and anticipated roving capability of the Mars Science Laboratory (MSL) position us to use new rover observations to test hypotheses generated on the basis of high-resolution orbital data. For example, orbital images and spectral data show that layered rocks have accumulated to thicknesses greater than a kilometer on some parts of the ancient Martian surface and comprise diverse lithologies (e.g. Bishop et al., 2008; Ehlmann et al., 2008a,b). What fundamental processes of particle generation, transport, and cementation made such accumulations possible, and what erosional processes govern present day exposures? MSL has the imaging capability to document and evaluate patterns of stratigraphic development, as well as the geochemical capacity to evaluate the sources of layered materials and their subsequent diagenesis. Bibring et al. (2005) have identified phyllosilicates by remote sensing of the Martian surface and hypothesized that these record an early, relatively wet epoch in Martian history, before the time of acid sulfate deposition recorded in the sediments at Meridiani Planum. MSL has the capacity to confirm phyllosilicate mineralogy and evaluate it in stratigraphic context, allowing us to understand more fully the significance of these minerals for reconstructing Martian environmental history. Finally, the hallmark of life is organic matter —do Martian strata preserve organic molecules that might illuminate the planet's early environmental, and possibly biological, history? MSL's Sample Analysis at Mars (SAM) instrument suite provides unprecedented potential to answer this question.

Knowledge of our own planet's biological and environmental history has developed through the integration of many types of observations. Arguably among the most important are: field mapping, the measurement and correlation of stratigraphic sections, and both paleontological and geochemical analyses of samples collected from measured sections located within mapped terrains. Through the strategic choice of a landing site using high-resolution orbital data, MSL promises a comparable integration for Mars. With this in mind, it is helpful, even necessary, to consider how geologists evaluate and select field sites on Earth. Surely, site accessibility and map data influence choice, as do accumulated observations by previous geologists. But there is one more consideration that governs site selection by geologists, geochemists, and paleobiologists: what types of deposits are most likely to preserve geological and possible biological signals of interest? Simply put, NASA will realize the greatest returns on its investment in the MSL payload if it targets outcrops that maximize the probability of organic deposition and preservation. It will maximize its return from the payload if it targets stratigraphic successions that place mineralogical measurements in temporal and paleoenvironmental context.

Working Group Objectives

The Preservation Working Group was assembled to assess whether current understanding of organic matter preservation on Earth might help guide site selection and both strategic as well as tactical planning during surface operations for the MSL mission. The Working Group was asked to provide general guidance on what specific geologic environments would be most favorable for preservation of potential biosignatures, including special consideration of organic carbon (Farmer and Des Marais, 1999).

Insert Text Box 1 and Box 2 hereabouts

It is essential to recognize that, on Earth, and in spite of a vital biosphere, the majority of biologically derived organic carbon exists as "fossil" organic carbon stored within layered sedimentary rocks. This sequestered organic matter is by some estimates 2×10^5 that the mass of the carbon stored in the living biosphere. On Mars, it appears reasonable to assume that if life exists or ever existed, it never evolved to the point of large differentiated, multi-cellular organisms (e.g., plants) that biosynthesize large quantities of recalcitrant biopolymers (e.g., lignin and cellulose) leading to potential accumulations of extensive organic matter rich sedimentary deposits (e.g., coal). There is general consensus that extant microbial life on Mars would likely exist (if at all) in the subsurface and at low abundance, making it difficult, if not impossible, to detect using sampling technologies foreseeable over the next decade.

Detecting an ancient subsurface biota may be even more difficult unless exhumed records of ancient subsurface environments can be confidently recognized and are accessible to a rover. Since all life requires an abundance of electron donors and acceptors to grow and to accumulate biomass, we would also need analyze the mineralogy and geochemistry of exhumed rocks to assess their bioenergetic potential. Even though the record of early life on Earth is reported to contain microstructures (e.g. Rasmussen, 2000; Brasier et al., 2006) purported to reflect subsurface life, significant doubt remains about their biogenicity. These remains are rare and notoriously difficult to interpret with confidence given their high degree of thermal alteration. In contrast, it is possible that the organic remains of extinct microbial life developed at Mars' surface, or subsurface, may persist and perhaps even be enriched in certain sedimentary rocks.

On Earth, microorganisms commonly exist communally in the water column and in sediment pore spaces or as attached biofilms. Biomass of these communities may be preserved in the rock record in concentrations sufficient to detect with the MSL payload elements (see Box 1). Furthermore, sedimentary processing (e.g., hydrodynamic sorting as occurs in fluvial and deltaic environments on Earth) may concentrate biologically derived carbonaceous particles into organic-rich horizons in sedimentary strata. A logical approach to establishing whether life ever existed on Mars is, therefore, to analyze appropriate sedimentary lithologies, seeking evidence of "fossilized" organic matter preserved in sedimentary deposits.

One issue that may add ambiguity in such a search is the fact that, throughout Martian history, organic-rich chondritic meteorites have undoubtedly rained upon the Martian surface. Weathering of chondritic meteoritic debris in an environment with minimal oxygen and no extensive surface biosphere (i.e., microbes and fungi capable of degrading chondritic organic matter) may lead to a persistence of extraterrestrial organic particles and, consequently, its accumulation into certain sedimentary rocks through hydrodynamic sorting. At the same time, strong oxidants in Martian regolith along with exposure to ionizing radiation might alter or destroy molecular signatures from meteorites or organisms. Notwithstanding the potential complexity of interpreting any organic material that may be detected, the simple detection of organic matter in rock or soil via the MSL mission will constitute a critically important result.

The membership and objectives of the Working Group were chartered by the Co-Chairs of NASA's MSL Project Science Group, John P Grotzinger and Michael A Meyer. The charge to the Working Group was to outline a search strategy that included consideration of the nature of the payload elements (PE), a ranked order of biosignatures detectable by those instruments and an evaluation of the types of environments conducive to the formation and, especially, preservation of these biosignatures. Four candidate landing sites remain at the time of writing and this strategy could serve as a guide to members of the Mars exploration community in deliberating whether potential landing sites have more or less appropriate lithologies for biosignature preservation. A second objective was to assess, in very general terms, how the MSL instrumentation may be best exploited for the analysis of any record of organic compounds (biogenic or abiogenic) that might be preserved in Martian sedimentary rocks. The working group was asked not to address the merits or otherwise of specific Mars localities. Nor were we asked to assess instrument specifications and how those instruments might be operated at the surface of Mars, as these are issues more appropriately addressed by very different groups of specialists. We were guided in our work by two recent publications from the National Academies namely the report on the *Limits of Life in Planetary Systems* (Baross et al., 2007) and an *An Astrobiological Strategy for the Exploration of Mars* (Jakosky et al., 2007).

Taphonomic Windows

Taphonomy is the term used by paleontologists to describe the processes by which living organisms become fossils. Taphonomy is commonly portrayed as "post-mortem information loss" because fossilized bones, shells, or microorganisms record only a small subset of the biological information originally present in their makers. With a different perspective, however, we might view taphonomy as "post-mortem information preservation" because, however selective it may be, fossilization provides our only permanent record of past life. In the context of MSL, we can broaden the concept of taphonomy to include the geologic preservation of the full suite of materials we might wish to measure using the rover's instrument package. What combination of processes, for example, maximizes the probability of preserving organic molecules, body fossils and sedimentary textures?

If we can understand the processes that facilitate preservation, then we can conceive of the likely operation of those processes in time and space. That is, we can define a taphonomic window – the sedimentary and diagenetic circumstances most conducive to preservation. We know that ancient organic molecules will preserve only if buried in sediments and long-term preservation will occur only if buried organics are shielded from oxidizing fluids. On Mars, surface oxidants and UV radiation will have altered or destroyed organic molecules (Benner et al., 2000; Navarro-Gonzâlez et al., 2006; Sumner, 2006). On Mars, surface oxidants and UV radiation will have altered or destroyed organic molecules at or near the surface (Benner et al., 2000; Navarro-Gonzâlez et al., 2006; Sumner, 2006). If we can identify generic features that can be used to characterize potential landing sites with respect to the presence or absence of specific taphonomic windows, then we can help maximize the chances of successful analyses by MSL.

Working Group Findings

A recent review of biosignatures and strategies for their use in life detection can be found in Botta et al., (2008). Our deliberations yielded the ranked order of biosignatures and taphonomic windows that are provided in Tables 1 & 2. However, we also recognized that, even on Earth with its vigorous and multi-billion-year-old biosphere, many of these biosignatures can be ambiguous and are preserved only under rare and exceptional circumstances.

Insert Table 1 hereabouts

Insert Table 2 hereabouts

Box 1: Biosignatures at a glance – summary of what can be observed with the payload elements (PE) of MSL. Note that environments can be reconstructed from physical and chemical features of ancient sediments that are not considered to be biomarkers. (see tables 1 & 2)

1 Organism Morphologies (cells, body fossils, casts)
PE: MAHLI
Minimum size would have to be greater than 100 µm and rock preparation techniques are not available to expose organisms within rock. Martian life is expected to be microbial, so the probability of detection is low
Potential as a biosignature: exceptionally high
Potential as an environmental indicator: low

2 Biofabrics (including microbial mats)
PE: MAHLI, MastCam
Accreted structures analogous to those on Earth are detectable; However, few bedding plane surfaces are exposed, so potential surface biosignatures will be difficult to detect
Potential as a biosignature: moderate
Potential as an environmental indicator: low

3 Diagnostic organic molecules; Organic carbon
PE: SAM, ±ChemCam only if very abundant. Detection potential high incl. atmospheric gases
Potential as a biosignature: exceptionally high
Potential as an environmental indicator: high

4 Isotopic Signatures
PE: SAM
Contextual knowledge is essential; results can be ambiguous and complex to interpret
Potential as a biosignature: moderate
Potential as an environmental indicator: low

5 Biomineralization & bioalteration
PE: CheMin, ±MAHLI, ±SAM, ±APXS
detection of specific minerals is good
morphological pattern may be useful but needs very fine spatial resolution
Potential as a biosignature: low
Potential as an environmental indicator: low

6 Spatial patterns in chemistry
PE: SAM, CheMin, ±ChemCam if very abundant
C, N, S elemental distributions; Detection potential on cm scale to facies scale
Potential as a biosignature: low on its own
Potential as an environmental indicator: low

7 Biogenic Gases (Non-equilibrium)
PE: SAM
Excellent capacity to detect gases
Potential as a biosignature: high (e.g., CH_4)
Potential as an environmental indicator: low

Site selection decision-making and landed operations of the MSL should support the search for all of the above-mentioned biosignatures. However, it is also clear that accumulations of organic matter above meteoritic background levels would be amongst the most easily detected and least ambiguous. If life ever existed on Mars, it was likely microbial and existed communally in fluids and/or sediments, either free-living or as biofilms. Biomass from such communities, whatever their physiological characteristics, might then be preserved in the Martian sedimentary rock record in sufficient concentration to be detectable with MSL payload elements. Notwithstanding the numerous possibilities for habitable niches on Mars, a first-order approach to evaluating the organic record there would be to seek evidence of sedimentary environments -- the preferred geological setting for study -- that may have elevated concentrations of biologically derived carbonaceous materials (Table 3). These may include standing water environments such as deltaic systems, that promote retention of *in situ* organics and environments that hydrodynamically concentrate organics. An alternative approach would be to seek concentrations of buried crystalline minerals, such as clays and evaporites which may protect organic matter from the destructive effects of ionizing radiation and strong oxidants. We also identify and order a range of other possibilities for environments conducive to the preservation of the signs of former and extant life (Tables 3 and 4).

