News & Views

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. Key Words: Astrobiology—Atmospheric gases—Mars—Biosignatures—Life detection. Astrobiology 11, xxx–xxx.

Introduction

IN THE FIRST DECADE of the 21st 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 the 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.,*

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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, 2008b). 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) 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, which will allow 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 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 geological environments would be most favorable for preservation of potential biosignatures, including special consideration of organic carbon (Farmer and Des Marais, 1999).

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, multicellular organisms (*e.g.,* plants) that biosynthesized large quantities of recalcitrant biopolymers (*e.g.,* lignin and cellulose) that led 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, which would make 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 accumulate biomass, investigators would also need to 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) that are 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 with which to establish whether life ever existed on Mars is, therefore, to analyze appropriate sedimentary lithologies and seek 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

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 biosignatures (see Tables 1 and 2).

(1) Organism morphologies (cells, body fossils, casts)
     PE: MAHLI
     Minimum size would have to be greater than $100\,\mu$m 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

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(3) Diagnostic organic molecules; organic carbon
     PE: SAM, $\pm$ ChemCam only if very abundant. Detection potential high including 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 and bioalteration
     PE: CheMin, $\pm$ MAHLI, $\pm$ SAM, $\pm$ 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, $\pm$ ChemCam if very abundant
     C, N, S elemental distributions; detection potential on centimeter 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

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 martian 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* (Committee on the Limits of Organic Life in Planetary Systems, 2007) and *An Astrobiological Strategy for the Exploration of Mars* (Committee on an Astrobiology Strategy for the Exploration of Mars, 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 geological 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 at or near the surface (Benner *et al.,* 2000; Navarro-González *et al.,* 2006; Sumner, 2004). 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 and 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.

Site selection decision-making and landed operations of MSL should support the search for all the above-mentioned biosignatures. However, it is also clear that accumulations of organic matter above meteoritic background levels would be among the most easily detected and least ambiguous. If life ever existed on Mars, it was likely microbial and existed communally in fluids or on sediments, either free-living or as biofilms, respectively. 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 evaluat-

ing 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, which 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 have demonstrated 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 and, in many cases, yield critical information regarding the identity of the organism through the presence of characteristic molecular biosignatures. Some common characteristics of molecular biosignatures 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 is amenable to characterization via pyrolysis gas chromatography–mass spectrometry as well and may be distinguished from biologically derived material through specific kinds of molecular distributions (Sephton and Botta, 2008 and references therein).

Aside from MSL's capabilities to provide high-resolution organic molecular information, the addition of Chemistry &

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TABLE 1. A RANKED ORDER OF BIOSIGNATURES THAT COULD BE DETECTED WITH MSL PAYLOAD CONSIDERING BOTH (1) HOW DEFINITIVE THE "BIOSIGNATURE" IS AND (2) HOW WELL IT CAN BE MEASURED. THUS, THE "BEST" BIOSIGNATURES WILL BE BOTH DEFINITIVE AND CONFIDENTLY MEASURED

Biosignatures detectable by MSL	How definitive as a biosignature?	How well can it 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 2. A Ranked Order of Biosignature Taphonomic Windows Including an Evaluation of Our Confidence in the Geological Context and How This Informs about Potential Biosignature Preservation

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

AU1 ▶ Mineralogy (CheMin) and Chemistry & Camera (ChemCam) to the traditional Alpha Particle X-ray Spectrometer (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 may remain and provide evidence consistent with the former presence of organic matter Finally, certain minerals that exist on Earth on a global scale are generally recognized to be the consequence of an active biosphere, for example, biogenic carbonates, hazenite $(KNaMg_2(PO_4)_2 \cdot 14H_2O)$, or brushite $(CaH-PO_4 \cdot 2H_2O)$. Hazen *et al.* (2008) listed and described 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 mineralogical evidence that may indicate the former presence 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 and 4). In this regard, mobility is critical. As the Mars Exploration Rover 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.

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 that extends upward from the rover deck and will be used to study the martian landscape, rocks, and soils; view frost and weather phenomena; and support the driving and sampling operations of the rover.