MSL's Unique Combination of Capabilities

The MSL rover houses a remarkable suite of analytical instrumentation within a mobile platform—a distinct advantage for field investigations. Once on the surface of Mars, this rover will support several years of exploration and sample analysis. The analysis of fossil organic matter entrained in sedimentary rocks requires a proven approach, which can be implemented by the SAM instrument. Extensive studies of fossil organic remains in terrestrial rocks demonstrate that in most cases macromolecular constituents make up the overwhelming bulk of geologically preserved organic material. Pyrolytic breakdown of biopolymeric material (or diagenetically modified biopolymeric material) into small, volatile and identifiable fragments in a specially engineered device at the front end of a gas chromatograph-mass spectrometer (GC-MS) is a proven and manageable analytical approach because it can provide a molecular fingerprint of fossil organisms, in many cases yielding critical information regarding the identity of the organism through the presence of characteristic molecular biomarkers. Some generic characteristics of biomarkers are summarized in Box 2. A combination of these features should be present in biomolecules, whatever their origin, and most of them are detectable with the SAM instrument. It is noteworthy that interstellar organic matter that may also be present in certain sedimentary rocks on Mars, also is amenable to characterization via pyrolysis GC-MS and may be distinguished from biologically derived material through specific kinds of molecular distributions (Sephton & Botta, 2008 and references therein).

Box 2: Molecular biosignatures at a glance

- Enantiomeric excess
  Homochirality characterizes terrestrial biochemicals; strong preference for one enantiomer over the other in a chiral molecule. Interpretation is complicated by the discovery of L- excess in meteoritic amino acids (Engel & Macko 1997, Cronin & Pizzarello 1997, Pizzarello 2006, Glavin & Dworkin 2009)
- Diastereoisomeric preference
  Strong isomer preferences in molecules with more than one center of asymmetry (Summons et al., 2007)
- Structural isomer preference
  Observing a limited subset of the possible stable structural isomers in a complex molecule (Summons et al., 2007)
- Repeating constitutional sub-units or atomic ratios
  Signifies complex molecules constructed from small common building blocks as in terrestrial biochemistry (McKay, 2004; 2007; Summons et al., 2007)
- Systematic isotopic ordering at molecular and intramolecular levels
  As above
- Uneven distribution patterns or clusters (e.g., C-number, concentration, $\delta^{13}C$) of structurally related compounds.
  As above

Aside from MSL's capabilities to provide high-resolution organic molecular information, the addition of CheMin and ChemCam to the traditional APXS broadens the capability to search for ancient life on Mars. The ability to determine quantitatively the major mineral and chemical constituents of prospective rocks will no doubt aid in assessing whether Mars had an active biosphere at a much earlier time in its history. In terrestrial rocks, the presence of biological organic matter can effect changes in local mineralogy by a number of different processes.

In some cases even if the organic matter has ultimately been destroyed through long-term exposure to oxidizing fluids, specific mineral associations with the now-absent organics may remain, providing a more persistent biomarker. Finally, certain minerals that exist on Earth on a global scale are generally recognized to be the consequence of an active biosphere, e.g., biogenic carbonates, hazenite ($KNaMg_2(PO_4)_2 \cdot 14H_2O$), or brushite ($CaHPO_4 \cdot 2H_2O$). Hazen et al. (2008) list and describe a large variety of mineral species that can be produced by biological processes. The presence of CheMin in the analytical suite of MSL is, therefore, of profound importance for the detection of ancient life.

The essential factor in addressing whether organic matter may be preserved in the Martian sedimentary record is the ability to access appropriate lithologies (Tables 3 & 4). In this regard, mobility is critical. As the MER mission has clearly demonstrated, only an "eyes-on-the-ground" approach can provide the information required to interpret the lithologies of outcrops. Integrating this mobile capability with analytical instrumentation provides the means to address whether organic matter preservation has occurred or not.

Insert tables 3 and 4 hereabouts

Brief description of the payload elements

Full descriptions of the MSL payload instruments can be found at: http://msl-scicorner.jpl.nasa.gov/Instruments/. In addition to the suite of analytical tools there are four cameras. The Mast Camera (MastCam), the Mars Hand Lens Imager (MAHLI), the Remote Micro-Imager on ChemCam (RMI) and the Mars Descent Imager (MARDI).

MastCam will take color images and color video footage of the Martian terrain. These can be stitched together to create panoramas of the landscape around the rover. MastCam consists of two camera systems mounted on a mast extending upward from the rover deck and will be used to study the Martian landscape, rocks, and soils; to view frost and weather phenomena; and to support the driving and sampling operations of the rover.

MAHLI will provide close-up views of the minerals, textures, and structures in Martian rocks and the surface layer of rocky debris and dust. The self-focusing, roughly 4-centimeter-wide (1.5-inch-wide) camera will take color images of features as small as 14 micrometers and will carry both white light and ultraviolet light sources making the imager functional both day and night. The ultraviolet light will be used to induce fluorescence to help detect carbonate and evaporite minerals, both of which would indicate that water helped shape the landscape on Mars.

RMI will provide telescopic views of the surfaces to be analyzed by LIBS, and will put LIBS analyses into their geologic context. However, the RMI can also be used to image textures whether or not the LIBS is used. The RMI has a field of view of 19 milliradians. Due to optimization of the telescope for LIBS, the RMI resolution is not pixel-limited, and is approximately 80 microradians. The RMI can clearly distinguish the submillimeter LIBS spot on a metal plate at a distance of at least 10 m. Therefore, this camera has the ability to make discoveries of texturally-based potential biosignatures, such as stromatolites and other textures suggestive of former microbial processes.

MARDI will take color video during the rover's descent toward the surface, providing an "astronaut's view" of the local environment. As soon as the rover jettisons its heat shield several kilometers above the surface, the Mars Descent Imager will begin producing a five-frames-per-second video stream of high-resolution, overhead views of the landing site. It will continue acquiring images until the rover lands, storing the video data in digital memory. After landing on Mars, the rover will transfer the data to Earth. MARDI will provide information about the larger geologic context surrounding the landing site.

ChemCam combines laser-induced breakdown spectroscopy with a remote micro-imager that provides images of the target. It will provide elemental analysis of spatially resolved solid samples at distances of 1-9 m. ChemCam's primary objective is to determine the chemical composition of rocks and regolith in order to characterize the materials in the vicinity of the rover.

The Alpha Particle X-Ray Spectrometer (APXS) will measure the abundance of chemical elements in rocks and soils. It will be placed in contact with rock and soil samples on Mars and will expose the material to alpha particles and X-rays emitted during the radioactive decay of curium. The MER rovers have used APXS successfully, but the greatest benefit of APXS will be when it is integrated with mineralogical analyses made by CheMin.

CheMin is a mineralogy instrument that will unequivocally identify and quantify the minerals present in rocks and soil delivered to it by the Sample Acquisition, Sample Processing and Handling (SA/SPaH) system. By determining the mineralogy of rocks and soils, CheMin will enable assessments of the involvement of water in their formation, deposition, or alteration. CheMin data will also be useful in the search for potential mineral biosignatures, energy sources for life, or indicators of past habitable environments. CheMin can unequivocally identify and quantify minerals above its detection limits in complex natural samples such as basalts, multi-component evaporite systems, and soils.

The Sample Analysis at Mars (SAM) Suite Investigation in the MSL Analytical Laboratory is designed to address the present and past habitability of Mars by exploring molecular and elemental chemistry relevant to life. SAM evaluates carbon chemistry through a search for organic compounds, the chemical state of light elements other than carbon, and isotopic tracers of planetary change. SAM is a suite of three instruments, a Quadrupole Mass Spectrometer (QMS), a Gas Chromatograph (GC), and a Tunable Laser Spectrometer (TLS). The QMS and the GC can operate together in a GC-MS mode for chromatographic separation and mass spectral identification of organic compounds. The TLS obtains precise stable isotope ratios for C and O in carbon dioxide as well as C isotopes and abundance of trace methane.

The Radiation Assessment Detector (RAD) will detect and analyze the most hazardous energetic particle radiation on the surface of Mars. Characterizing and understanding the radiation environment on the Martian surface is fundamental to quantitatively assessing the habitability of the planet (both past and present) and is essential for future manned Mars missions. RAD will address radiation effects on biological potential and past habitability, as well the contribution to chemical alteration of the regolith due to impinging space radiation.

REMS is designed to record six atmospheric parameters: wind speed/direction, pressure, relative humidity, air temperature, ground temperature, and ultraviolet radiation. All sensors are located around three elements: two booms attached to the rover Remote Sensing Mast (RSM), the Ultraviolet Sensor (UVS) assembly located on the rover top deck, and the Instrument Control Unit (ICU) inside the rover body.

The Dynamic Albedo of Neutrons (DAN) instrument is an active/passive neutron spectrometer that measures the abundance and depth distribution of H- and OH-bearing materials (e.g., adsorbed water, hydrated minerals) in a shallow layer (0.5-1 m) of Mars' subsurface along the path of the MSL rover.

The Sample Acquisition/Sample Processing and Handling subsystem (SA/SPaH) for MSL consists of a powdering drill (Powder Acquisition Drill System or PADS) together with a scooping, sieving, and portioning device (Collection and Handling for Interior Martian Rock Analysis or CHIMRA) mounted on a turret at the end of a robotic arm. There is also a dust removal tool (DRT) for clearing the surface of rocks prior to sampling. The drill enables powder to be acquired from depths of 20 to 50 mm over a wide range of rock hardness with the top ~15-20 mm being discarded. The scoop also enables samples of soil to be acquired, sieved and apportioned. Five bricks of a silicon dioxide ceramic organic check material (OCM) are mounted in canisters on the front of the rover to help assess end-to-end sample handling and potential organic contamination at different times during the mission. Each brick, which is sealed under vacuum in its own canister, can be drilled, sieved and portioned in CHIMRA. The powder is then delivered to SAM or CheMin following the same pathway as for Martian rock samples. The bricks are doped with traces of non-natural volatile fluorinated compounds. The sampling tools and protocols are subject to equivalent and, as far as is known, benign impacts on biosignature integrity as those used in terrestrial laboratories.

These instruments have been developed specifically for the MSL mission. Many aspects of their specifications and ultimate performance, individually or in concert, are still being evaluated.

Brief synopsis of environmental and physical features detectable with MSL payload

In the MSL payload, SAM can detect traces of organic matter in rocks and sediment. It does so in a variety of ways—from bulk organic carbon detection (by the difference between combusted total carbon and inorganic carbon) or non-specific molecular detection by evolved gas analysis (Bibring et al., 2005) to gas chromatographic (GC) separation and structural identification of discrete molecules volatilized directly or after reactions with chemical derivatizing reagents that enhance volatility and thermal stability (Tables 2, 5-8). It also detects traces of volatile organics in the atmosphere, such as C1-C6 hydrocarbons and other gases, and it can precisely measure carbon isotopic composition of methane and carbon dioxide.

The camera systems are designed document color and grain size variations in rocks and sediments that reflect sedimentary structures, mineral growth processes, weathering and biofabrics, if present (see Noffke, 2009; Tables 9-12). These features provide essential data for interpreting the processes forming the rocks as well as their alteration. Images are essential for sample selection in addition to providing a context for chemical analyses.

ChemCam can remotely detect carbon in soils and rocks (>1% carbon subject to final testing and calibration) but the ChemCam does not directly discriminate between organic and inorganic carbon (Tables 5 & 6). This is in contrast to the SAM capability of detecting sub ppb levels of organic compounds that are <535 dalton via Evolved Gas Analysis (EGA) and pyrolysis.

CheMin in XRD mode cannot detect organic carbon, but it can detect and identify any crystalline inorganic hosts of carbon and sulfur, for example (Tables 11 & 12). Used in conjunction with SAM, it can be particularly useful in providing more accurate discrimination between organic and inorganic hosts. Thus, the MSL payload is capable of mapping the distribution of organic carbon and its molecular composition in rocks and sediments in stratigraphic, geomorphic, and/or chronologic context. This distribution, the types of molecular structures detected, their redox state, polarity, volatility, and their relationship to other elements and minerals detected by other MSL payload instruments would provide critical insight to deciphering biosignatures, other organic matter sources (abiogenic and meteoritic), environmental records, surface processes and carbon cycling.

Insert Tables 4 and 5 hereabouts

Carbon isotopes as potential biosignatures on Mars

The patterns of isotopic composition ($^{13}C/^{12}C$ ratios) of Martian crustal and atmospheric constituents reflect the compositions of their original sources as well as any isotopic discrimination associated with the network of physical, chemical (and biological?) processes that created and cycled these constituents (Tables 7 & 8). Fig. 1 depicts the terrestrial C cycle consisting of C reservoirs (boxes) and processes (arrows) in the atmosphere, crust, and interior. The caption for Fig. 1 addresses these processes. An illustration of the S cycle would be analogous to Fig. 1, except sulfide and sulfate reservoirs would be substituted for organic and inorganic C reservoirs, respectively. The figure is included to illustrate the complexity of known reservoirs, the timescales over which they interact and range of isotopic values on Earth. This picture has only emerged gradually over many years through extensive study through direct observation of the chemical, biological, isotopic and geological aspects of carbon cycling (e.g. see Des Marais, 2001).

Insert Figure 1 Hereabouts

Insert Table 7 hereabouts

Overall, the terrestrial C-cycle consists of multiple nested cyclic pathways that differ with respect to reservoirs, processes and timescales. Carbon is exchanged between the atmosphere and shallow crust by processes which act on relatively short timescales. Carbon deeper within the crust is cycled more slowly by processes of burial and exhumation under tectonic control. These processes are now probably negligible due to the presumed absence of subduction on Mars. Processes which exchange carbon between the crust and atmosphere of Mars might be somewhat active as indicated by the recent indications of methane in the Martian atmosphere (Mumma et al., 2009). This methane almost certainly has a subsurface source that very likely involves aqueous processes, possibly including life, which we discuss further below.

The $^{13}C/^{12}C$ ratios of the carbon reservoirs reflect isotopic discrimination associated with the above processes. On Earth, isotopic discrimination associated with organic biosynthesis has been principally responsible for determining the $^{13}C/^{12}C$ ratios observed in organic and inorganic crustal reservoirs. Biological processes can change these values by several percent (e.g., Des Marais, 2001). Accordingly $^{13}C/^{12}C$ ratios might serve as biosignatures of any past or present life on Mars if key components of the C-cycling system can be constrained. However Jakosky et al. (1994) calculated that processes that caused loss of C to space were isotopically selective and increased by several percent the $^{13}C/^{12}C$ ratios of the remaining atmospheric and near-surface crustal C reservoirs. These increases might equal or exceed, and thus obscure, any changes in $^{13}C/^{12}C$ ratios due to biological processes. Note, as well, that abiotic processes of organic synthesis involve C-isotopic fractionation, further complicating the isotopic interpretation of any organic compounds that may be detected (Chang et al., 1983). To the extent that carbon situated in deeper interior reservoirs was isolated from these atmospheric escape processes, its $^{13}C/^{12}C$ value would be less affected and therefore lower, and perhaps most closely reflect initial Martian $^{13}C/^{12}C$ ratios. Consequently we cannot be entirely sure whether any measured $^{13}C/^{12}C$ patterns might indicate life or whether they reflect principally the effects of atmospheric escape or other environmentally sensitive equilibrium fractionation processes. Another difficult challenge for interpretation of C-isotopes on Mars is establishing whether organic matter and any inorganic carbon in a given sample have a genetic relationship. If, for example, the OM is meteoritic and carbonate originated hydrothermally, an isotopic separation is likely to be meaningless.

Precise and accurate carbon isotopic compositions of methane and carbon dioxide from the TLS in SAM may provide important benchmarks for understanding planetary-scale carbon cycling on Mars. For atmospheric measurements these experiments are rapid and not resource intensive and, thus, could be included in a regular sampling scheme. Detection and quantification of atmospheric methane by MSL would provide an important verification of the Earth-based and orbital spectroscopic detections of methane at ppb levels (Formisano et al., 2004, Krasnopolsky et al., 2005; Mumma et al., 2009). Temporal variations in methane concentration would be detectable by MSL and could potentially distinguish between episodic release of subsurface methane or methane destruction from photolytic, oxidative or dust reactions in the modern environment (Atreya et al., 2006). Spatial variations in methane concentration are not expected to be observable unless MSL is proximal to a subsurface hydrothermal, volcanic or unstable hydrate point source. Using C-isotopic data to constrain the origins of atmospheric methane on Mars, however, presents a formidable problem. Abiogenic methane production associated with serpentinization, that is, aqueous alteration of olivine- and/or pyroxene-rich rocks, is a process likely to have been prevalent early in Mars history and which feasibly continues today (Oze and Sharma, 2005). Multiple carbon and hydrogen isotopic data suggest the methane that is abundant in the fluids emanating from the Lost City hydrothermal field, a site of contemporary serpentinization on Earth, has an abiogenic origin. However, it is known that methanogenic Archaea are also active in this system (Bradley et al., 2009). Accordingly, carbon isotopes are of limited value in discriminating between biological and abiogenic sources where multiple processes can contribute to a pool of methane and reservoir affects provide added complications (Bradley and Summons, 2010). This is the situation on Earth where the biochemistry of methanogenesis is reasonably well understood and even more uncertainly would accompany methane measurements on Mars. Carbon isotopic data might discriminate between abiogenic and biogenic methane sources only if the fractionation between methane and co-existing CO_2 were well in excess of the equilibrium values modeled for feasible P-T conditions, thereby implying kinetic (i.e., enzymatic) control on methanogenesis.

Variations in C-isotopic compositions of carbon dioxide are less likely as it is the dominant atmospheric species. SAM design also enables isotopic measurements of trace amounts of bulk inorganic and organic carbon by comparing CO_2 evolved under inert conditions with CO_2 generated from combustion with O_2. Mapping variations in these isotopic compositions could further our understanding of redox processes, isotopic fractionation pathways (including biosignatures, abiogenic processes, and possibly meteoritic contributions), and environmental carbon cycling (Table 8). The TLS can also measure oxygen isotopes of carbon dioxide and deuterium/hydrogen in water, which may indicate the effects of surface and atmospheric cycling. Oxygen isotopes of carbon dioxide evolved from carbonates in SAM will help with assessment of post-depositional alteration by subsurface fluids.

Sulfur isotopes as potential biosignatures on Mars

Observed $^{34}S/^{32}S$, and $^{33}S/^{32}S$ values presumably reflect processing by redox reactions in the atmosphere (e.g. photochemistry, see Farquhar et al., 2000) and crust (e.g. weathering, hydrothermal and life). On Earth, microbial reduction of sulfate and sulfur disproportionation reactions occurring at ambient temperatures have created large $^{34}S/^{32}S$ differences (several percent) between oxidized and reduced sulfur reservoirs (Canfield, 2001). Because microorganisms are required to catalyze S-isotopic exchange reactions having significant fractionations at low ambient temperatures, large $^{34}S/^{32}S$ differences in sedimentary rocks can be reliably interpreted as biosignatures in many cases. However, a careful assessment of the original environment of deposition is always essential. Accordingly, before stable isotopic patterns can serve as potential biosignatures on Mars, we must characterize the isotopic composition of major sulfur reservoirs and also understand more fully the consequences of key non-biological processes.

Tests on a SAM breadboard QMS instrument have shown that sulfur isotope measurements of sulfur dioxide evolved from the thermal degradation of sulfate minerals are possible (Franz et al., 2007). However, these measurements are complicated by overlapping spectra and the evolution of gas from multiple sulfur species. Unlike the sub-per-mil precision from Earth-based instrumentation, the SAM QMS may provide percent precision. These data may still be valuable on Mars, especially if basaltic sulfur, which shows <1% variability on Earth and meteorites, provides a reference point for comparing sedimentary and hydrothermal sulfur analyses (Table 8). On Earth, sedimentary sulfides show 4% variation, reflecting biological cycling of S, a sensitive redox element (Canfield, 2001; Farquhar et al., 2003). If a similar record were to exist on Mars, sulfur isotopic detection by the SAM QMS may detect it. Sulfur isotopic compositions of sulfate and reduced-sulfur minerals may also provide valuable information of environmental sulfur cycling by abiogenic hydrothermal (Rye, 2005; Greenwood et al., 2000) and atmospheric processes (Farquhar et al., 2000).