The Mars Hand Lens Imager 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 cm wide (1.5 in. wide) camera will take color images of features as small as 14 μm and will carry both white light and UV light sources, which make the imager functional both day and night. The UV 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.

The Remote Micro-Imager will provide telescopic views of the surfaces to be analyzed by laser-induced breakdown spectroscopy (LIBS) and will put LIBS analyses into their ◀ AU2 geological context. However, the RMI can also be used to image textures regardless of whether 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.

The Mars Descent Imager will take color video during the rover's descent toward the surface and provide an "astronaut's view" of the local environment. As soon as the rover jettisons its heat shield several kilometers above the surface, MARDI 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, at which time it will store the video data in digital memory and transfer the data to Earth. MARDI will provide information about the larger geological context surrounding the landing site.

ChemCam combines LIBS 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 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 Mars Exploration 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

TABLE 3. SUMMARY OF EARLY MARS SEDIMENTARY ENVIRONMENTS THAT COULD BE ENCOUNTERED BY MSL WITH AN ASSESSMENT OF THEIR POTENTIAL TO SUPPORT ORGANIC MATTER (OM) FORMATION THROUGH BIOTIC AND ABIOTIC PROCESSES, THEIR CAPACITY TO CONCENTRATE AND PRESERVE OM AND OUR ABILITY TO DETECT BY REMOTE SENSING AND MSL

Martian context → early Mars environment	Support biotic OM formation	Support for abiotic OM formation	Support OM concentration	Support preservation	Potential for recent exhumation*	ID by remote sensing			ID by MSL
						Geomorphic	Mineralogical	Stratigraphic	
Eolian sediments (sand)	low	low	low	low	low ??	high	n/a	mod	high
Altered eolinites (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)(SO$_4$)	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

mod, moderate; n/a, not available.
*Poorly constrained estimates; require improved knowledge of erosional processes and timescales.

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TABLE 4. SUMMARY OF EARLY MARS VOLCANIC AND HYDROTHERMAL ENVIRONMENTS, THEIR ABILITY TO SUPPORT SYNTHESIS, CONCENTRATION AND PRESERVATION OF ORGANIC MATTER (OM), AND THEIR DETECTABILITY BY REMOTE SENSING AND THE MSL INSTRUMENT PACKAGE

Specific cases	Support biotic OM formation	Support for abiotic OM formation	Support OM concentration	Support preservation	Potential for recent exhumation*	ID by remote sensing			ID by MSL
						Geomorphic	Mineralogical	Stratigraphic	
Pyroclastic deposits (unaltered)	low	low	low	low	low?	mod	low	high	high
Volcanic flows	very low	low	low	low	low?	high	high	mod	high
Pyroclastics—aqueous altered at surface	low	low	low	mod-high	low?	low	mod	low	mod
Pyroclastics—aqueous altered in subsurface	low	low	low	mod-high	low?	low	mod	low	mod
Volcanic flows—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
Volcanic flows—aqueous altered in subsurface	mod	mod	low	low-mod	mod	low	mod	low	mod
Hydrothermal (<100°C) subsurface	mod	mod (F/T)	mod-low	mod	mod	mod	mod-high	n/a	high
Hydrothermal (<100°C) surface	high	low	mod-high	mod	mod	high	mod-high	low	high
Mafic and ultramafic subsurface (<100°C)	high	low	mod-high	mod	mod	high	mod-high	low	high

Ultramafic serpentinizing systems can support both biotic and abiotic formation of organic matter (McCollom and Seewald, 2006, 2007; Bradley *et al.*, 2009). The potential for long-term organic preservation in subsurface serpentine and hydrothermal systems is presently not well understood although Walter (1996) identifies several promising examples.

mod, moderate; n/a, not available.

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

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 (Cronin and Pizzarello, 1997; Engel and Macko, 1997; Pizzarello; 2006; Glavin and 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, δ^{13}C) of structurally related compounds.
  As above

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soil delivered to it by the Sample Acquisition/Sample Processing and Handling 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, multicomponent evaporite systems, and soils.