Other isotopic data

Noble gas isotope measurements and elemental ratios are regarded as isotopic tracers of mantle and atmospheric evolution (Swindle, 2002) and possible comet-borne contributions (Owen et al., 1992). Although they do not provide direct insight into environmental conditions preserved in the sedimentary record, they can supplement the larger context of Mars chemical and environmental evolution. These data may help explain other isotopic records.

Environmental conditions

Sedimentary and other near-surface materials can serve as recorders of environmental conditions that prevailed during previous epochs of Martian history. Insights into ancient environmental conditions might help to identify potential processes responsible for setting the observed isotopic patterns. Paleotemperatures often can be inferred by measuring stable isotopic compositions of pairs of minerals or fluids that equilibrated isotopically when they formed. Oxygen isotopes have been utilized most frequently to infer paleotemperatures within the habitable range (<120^{o}C). Elevated temperatures have been inferred using sulfur (>150^{o}C) and carbon (>300^{o}C) isotopes. Stable isotopic compositions of preserved minerals can also help to elucidate the nature of fluids associated with their formation. For example, elevated $^{18}O/^{16}O$ values might indicate the former presence of brines in evaporitic environments. Many additional examples can be cited where stable isotopic patterns have helped to constrain paleoenvironmental conditions.

Insert Table 8 hereabouts

Preservation potential

To the extent that sediments, cements, and other surface materials have escaped alteration subsequent to their formation, they can preserve information about earlier environmental conditions and, potentially, biosignatures (Tables 9 & 10). Preservation can be compromised by weathering and erosion or by alteration *in situ* by oxidation and migrating fluids, for example.

The following minerals can isolate and preserve biosignatures (listed in order of increasing crustal residence times on Earth): ice, halite, sulfates (e.g. Aubrey et al., 2005; Panieri et al., 2010), carbonates (e.g. Birgel et al., 2008), phyllosilicates (e.g. Hedges and Keil, 1995; Butterfield, 1990), silica (e.g. Knoll, 1985), hematite (Fernadez Remolar and Knoll, 2008) and phosphates (e.g. Xiao & Knoll, 1999; Farmer & Des Marais, 1999). For example, carbonates deposited as a consequence of microbial metabolisms sometimes hold an excellent record of those processes as is the case with methane seep limestones (e.g. Birgel et al., 2008) or hydrothermal systems like Lost City (Bradley et al., 2009). Silica-rich water derived from hydrothermal systems is another well-established medium that promotes faithful preservation (e.g. Knoll et al., 1985; Trewin, 1996). In fact, Walter (1996) has identified numerous fossil hydrothermal systems on Earth, both terrestrial and marine, that are known and potential repositories of paleobiological information. Preservation is optimized when temperatures remain low and mineral matrices form during sedimentation/precipitation and reduce the permeability of the sediments to near zero. Detailed $^{18}O/^{16}O$ values of some of these minerals can help to assess the extent to which invading fluids caused post-depositional alteration.

Hydrated mineral phases

The presence of hydrated minerals reflects specific chemical conditions, including the activity of water (Table 12). Specific implications of different hydrous phases vary with the composition and context of the minerals. Some, such as hydrous Mg-sulfates, require low temperatures and/or substantial humidity to remain stable. Their hydration states reflect local current conditions due to their rapid dehydration kinetics, although their formation may reflect older conditions. Other hydrous minerals, such as the clay minerals, remain metastable for long periods of time and provide a record of past hydrous activity. Extracting the history of water on Mars requires careful characterization of hydrous minerals within their environmental context.

Textural features preserved in sediments and hydrothermal systems

Physical, chemical and biological processes all influence the preservation of biosignatures in hydrothermal and sedimentary systems on Earth, and we can use our understanding of these processes to predict their impact on possible biosignature preservation on Mars (Tables 9 & 10).

Purely physical and chemical processes should be comparable on Earth and Mars. For subsurface, hydrothermal and sedimentary systems, physical and chemical processes can provide substantial insights into the history and habitability of the system. For example, in sedimentary systems, physical processes such as sediment transport produce structures that are characteristic of specific processes, e.g., types of flows. These can be used to interpret processes in the depositional environment, providing invaluable constraints on habitability and guiding the search for biomarkers. There are some non-negligible differences due to the lower g of Mars, however, these do not affect the overall interpretation of transport-related suites of sedimentary structures (Grotzinger et al., 2005). Similarly, chemical processes leave distinctive signatures, whether they are active in the depositional environment or within the rock. They can be used to evaluate the habitability of the environment and rocks at different points in time, including the potential for subsurface colonization of rocks of volcanic, hydrothermal or sedimentary origins.

Insert tables 9 & 10 hereabouts

On Earth, biological processes are very active in almost all sedimentary and lower-temperature hydrothermal systems. Biological processes in terrestrial hydrothermal systems provide a diverse suite of potential biomarkers, including concentrations of organics and minerals that reflect mats, stromatolites, roll-ups, biofilms, streamers, etc. (Tables 9 & 11). Concentrations of elements and high concentrations of migrated organics are also characteristics of some terrestrial hydrothermal systems. Preservation of these indicators of biological activity is strongly affected by physical and chemical processes. The high temperatures and abundant water flow tend to degrade biomarkers. Hydrothermal systems commonly experience intense brecciation and fracturing due to high-pressure fluids. This type of fracturing leaves distinctive textural features that are best avoided when looking for a good biosignature preservation window. Chemical processes also affect preservation. Mineral precipitation can entomb organics and biological processes can influence the distribution of minerals. In hydrothermal settings, a good preservation window is created by precipitation of non-redox sensitive, low-porosity minerals. However, minerals can also recrystallize and dissolve, particularly when exposed to high-temperature fluids, making preservation of biosignatures less likely. When looking for a good preservation window, one wants to avoid recrystallized areas, those that have experienced intense oxidation, and those exposed to high temperatures or ionizing radiation (e.g. Dahl et al., 1988).

Sedimentary systems on Earth also have substantial potential for preserving biosignatures because of the intensity of biological activity, and their natural tendency to concentrate or high-grade organic matter across hydraulic gradients. Again, these terrestrial processes serve as models for predicting good preservation windows on Mars (Tables 10 & 12). Biomass accumulation in terrestrial systems is reflected in mats, stromatolites, roll-ups, wrinkle structures, etc. For preservation, these accumulations need to incorporate sediment or be mineralized prior to degradation of the organics. Biological processes can also create fenestrae (gas-produced pores), affect grain sizes, and influence elemental concentrations. These features can be well preserved if they are lithified early and do not experience significant alteration. Physical processes such as dewatering, hydration changes and structural deformation can destroy these signatures. Similarly, chemical processes such as recrystallization, redox changes and metamorphism destroy biomarkers. Thus, for biomarker preservation, one should identify areas with an appropriate sedimentary environment that was lithified early and experienced minimal post-depositional alteration (Farmer and Des Marais, 1999).

Elemental concentrations and mineral distributions in hydrothermal and deep subsurface systems

Hydrothermal environments can preserve potential biosignatures in the form of elemental concentrations and mineral distributions (Table 11). Thermally driven aqueous convection can significantly alter environmental conditions through selective mineral dissolution, alteration, and precipitation; element leaching and subsequent transport; and oxidation and reduction (redox) chemistry. On Earth, each of these processes can occur with or without biological mediation, but through careful analysis with multi-faceted approaches, the role of biology can often be assessed.

If life emerged on Mars and prospered in hydrothermal systems, these alteration processes likely include biotic and abiotic components (Tables 9 & 11). Each yields an array of features including specific mineralogy that is characteristic of certain hydrothermal conditions and chemistries, element gradients and zonation within those minerals and spatial distribution of alteration minerals and precipitates at scales from µm to km (Table 11). The identification and chemical analysis of chlorite, amorphous silica or quartz, sulfide minerals, kaolinite and other clays, hematite and other ferric (hydr)oxides, carbonates, and sulfates can be used to determine formation temperatures, redox conditions, and pH. For example, specific sulfides (PbS, ZnS, CuS) and sulfates ($BaSO_4$, $CaSO_4{\cdot}2H_2O$)or mineral assemblages (e.g., sulfate and/or sulfide together with saddle dolomite) can point to specific formation temperatures. The presence of jarosite, alunite, or kaolinite indicate low-pH environments, and discrimination between crystalline silica minerals (e.g., quartz or cristobalite) and non-crystalline silica phases, such as opal-CT, is most effective when chemical data are combined with mineralogical information (e.g., XRD data). Other minerals bearing S, Fe, Mn, U, As or other redox-sensitive elements can provide further constraints on Eh and, if present above the minimum detection limits for CheMin, could be detected by XRD. All of these features would help constrain the possibility, probability, and physiology of potential life forms on Mars. However, because hydrothermal systems are dynamic, high-energy environments, the preservation of labile features (e.g. organic matter, amorphous solids) would undoubtedly require encasement or entombment in protective minerals or other removal from the destructive forces of oxidation, metamorphism, and continued hydrothermal activity.

Insert Table 11 hereabouts

Elemental concentrations and mineral distributions in sedimentary systems

Sedimentary environments present both similarities and differences to the hydrothermal case highlighted above. The preservation potential of environmental signatures is determined principally by the sedimentary material, the chemical composition and flux of the aqueous solutions responsible for the sediment transport, the redox state and pH of that solution, and any post-depositional chemical processes (including putative microbe-mineral interactions) that may have operated (Table 12). The most informative environmental signatures include sedimentary structures and redox-sensitive (e.g., S, Fe, and Mn-bearing) and pH-sensitive (e.g., jarosite, alunite, kaolinite, carbonates) mineral assemblages and abundances. Many sedimentary environments on Earth or Mars also host evaporite minerals (including sulfates and chlorides) and corresponding trace element distributions, as well as oxides, carbonates, sulfides and, perhaps, phosphate precipitates resulting from microbe-mineral interactions. The preservation potential of these environmental features is particularly enhanced by early lithification of the sediments. In addition, the greatest scientific return would likely come from sedimentary systems, lacustrine or marine, that have not been subjected to significant recrystallization, prolonged strong oxidizing conditions, dissolution and solute removal, major structural alteration, or significant thermal metamorphism. As closed basins, lakes in particular, represent terminal receptors for both primary and transported organics together with the clays, which preserve OM due to strong absorption capacity, low reactivity, and low permeability when compacted (Farmer and Des Marais, 1999; Meyers and Ishiwatari, 1995).

Insert Table 12 hereabouts

Critical Mars - Earth contrasts: considerations for MSL decision-making

Any martian biomass must be, and probably would have been, less abundant than biomass on Earth throughout its history. Land plants dominate modern biomass on Earth, and marine organic matter is created almost exclusively by photosynthetic biota and it is pervasively concentrated at the margins of continents. Only a relatively small percentage of all primary productivity (~0.1%) survives remineralization and becomes preserved in sediments. If life colonized Mars, its global primary productivity is expected to have been much lower, given the less clement and more ephemeral surface habitable environments and the presumed absence of plants. The fraction of any biomass that was preserved in martian sedimentary rocks is, of course, unknown.

Meteorite impacts delivered organic matter to the martian surface. The early solar system had a greater abundance of debris and thus experienced a higher rate of impacts than later in its history. The size distribution of impactors may also have been different. Radiometrically dated samples from the moon make it possible to associate an absolute age with a certain crater density. The relation is non-linear because the flux of impactors was higher before 3.5 Ga, but subsequently the flux has apparently remained nearly constant. The following major questions persist: 1) Did the early impact flux decrease steadily or did an “impact spike” occur at ~4 Ga (known as the “Late Heavy Bombardment”)? 2) There is a large uncertainty (factor of about 2) for young ages (≤ 1 Ga). Because Mars is closer to the asteroid belt the number of impacts on Mars is estimated to be 3±1.5 times the number of impacts on the Earth-Moon system. However the accumulation of meteoritic organics in the martian crust also depends upon the fraction of material that is actually preserved.

The Late Heavy Bombardment is an important consideration in estimating organic matter preservation on Mars. As far as we know, virtually all of the biogenic organic matter that persists on Earth today was formed after 3.8 Ga and most of that was formed within the most recent 500 million years. If a biosphere existed in the first 500 million years of martian history a substantial fraction of its remains might have been altered or destroyed during the Late Heavy Bombardment. Smaller, relatively recent impacts might have exumed any remnants of an early biosphere.

The tectonic regimes of Mars and Earth are distinctly different, as reflected by significantly older surface ages and relatively minor regional metamorphism on Mars. Organic carbon accumulation on Earth is, and has been, modulated by a vigorous tectonic cycle, and the residence time of organic carbon in the crust is consistent with the Wilson cycle period (i.e., modern plate tectonics). Most importantly, tectonic processes drive biogeochemical cycles by sustaining nutrient availability and creating the spaces for subaqueous accumulations of sediment and its entrained organic matter.

Mars currently has no global dynamo-driven magnetic field, but strong local crustal fields indicate that a global field likely existed in the past. However, magnetic field age and strength are not known to directly influence organic matter formation preservation except that a global magnetic field would have attenuated the flux of deleterious radiation and reduced losses of atmospheric species to space. The radiation environment on Earth is conducive to harvesting solar energy and forming organic matter through photosynthesis. A dense atmosphere, the pervasiveness of liquid water on Earth's surface and the operation of a magnetic field all can reduce deleterious radiation. Widespread photosynthesis on Earth has clearly enhanced organic matter production in environments that also favored its preservation in aqueous sediments.

Processes operating in such favorable sedimentary environments can concentrate organic matter prior to burial. Important concentrating mechanisms include the following: density sorting during transport, adherence to the fine particles of clay minerals, and ballasting of organics on biogenic minerals. Differences in the hydrological cycles of Mars and Earth would have affected any potential concentration or organics during transport.

Sedimentary rocks with anomalously high concentrations of organic matter (> few percent) are a historically pervasive feature of Earth's sedimentary rock record; they occur even in the early Precambrian record. However organic-rich and biomarker-bearing deposits are typically non-uniformly distributed and unpredictable. No known example of subaerial fossilized deposits on Earth have a total organic carbon content exceeding 1% by weight; Mars is expected to be similar.

Aeolian transport processes lead to destruction of organic matter by continually refreshing its contact with oxidizing agents and UV radiation. The fate of organic matter transported in this way is expected to be similar on Mars to what it is on Earth or, possibly, worse.

Therefore, on modern Earth, biomass has been detected in almost every wet environment, including very harsh and extreme sites in terms of temperature, pH, water activity, intermittent desiccation, and pressure. Essentially every wet environment below the upper thermal limit of life can be considered habitable. However the production, concentration and preservation of organics have varied substantially and have been controlled by the spatial and temporal distribution of subaqueous environments and sedimentary processes. The search for martian biosignatures has become more promising due to the discovery that surface and near-surface aqueous environments existed on Mars at the same time when biological organic matter was being preserved in ancient aqueous sediments on Earth.

In its quest to find organic-bearing strata, MSL should investigate, ideally, a subaqueously deposited and rapidly buried suite of strata that represents the longest duration possible, i.e., the thickest section in the absence of other age constraints (Farmer and Des Marais, 1999). If the record at Meridiani Planum is representative of other early martian sedimentary environments, at least some beds might have been deposited in water even if the stratigraphic succession is predominantly eolian in origin (Grotzinger et al., 2005).

Consideration of planetary age

Planetary evolution strongly influences biosignature preservation, particularly on a planet like Mars that has experienced significant geological and climate variations. Changes in habitability through time affect the abundance and diversity of potential biosignatures. For example, loss of the Martian magnetic field strongly affected surface environments through atmospheric loss and increased radiation; this change significantly degraded surface habitability, reducing the chances of biosignatures in the rock record. Changes in temperature and moisture also clearly affect habitability both on the surface and in subsurface aquifers. Hydrothermal activity tied to volcanism and impacts was more abundant on early Mars and more abundant and continuous hydrothermal activity is more likely to support a biosphere that could leave signatures. Also, it is critical to understand long term climate evolution when choosing the best places to look for biosignatures; rocks deposited during warm and wet intervals, e.g. early Mars, are more promising for biosignature development. Preservation of any biosignatures also depends on climate-dependent sedimentary processes. Clay minerals preserve biosignatures in ways that are fundamentally different to what occurs in carbonate or sulfate minerals (Hedges and Keil, 1995). Therefore, long term changes in the relative abundance of certain minerals affect the likelihood of specific biosignature preservation in rocks of a particular age. Thus, the specific evolution of Mars as a planet suggests that the best time interval for the search for biosignatures would be represented by early to mid-Noachian rocks, when clays were thought to be forming. This is not to say that clays did not form in younger times, in fact, tests of this hypothesis could be one outcome of the MSL mission.

Potential biological sources of organic carbon on Mars

On Earth today, photoautotrophy is by far the dominant physiology leading to organic matter synthesis. With a seemingly unlimited solar energy source, photoautotrophs in the ocean and on land can produce copious amounts of organic matter compared with chemoautotrophs (orders of magnitude more). In present-day aquatic environments chemoheterotrophs thrive on chemical energy from the decomposition of organic matter from photosynthetic communities using electron acceptors that are also regenerated by photoautotrophs.

Chemoautotrophs thrive by carbon fixation using electron donors that are also generated or regenerated via light-harvesting processes. In the absence of photoautotrophy, primary biomass production would be limited to chemoautotrophs that harvest chemical energy from geological processes—namely those occurring in hydrothermal vents in the oceans and terrestrial geothermal springs (see Table 4) and subsurface microenvironments within the fractures and pores of ultramafic and mafic rocks. The Lost City Hydrothermal Field (Kelley et al., 2005), a low-temperature marine ultramafic hydrothermal system is one model for an environment that could support life in the absence of photosynthetic light harvesting (Martin & Russell, 2007; Martin et al., 2008). Such a system could conceivably occur anywhere that water circulates through ultramafic rock. Although ultramafic rock is rare on the ocean floor today, occurring mainly at ultraslow-spreading ridges, it could have been more prevalent in the geological past

(Sleep et al., 2004; Sleep and Bird 2007). Molecular and isotopic data indicate that Lost City fluids sustain a flourishing microbial community of methanogens and sulfate-reducing bacteria (SRB) (Bradley et al., 2009; Brazelton et al., 2006). Although the SRB would be sulfate-limited if disconnected from a sulfate supply that is ultimately coupled to oxygenic photosynthesis or abiotic oxidation reactions occurring at the surface or subsurface, there appear to be no such constraints on the activity of methanogens that require only hydrogen and CO_2. In addition, thermodynamic calculations showed that Lost City-type vent fluids mixed with seawater are energetically favorable for biomass synthesis (Amend & McCollom, 2009). Thus, the recent detection of serpentine deposits in Noachian terrains on the surface of Mars (Ehlmann et al., 2010) identifies the probable past occurrence of hydrogen-producing water-rock reactions and, therefore, an established set of processes that would both support chemosynthetic life and preserve a molecular and/or isotopic record of its prior existence (e.g. Kelly et al., 2005; Bradley et al., 2009)

At life's origin, the dominant energy source was unlikely to have been sunlight. Energy flowing from chemical and thermal disequilibria and particularly from the interaction of hot rocks with water is more likely. Perhaps the same was the case for early Mars. In aqueous depositional environments, chemoautotrophs may have been the cornerstone of microbial communities relying on fermentation and heterotrophy fueled by a weak oxidant flux from chemoautotrophy or irradiative oxidation. If Mars evolved a biosphere, it may not have progressed to photoautotrophy or a dependence on photoautotrophy as it did on Earth. Thus, in the consideration of Martian environments conducive to producing molecular biosignatures, targeting depositional environments that had a strong chemical energy flux and sustained redox gradients for long periods by biogeochemical cycling is a most promising strategy.

One additional possibility for chemoautotrophy is energy derived from radiolysis of water (Pratt et al., 2006). The recent discovery of a microbial biome dominated by thermophilic sulfate reducing bacteria in a c. 3km deep saline aquifer in Archean metabasalt seems to required that they were sustained by geologically produced sulfate and hydrogen at concentrations sufficient to maintain biological activity for millions of years (Chivian et al., 2008; Lin et al., 2006). Radiolysis of water coupled to oxidation of sulfide minerals could have provided the energy drive for low-biomass, low-diversity subsurface ecosystems.