The 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 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 assessing the habitability of the planet quantitatively (both past and present) and is essential for future manned Mars missions. The Radiation Assessment Detector will address radiation effects on biological potential and past habitability, as well as the contribution to chemical alteration of the regolith due to impinging space radiation.

AU3 ▶   The Rover Environmental Monitoring Station is designed to record six atmospheric parameters: wind speed/direction, pressure, relative humidity, air temperature, ground temperature, and UV radiation. All sensors are located around three elements: two booms attached to the rover Remote Sensing Mast, the Ultraviolet Sensor assembly located on the rover top deck, and the Instrument Control Unit inside the rover body.

The Dynamic Albedo of Neutrons 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 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 for clearing the surface of rocks prior to sampling. The drill enables powder to be acquired from depths of 20–50 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 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 nonspecific molecular detection by evolved gas analysis (Bibring *et al.,* 2005) to gas chromatographic 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 to 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 that formed the rocks as well as those involved with 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 ChemCam does not directly discriminate between organic and inorganic carbon (Tables 5 and 6). This is in contrast to the SAM capability of detecting sub-part-per-billion levels of organic compounds that are <535 Da via evolved gas analysis (EGA) and pyrolysis.

CheMin in X-ray diffraction (XRD) mode cannot detect organic carbon, but it can detect and identify any crystalline inorganic hosts of carbon and sulfur, for example (Tables 11 and 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 chronological 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.

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 and 8). Figure 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 the range of isotopic values on Earth. This picture has only emerged gradually over many years through extensive study and direct observation of the chemical, biological, isotopic, and geological aspects of carbon cycling (*e.g.,* see Des Marais, 2001).

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 that 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 that 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

TABLE 5. SUMMARY OF HYDROTHERMAL AND DEEP SUBSURFACE ENVIRONMENTS AND PROCESSES NEEDED TO FORM, TRANSPORT, CONCENTRATE, AND PRESERVE ORGANIC MOLECULES ON EARLY MARS AND THE PAYLOAD ELEMENTS THAT CAN BE USED TO CONFIRM ENVIRONMENTAL FEATURES SPECIFIC TO THESE PROCESSES

	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.,* H_2/Fe/S/C metabolisms)	X	X	X	X	X	
Conc process	Adsorption to mineral surfaces			X	X	X	
	Immiscibility and 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)

Only environments with rankings that were at low-mod or higher for "support organic carbon" and "support preservation" from Tables 3 and 4 are considered. Only hydrothermal (<100°C) subsurface + surface environments are considered for the hydrothermal category.

TABLE 6. AS FOR TABLE 5, BUT APPLIED TO SEDIMENTARY ENVIRONMENTS AND PROCESSES

	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

Only fluvial floodplain, deltaic, lacustrine (perennial and evaporitic) environments are considered.
*By measuring carbon abundances, SAM and APXS can address concentration processes.

synthesis involve C-isotopic fractionation, which further complicates 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 organic matter 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; thus

TABLE 7. SUMMARY OF PAYLOAD ELEMENTS THAT CAN BE USED TO CONFIRM ENVIRONMENTAL FEATURES THAT ARE RELEVANT TO INTERPRETATION OF STABLE ISOTOPIC COMPOSITIONS IN HYDROTHERMAL ENVIRONMENTS

	Specific processes	EGA-TLS	EGA-QMS	GCMS	APXS	CheMin	ChemCam	MAHLI
Fractionation-related processes	Impacts (excavation for access to deep-carbon sources)	X	X					
	Atmospheric processes (e.g., photolysis)	X	X?					
	Biology	X	X?			X		
	Hydrologic cycle (over martian history indirectly understood via CO_2 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 and 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. Summary of Payload Elements That Can Be Used to Confirm Environmental Features That Are Relevant to Interpretation of Stable Isotopic Compositions in Sedimentary Environments