Abiotic sources of organic carbon on Mars

Sources of abiotic organic matter on Mars could have been similar to those hypothesized to have been present or formed on the early Earth. This would have included organic matter delivered by meteorites and interplanetary dust (Anders, 1989), organic matter produced as a result of atmospheric photochemistry (Chang et al., 1983) and organic matter produced during fluid mixing in hydrothermal systems (Shock & Schulte, 1998). The Lost City hydrothermal system also serves as an example of another route to abiotic organic compounds. The isotopic composition and chain length distributions of hydrocarbon gases isolated from Lost City fluids have been interpreted to signify an abiotic source (Proskurowski et al., 2008; Sherwood Lollar et al., 2006). Hydrogen produced in high concentration by serpentinization chemistry leads to a thermodynamic drive for CO_2 reduction (Shock & Schulte, 1998). Methane and higher hydrocarbons may be thus produced abiotically in ultramafic hydrothermal systems by Fischer-Tropsch type processes that comprise polymerization reactions leading to methane and higher hydrocarbons (Horita & Berndt, 1999; McCollom & Seewald, 2006; McCollom & Seewald, 2007).

Steele and co-workers (2007) have identified macromolecular carbon, in an intimate association with magnetite, through imaging and Raman spectroscopic studies of carbonate globules in the Mars meteorite ALH84001. This abiotically-formed organic matter appears to be native to Mars. It is hypothesized to have formed formation via reactions of the Fe-C-O system for which there is a terrestrial analogue in the Bockfjorden volcanic complex of Svalbard.

Interstellar organic matter

Irrespective of whether extensive abiotic organic synthesis of predominantly hydrocarbons occurred on the early Earth and, potentially, on Mars, chondritic meteorites and interplanetary dust particles (IDPs) have delivered abiotic organic matter to the Martian surface. Carbonaceous chondritic (CC) meteorites consist of up to 2 wt % of organic matter finely intermixed with matrix silicates (Alexander et al., 2007). It is well known that some CCs contain relatively high abundances of small, polar organic molecules, e.g. amino acids. The highest reported concentration of amino acids, however, is not very high, being on the order of 250 ppm (Martins et al. 2007). The primary form of organic matter in all classes of chondritic meteorites is Insoluble Organic Matter (IOM), a chemically complex macromolecule (e.g. Cody & Alexander 2005) that is by definition insoluble in any solvent and is in many cases 99 % of the organic matter in a given chondrite (Botta, 2005; Sephton, 2002; Sephton et al., 2004). Among the meteorites collected as finds in Antarctica, 0.8 % are CCs, the majority, 77 %, are ordinary chondrites (OCs) (http://curator.jsc.nasa.gov/antmet/ppr.cfm). While ordinary chondrites do contain IOM, its abundance is considerably lower than that in CCs (Alexander et al. 2007) and, even in the least metamorphosed OCs, the IOM has been significantly altered through long term thermal processing yielding highly aromatized macromolecular structures (Cody et al., 2008). If the distribution of meteorite types on Mars was and is similar to that of Earth, it is reasonable to assume that the predominant IOM would be exceptionally stable over geological timescales even under the harsh Martian surface conditions. An instrument analogous to SAM flew on the Viking mission and did not detect organics via pyrolytic analysis. All evidence suggests that the Viking technical approach and instrument worked according to its design (Biemann, 1979, Biemann, 2007) so these Viking results do not exclude the potential presence of abundant IOM, if the IOM was derived predominantly from OCs. IOM in OCs has already been subjected to extensive natural pyrolysis in the OC parent body (Cody et al., 2008). Minimal, if any, pyrolysate remains to be derived, therefore, from thermally metamorphosed IOM. Pyrolysate from chondritic IOM might be detected only if the abundance of CCs that accumulate on the Martian surface exceeds what is observed in the Antarctic collections.

Finally, there is the issue of Interplanetary Dust Particles (IDPs) that, in case of the Earth, constitute a much greater influx of extraterrestrial matter. IDPs typically contain considerably more organic matter than CCs and the organic macromolecule bears significant spectroscopic resemblance to IOM derived from primitive CCs. Lacking the silicate matrix protection afforded to CC IOM, it appears likely that IDPs will be subjected to more degradation than CC IOM on the Martian surface. Under ideal conditions, however, IDPs could survive on Mars, and be detectable via pyrolysis GCMS. The SAM instrument has enhanced sensitivity and experiment flexibility compared to Viking. However, an even more important quality is the mobility and composition of the entire MSL package as this enables optimization of sample selection and handling.

Distribution and importance of phyllosilicates for habitability and organic preservation

It has long been recognized that, on Earth, there is a close association between organic matter and phyllosilicate minerals. This is the case for both modern environments, particularly in large aqueous catchments where fine-grained particulates often rich in phyllosilicate minerals can settle from the water column (lakes and ocean margins), and in ancient sediments (e.g. shale and organic-rich mudstones). Certainly, low porosity and permeability of compacted phyllosilicate sheets aid in entombing and protecting organic matter from oxidizing fluids and biological activity over geological time scales. Abundant experimental data show that many phyllosilicates, particularly smectites, interact strongly with organic molecules and are capable of adsorbing and preserving them. However, the specific mechanisms that give rise to this association are not well understood and are the subject of ongoing investigations. Accordingly, we should be very careful in extending empirical observations made on Earth to the situation on Mars. Rather, the combined ability of the MSL to detect both organic carbon and clay mineral assemblages on Mars offers us an unprecedented opportunity to learn much about this particular issue during the landed operations.

Phyllosilicates such as smectites, chlorites, and kaolin minerals form during the weathering of minerals in soils and in hydrothermal systems. Phyllosilicates all have sheet-like structures and can accommodate a large variety of cations, most commonly including Fe, Mg, and Al in their octahedral sheets and Na, Ca, and K between the layers in the so-called interlayer region. Fine-grained, disordered phyllosilicates are often called clay minerals, and they have high surface areas and the ability to exchange their interlayer cations and adsorb H_2O molecules, as a result of negatively charged interlayer regions. Many organic compounds can be adsorbed onto surfaces and into the interlayer regions, in some cases forming weak bonds with phyllosilicate surfaces. Adsorption of organic molecules into the interlayer region is particularly important for very low molecular weight compounds, such as amino acids (Hedges & Hare, 1987) and polysaccharides (Dontsova and Bigham, 2005) as well as higher molecular weight material (Mayer, 1994a, b; Kennedy, et al., 2002). Organic molecules compete with other polar species in the environment (e.g., water, cations, etc.) for active sites on phyllosilicate minerals. However, a key factor for enhanced organic matter preservation by phyllosilicates is coincidental timing of organic matter diagenesis and phyllosilicate mineral formation (Hedges & Kiel, 1995). Specifically, it requires synchronous availability of organics and clay mineral formation. To grasp the significance of this timing issue, it is also important to understand how organic matter ends up in sediments and ultimately the rock record.

On Earth, most sedimentary and hydrothermal organic matter is macromolecular. In these terrestrial settings, polymerization to macromolecules may begin at the point of formation (i.e., cellular and biopolymer material), during diagenesis in the water column, or in pore waters of sediments as dissolved organic matter. It is composed of smaller constituents cross-linked together by covalent bonds into a three-dimensional material. Initially, it is porous, internally and externally charged, and has varying degrees of hydrated surfaces giving rise to hydrophilic (i.e., charged with functional groups having O, N, and S moieties) and hydrophobic regions (i.e., dominated by C and H). It also has a high affinity for complexation with trace elements and sorption to particles (Guo & Santschi, 1997), such as phyllosilicates (Ohashi & Nakazawa, 1996). Once deposited, the chemistry, porosity, and overall activity of macromolecular organic matter become more stable as it equilibrates with the sedimentary and eventually, lithified, environment. On Earth, this environment may be oxidizing and lead to overall degradation and loss of the organic macromolecules, potentially leaving behind the minerals, trace elements, and morphologies associated with the original material. This is commonly the case for subaerial environments. However, organic macromolecules stand a better chance of preservation if they are quickly stabilized in sediments. There are two primary mechanisms for this. One, common in the anoxic marine realm on Earth, is where hydrophilic functional groups of organic macromolecules are effectively 'quenched' and replaced by sulfide during diagenesis. The second mechanism, potentially more important on Mars, is rapid burial and lithification of organic macromolecules. Organic macromolecular sorption to mineral surfaces significantly aids in burial of organic matter (e.g., Bock & Mayer, 2000; Kennedy et al., 2006). On Mars, the environments that may have allowed for this diagenetic complexation between dissolved organic macromolecules and phyllosilicates would thus provide promising sites for organic molecular preservation and detection by MSL. These environments must also be proximal to sources of both phyllosilicates (e.g., weathering regolith or hydrothermal) and organic matter. Therefore, Martian hydrothermal and stable aquatic sedimentary environments may be very favorable for both phyllosilicate and organic matter accumulation (Farmer and Des Marais, 1999).

Assessments of potential carbon accumulation and preservation in sediments and hydrothermal systems

Terrestrial models of organic carbon accumulation and preservation provide predictive capability in respect to these processes in the regolith of Mars. However, due to differences in processes and chemical environments, our estimates of the propensity for early Mars environments to support organic matter formation and preservation are necessarily crude (Table 3). However, our understanding of terrestrial environments makes estimating the possibility of particular observations of potential biomarkers on Mars possible, even if limited. Estimates are thus scaled as high, medium or low. For example, the potential for biosynthesis of organic matter is highest in near-surface hydrothermal systems and in deltaic and lacustrine environments. The potential for hydrodynamic processes to concentrate those organics is ranked as high for the deltaic and perennial lacustrine environments but lower for the surface and subsurface hydrothermal systems as well as for evaporitic environments. Three columns toward the right of the table rank the potential to recognize such environments using remote sensing and criteria that are geomorphic, mineralogical, or stratigraphic, respectively. Finally, the right-hand column makes an assessment of the MSL instrument package's potential to gather data identifying such environments.

The potential for organic matter formation and accumulation on early Mars is assessed as low in the volcanic pyroclastic and flow deposits and moderate in hydrothermal environments (Table 4). Any organic matter that accumulated in such places would stand a moderate chance of being preserved over time. In tables 5 and 6 we evaluate how the MSL payload elements could be used to confirm environmental features specific to processes needed to form, transport, concentrate and preserve organic molecules on early Mars. Only environments identified in Table 1 as having moderate to high potential to support organic carbon formation and preservation that were at moderate or higher are considered for the sedimentary category (i.e., fluvial floodplain, deltaic, lacustrine (perennial), lacustrine (evaporitic). Only hydrothermal (<100℃) subsurface + surface environments are considered for the hydrothermal category.

An assessment of processes essential to the preservation of isotopic abundances in Mars sediments and hydrothermal systems

Interpretation of the stable isotopic compositions of carbon and sulfur in Mars gases, organics and minerals requires a thorough understanding of the environmental context under which the fractionation occurred and the degree to which original features may have been preserved. Such understandings can be gained, to some degree, by using the MSL payload elements as summarized in Table 7 for hydrothermal environments and in Table 8 for sedimentary environments. Interpretations of isotopic data are likely to be complex and prone to significant ambiguity.

Synthesis

The MSL instrument package has the potential to detect biosignatures if they are present at the landing site on Mars. Our understanding of the formation and preservation of biosignatures on Earth can guide our expectations of how and where they might have developed and be preserved on Mars even though the planets have distinct histories. The classes of biosignatures that could be detected and identified on Mars given appropriate biosignature formation and preservation include: diagnostic organic molecules, biogenic gases, body fossils, biofabrics, mineralogy affected by biomineralization and bioalteration, spatial patterns in chemistry due to metabolic processes, and isotopic signatures reflecting metabolic processes.

Diagnostic organic molecules and biogenic gases are the most definitive as biosignatures and are also readily detectable with the SAM instrument. However, they require sequestration from oxidative processes for preservation. Clay minerals promote the preservation of diagnostic organic molecules on Earth, and accumulations of sedimentary clay minerals commonly preserve organic molecules. Thus, using Earth as a model, a MSL landing site in a sedimentary basin containing clay minerals is ideal for maximizing the chances of detecting diagnostic organic molecules. Carbonates and other minerals deposited as a consequence of microbiological activity (microbialites) can also preserve diagnostic organic molecules.

Body fossils and biofabrics can also be definitive biosignatures if they are sufficiently complex and can be observed in context. For detection by MSL, body fossils and biofabrics must be large enough to be observed by MAHLI. Many terrestrial biofabrics are sufficiently large, but body fossils of bacteria are not. Biofabrics are easily preserved in hydrothermal and sedimentary rocks if protected from extensive recrystallization. Thus, detection of biofabrics by MSL is possible if microbial communities developed on Mars and an appropriate landing site is chosen. Low temperature hydrothermal and persistently wet sedimentary environments are most likely to develop and preserve biofabrics.

Biomineralization and bioalteration effects on the spatial patterns in chemistry rarely produce definitive microbial biosignatures due to substantial overlaps in abiotic and biotic processes. However, preserved disequilibrium mineral distributions or variations in chemistry can indicate good sites to look for more definitive biosignatures. CheMin, ChemCam and APX can all help characterize minerals and chemical patterns that have the potential to be biosignatures.

Stable isotopic signatures are commonly used in terrestrial materials to characterize the extent of biological chemical activity. However, such interpretations require a detailed knowledge of the biogeochemical context, including cycles, of the activity. Without that context, stable isotopic signatures rarely provide strong evidence for biological activity. SAM can characterize the isotopic composition of various important materials. If the proper environment is encountered on Mars, we have the potential to identify stable isotopic biosignatures if present. However, definitive biosignature detection would require characterization of co-occurring elemental reservoirs, preferably of carbon and sulfur with different oxidation states. To date, we have not identified such an environment on Mars.

Early Earth is the best analogue we have currently for guiding the search for biosignatures on Mars. Still, we must be constantly aware of the limits of our understanding of terrestrial processes of biosignature formation and preservation, especially as they relate to the Earth's earliest sedimentary record. The MSL is at the heart of the first NASA Astrobiology mission and provides an extraordinary opportunity to learn more about martian environments and processes, particularly in localities that might have been inhabited by microorganisms.

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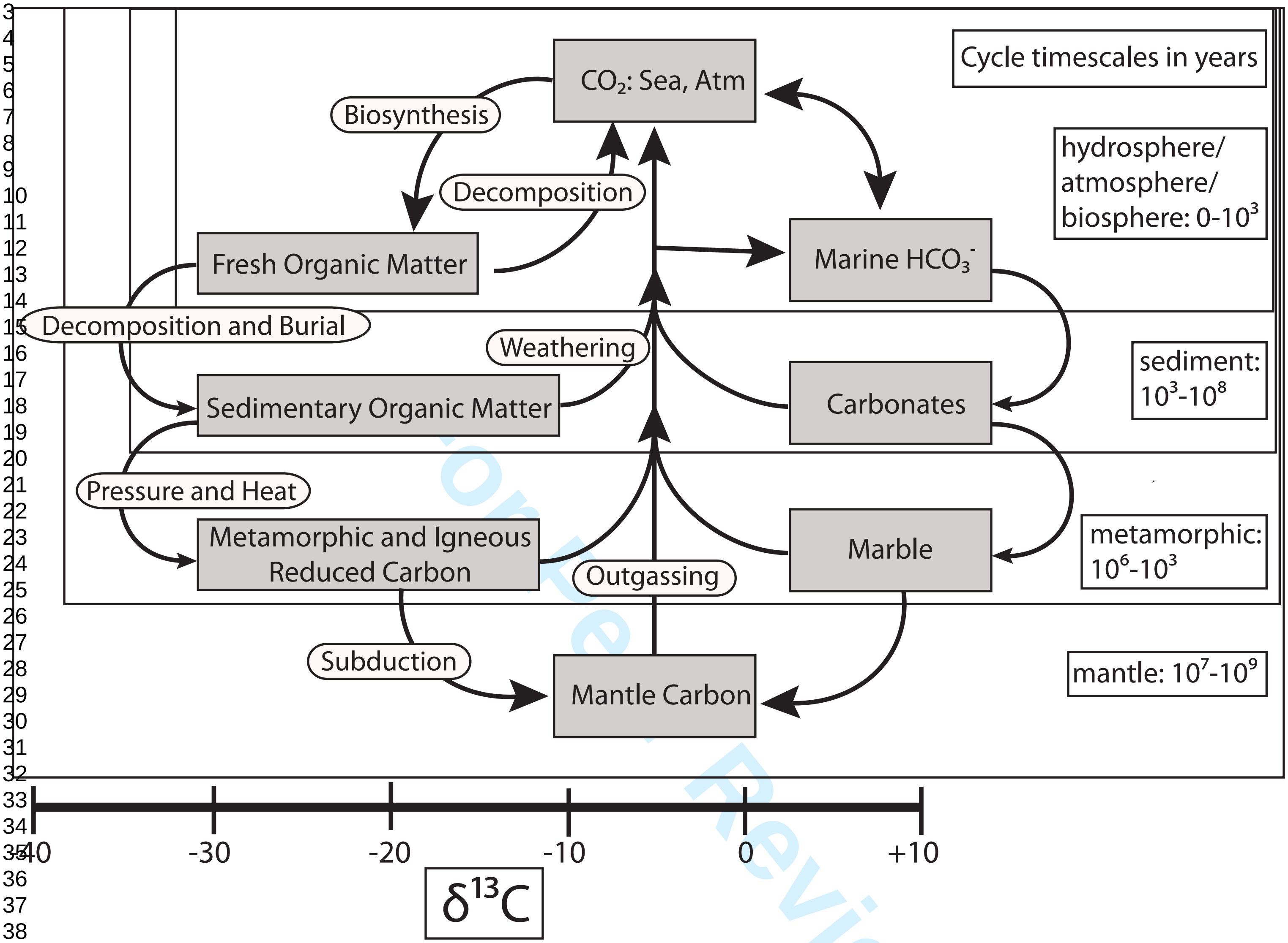
Cycle timescales in years
CO_2: Sea, Atm
Biosynthesis
Decomposition
Fresh Organic Matter
Marine HCO_3^-
hydrosphere/ atmosphere/ biosphere: 0-10^3
Decomposition and Burial
Weathering
Sedimentary Organic Matter
Carbonates
sediment: 10^3-10^8
Pressure and Heat
Metamorphic and Igneous Reduced Carbon
Outgassing
Marble
metamorphic: 10^6-10^3
Subduction
Mantle Carbon
mantle: 10^7-10^9
-40
-30
-20
-10
0
+10
$\delta^{13}C$

Biosignatures detectable by MSL	How definitive as a biosignature?	How well it can be measured by MSL?
biogenic organic molecules	highly definitive	readily with SAM
biogenic gases	often definitive	readily with SAM
body fossils	often definitive	with MAHLI if large enough
biofabrics	sometimes definitive	with MAHLI , MastCam
stable isotopic compositions	occasionally; context critical	readily with SAM
biomineralization/ alteration	rarely definitive	detectible with CheMin, ChemCam
spatial chemical patterns	rarely definitive	detectible with CheMin, ChemCam

Table 1

Biosignatures taphonomic window	Confidence in the geological context	How this informs about potential biosignature preservation
atmospheric gases	very high	predictable via chemical modeling
crystalline sedimentary mineral entrainment of organics	very high	can deduce formation mechanism and subsequent history
biofabric lithification	very high	can deduce history from lithology and stratigraphic relationships
body fossil preservation	very high	can deduce history from lithology and stratigraphic relationships
mineral replacement of body fossil	high	can deduce from mineralogy

Table 2

						ID by remote sensing			
Martian context --> Early Mars Environment	**Support biotic OM formation**	**Support for abiotic OM formation**	**Support OM conc'n**	**Support preservation**	**Potential for recent exhumation***	**Geo-morphic**	**Mineral-ogic**	**Strati-graphic**	**ID by MSL**
Aeolian sediments (sand)	low	low	low	low	low ??	high	n/a	mod	high
altered aeolinites (dust)	very low	low	low	low	low ??	low	n/a	n/a	high
Fluvial channel	low	low	low	low	high	high	n/a	high	high
Fluvial floodplain	low-mod	low	mod	mod	possible ??	high	n/a	high	high
alluvial fan	low	low	low	low	low ??	high	n/a	high	high
Deltaic	high	low	high	high	low ??	high	n/a	high	high
Lacustrine (perennial)	high	low	high	high	high	mod	mod	mod	high
Lacustrine (evaporitic)(Cl)	low	low	high	high-very high	high	mod	high	mod	high
Lacustrine (evaporitic)(SO4)	mod	low	high	high-very high	high	mod	high	mod	high
Regional groundwater pore system	low	low	low	low	high ??	n/a	n/a	n/a	mod
Glacial deposits	low	low	low	low	high	high	n/a	low	high
permafrost	low	low	low	mod	mod	high	n/a	n/a	high
soil (surface fines chemically altered by atmosphere)	low	low	low	low	low	n/a	n/a (albedo and TI)	n/a	high
Regolith/Fractured Bedrock (not soil)	low	low	low	low	low	high	n/a	n/a	high

* Poorly constrained esimates;require improved knowledge of erosional processes and timescales

Table 3

						ID by remote sensing			
Specific cases	**Support biotic OM formation**	**Support for abiotic OM formation**	**Support OM conc'n**	**Support preservation**	**Potential for recent exhumation***	**Geo-morphic**	**Mineral-ogic**	**Strati-graphic**	**ID by MSL**
Pyroclastic Deposits (unaltered)	low	low	low	low	low?	mod	low	high	high
Volcanic flows	very low	low	low	low	low?	high	high	mod	high
aqueous altered at surface	low	low	low	mod-high	low?	low	mod	low	mod
aqueous altered in subsurface	low	low	low	mod-high	low?	low	mod	low	mod
aqueous altered at surface	low	low	low	low-mod	low?	low	mod	low	mod
Volcanics-hydrothermal altered	mod	low	low	mod	mod	mod	mod	low	high
aqueous altered in subsurface	mod	mod	low	low-mod	mod	low	mod	low	mod
Hydrothermal (<100C) subsurface	mod	mod (F/T)	mod-low	mod	mod	mod	mod-high	n/a	high
Hydrothermal (<100C) surface	high	low	mod-high	mod	mod	high	mod-high	low	high
ultramafic subsurface (<100C)	high	low	mod-high	mod	mod	high	mod-high	low	high

* Poorly constrained esimates;require improved knowledge of erosional processes and timescales

Table 4

	Specific Processes	EGA	GCMS	APXS	CheMin	ChemCam	MAHLI
Abiotic Processes	F/T and catalyzed polymerization	X	X	X	X		
Bioprocess	Redox dependent metabolisms (e.g. H2/Fe/S/C - metabolisms)	X	X	X	X	X	
Conc Process	Adsorption to mineral surfaces			X	X	X	
	Immiscibility & migration	X					X
Preservation Process	Adsorption to mineral surfaces			X	X	X	
	mineral encapsulation (trapping)	X				X	X
	thermal polymerization (pyrobitumen formation)	X			X	X	X (UV)

Table 5

	Specific Processes	EGA	GCMS	APXS	CheMin	ChemCam	MAHLI
Abiotic Processes	Cosmic (footnote:specific targets for PE are organic molecules and Cr, Ni anomalies)		X	X	X		
	Atmospheric photolytic synthesis		X	X	X		
Bioprocess	chemosynthesis		X	X	X		
	photosynthesis	X (%TOC)	X	X	X		
Conc Process	sorting of transported organics and organics in/on minerals		X$^{\#}$	X$^{\#}$	X	X	X
Preservation Process	lithification (includes cementation)	X		X	X	X	X
	Adsorption to mineral surfaces			X	X	X	X
	Burial			X	X	X	X
	Co-precipitation (sorption) of mineral/organics	X		X	X	X	X

Table 6

	Specific Processes	EGA-TLS	EGA-QMS	GCMS	APXS	CheMin	ChemCam	MAHLI
Fractionation-Related Processes	impacts (excavation for access deep-carbon sources)	X	X					
	atmospheric processes (e.g. photolysis)	X	X?					
	Biology	X	X?			x		
	hydrologic cycle (over martian history indirectly understood via CO2 record)	X			x	x		
	Global C cycling	X			x	x		
	Global S cycling		X		x	x		
	other biogeochemical cycling	X	X		x	x		
	volcanism	X	X		x	x		
Environmental State	atmospheric composition (past & present), temperature, pressure	X	X					
	water inventories, state, and activity	X	X			x		
	Redox state	X	X		X	x		
	pH	X	X		X	x		
	surface materials (in exchange with atmosphere)	X	X			x		
Preservation Process	lithification (includes cementation)	X	X		X	X	X	X
	Adsorption to mineral surfaces	X			X	X	X	X
	Burial	X			X	X	X	X
	Co-precipitation (sorption) of mineral/organics	X	X		X	X	X	X

Table 7

	Specific Processes	EGA-TLS	EGA-QMS	GCMS	APXS	CheMin	ChemCam	MAHLI
Processes	impacts (excavation for access deep-carbon sources)	X	X					
	cosmic (influx and loss)	X	X					
	weathering	X	X					
	atmospheric processes (e.g. photolysis)	X	X?					
	Biology	X	X?			X		
	hydraulogic cycle (over martian history indirectly understood via CO2 record)	X			X	X		
	C cycling	X			X	X		
	S cycling		X		X	X		
	other biogeochemical cycling	X	X		X	X		
	volcanism	X	X		X	X		
	aeolian (fractionation via oxidation of materials or concentration of materials from particular sources)	X	X			X		
Environmental State	atmospheric composition (past & present), temperature, pressure	X	X					
	water inventories, state, and activity	X	X			X		
	Redox state	X	X		X	X		
	pH	X	X		X	X		
	surface materials (in exchange with atmosphere)	X	X			X		
Preservation Process	lithification (includes cementation)	X	X		X	X	X	X
	Adsorption to mineral surfaces	X			X	X	X	X
	Burial	X			X	X	X	X
	Co-precipitation (sorption) of mineral/organics	X	X		X	X	X	X

Table 8

	Processes	Features	Preservation Window
Physical	Brecciation Fracturing	hydraulic breccia/fractures	Avoidance of strong structural deformation and very high thermal metamorphsm
Chemical	Mineral Precipitation +- Alteration, Dissolution	cement distribution & composition, alteration crusts, porosity, dissolution surfaces, laminations, terraces, mounds	Avoidance of recrystallization & dissolution, increases in oxidation state (e.g. Fe/Mn, perchlorate, sulfate, clay hydration); avoidance of structural deformation and very high thermal metamorphsm
Biological	Biomass Accumulation	"mats, stromatolites, etc; roll-ups, streamers, elemental concentrations, coking	Avoidance of strong structural deformation and very high thermal metamorphsm; coke in fractures

Table 9

	Processes	Features	Preservation Window
Physical	Sediment Transport; Soil/permafrost	grain size, sorting, rounding, composition cross strat laminations, cracks/fracturing soft sediment deposition	dewatering, recrystallization of sulfates, hydration changes; structural deformation and very high thermal metamorphsm
Chemical	Mineral Precipitation +- Alteration, Dissolution	cement distribution and composition alteration crusts porosity dissolution surfaces concretions displacive recrystallization lamination	Avoidance of recrystallization & dissolution, increases in oxidation state (e.g. Fe/Mn, perchlorate, sulfate, clay hydration); avoidance of structural deformation and very high thermal metamorphsm
Biological	Biomass Accumulation	mats, stromatolites, etc roll-ups, wrinkled structures elemental concentrations fenestrae grain size variations	Avoidance of recrystallization, hydration, elemental mobility, organic remineralization; Avoidance of structural deformation and very high thermal metamorphsm

Table 10

Table 11: Chemical and Mineralogic Features of Hydrothermal Environments

Processes		Features	Environmental Indicators	Preservation Window	Payload elements
Environmental	Fluid Convection, selective mineral phase dissolution, alteration, migration, and precipitation; element leaching and transport; Redox chemistry; cooling/heating;	mineral and element zonation/gradients (i.e. characteristic mineralogy associated with variations of hydrothermal environments, such as: chlorite,silica sulfides, kaolinite, hematite, gold, carbonates, sulfates; etc.); spatial distribution of alteration minerals and precipitates; mineral assemblages for redox and temperature*; fracture fills; pH differences; m-km scale mineral zonation		encasement of sensitive phases in less sensitive phases (e.g. silica or organic entombment of minerals); avoidance of oxidation, metamorphism, continued hydrothermal activity	Mastcam, APXS, Chemcam, CheMin, SAM-EGA
Biological	Accelerated redox reactions, organic synthesis, altered mineral assemblages	Altered mineral or elemental abundances, corroded (e.g., bored) minerals, biofabrics, organic matter	Mineral, elemental and textural indicators of aqueous conditions and mineral precipitation	Entombment in minerals formed during cooling or other changes that favor precipitation	MAHLI, APXS, Chemcam, CheMin, SAM-EGA
Physical	Fluid Convection	Hydraulic brecciation; Geomorphic evidence of springs; Overall architecture of system	Heat source	Broad due to large scale	MastCam
	Temperature Changes	Heat flow; Induces variations in chemical properties in time and over spatial scales from m to km	Heat source; Flow patterns	Large scale variations have high preservation potential; small scale changes require avoidance of recrystallization and elemental leaching	Mastcam, MAHLI, ChemCam
Chemical, Potentially Biological	Mineral Precipitation	Evidence of water chemistry & temperature; Springs mounds & terraces; Some mineral precipitation can be localized by organic carbon	Temperature indicators from low T to high T: BaSO4, PbS, ZnS, SO4/Sulfides together, saddle dolomite, CuS, CaSO4; Low pH indicators: jarosite, abundant kaolinite, alunite vs carbonate	Encasement of sensitive phases in less sensitive phases (e.g. silica or organic entombment of minerals); Avoidance of oxidation, metamorphism, continued hydrothermal activity	MastCam, MAHLI, APXS, ChemCam, CheMin, SAM-EGA
	Minieral Alteration & Dissolution	Evidence of changes in water chemistry			
	Elemental Leaching & Transport	m to km-scale spatial gradients in elemental composition			
	Redox Changes	Important redox indicators: S2-, S0, S6+, Fe2+, Fe3+, Mn2+, Mn4+, U2+, U4+, As3+, As5+			

*** Temp mineral assemb.**

mod T	SO4/sulfide together
	saddle dolomite
Low T --> high T	PbS, ZnS, CuS
Low T --> high T	BaSO4--> CaSO4

*** Redox mins**

S2- --> S0-->S6+
Fe2+ --> Fe3+
Mn2+ --> Mn4+
U2+ --> U4+
As3+ --> As5+

*** low pH mins**

jarosite, large kaolinite conc., alunite vs carb.

Important factors	Factor related Feature	Preservation Window	Payload elements
Sediment source	detrital mineral assemblages	Early lithification is favorable. Avoid the following: sediments altered by recrystallization and dissolution (especially evaporites), redox changes toward oxidizing conditions, and strong structural alteration and strong thermal metamorphism	Mastcam, MAHLI, APXS, Chemcam, CheMin, SAM-EGA
H_2O solute chemistry and flux	evaporite assemblages and trace element distribution		
Redox and pH	Redox sensitive (Fe, Mn, S, U, etc.) and pH sensitive (Jarosite, alunite, kaolinite, etc. Vs carbonates) mineral phase and abundance		
bio-mineral interactions	bio-magnetite, bio carbonate, bio-sulfides, oxides, phosphate precipitation; bioleaching and dissolution products		

Table 12