	Specific processes	EGA-TLS	EGA-QMS	GCMS	APXS	CheMin	ChemCam	MAHLI
Processes	Impacts (excavation for access to 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		
	Hydrologic cycle (over martian history indirectly understood via CO_2 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		
	Eolian (fractionation via oxidation of materials or concentration of materials from particular sources)	X	X			X		
Environmental state	Atmospheric composition (past and 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

they 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 part-per-billion levels (Formisano *et al.,* 2004, Krasnopolsky *et al.,* 2004; 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- or pyroxene-rich rocks, or both, is a process that was likely prevalent early in Mars' history and, feasibly, continues to the present day (Oze and Sharma, 2005). Multiple carbon and hydrogen isotopic

Table 9. An Assessment of Identifiable Textural Features, and Their Corresponding Preservation Windows, That May Be Encountered in Mars' Hydrothermal Environments

	Processes	Features	Preservation window
Physical	Brecciation fracturing	Hydraulic breccia/fractures	Avoidance of strong structural deformation and very high thermal metamorphism
Chemical	Mineral precipitation ± alteration, dissolution	Cement distribution and composition, alteration crusts, porosity, dissolution surfaces, laminations, terraces, mounds	Avoidance of recrystallization and dissolution, increases in oxidation state (*e.g.,* Fe/Mn, perchlorate, sulfate, clay hydration); avoidance of structural deformation and very high thermal metamorphism
Biological	Biomass accumulation	Mats, stromatolites, etc.; roll-ups, streamers, elemental concentrations, coking	Avoidance of strong structural deformation and very high thermal metamorphism; coke in fractures

Table 10. An Assessment of Identifiable Textural Features, and Their Corresponding Preservation Windows, That May Be Encountered in Mars' Sedimentary Environments

	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 metamorphism
Chemical	Mineral precipitation $\pm$ alteration, dissolution	Cement distribution and composition alteration crusts porosity dissolution surfaces concretions displacive recrystallization lamination	Avoidance of recrystallization and dissolution, increases in oxidation state (*e.g.,* Fe/Mn, perchlorate, sulfate, clay hydration); avoidance of structural deformation and very high thermal metamorphism
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 metamorphism

data suggest that 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 effects provide added complications (Bradley and Summons, 2010). This is the situation on Earth, where the biochemistry of methanogenesis is reasonably well understood; 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 coexisting CO_2 were well in excess of the equilibrium values modeled for feasible pressure-temperature conditions, which thereby implies kinetic (*i.e.,* enzymatic) control on methanogenesis.

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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 postdepositional 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 re-

duction of sulfate and sulfur disproportionation reactions that occur 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, in many cases, be reliably interpreted as biosignatures. 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 understand more fully the consequences of key nonbiological 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-mill 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, which reflects biological cycling of S, a sensitive redox element (Canfield, 2001; Farquhar *et al.,* 2003). If a similar record were to exist on Mars, the sulfur isotopic detection capability of 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 (Greenwood *et al.,* 2000; Rye, 2005) 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 contri-

Table 11. Features Relevant to Biosignature Preservation in Hydrothermal Environments on Early Mars

	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); spatial distribution of alteration minerals and precipitates; mineral assemblages for redox and temperature*; fracture fills; pH differences; m to 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

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TABLE 11. (CONTINUED)

Processes	Features	Environmental indicators	Preservation window	Payload elements
Mineral precipitation	Evidence of water chemistry and temperature; springs, mounds, and terraces; some mineral precipitation can be localized by organic carbon	Temperature indicators from low T to high T: $BaSO_4$, PbS, ZnS, SO_4/sulfides together, saddle dolomite, CuS, $CaSO_4$; 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
Mineral alteration and dissolution Elemental leaching and transport	Evidence of changes in water chemistry m to km scale spatial gradients in elemental composition			
Redox changes	Important redox indicators: S^{2-}, S^0, S^{6+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+}, U^{2+}, U^{4+}, As^{3+}, As^{5+}			
*Temp mineral assemb.	*Redox mins		*Low pH mins	
mod T SO$_4$/sulfide together saddle dolomite	$S^{2-} \rightarrow S^0 \rightarrow S^{6+}$ $Fe^{2+} \rightarrow Fe^{3+}$			
Low $T \rightarrow$ high T Low $T \rightarrow$ high T PbS, ZnS, CuS $BaSO_4 \rightarrow CaSO_4$	$Mn^{2+} \rightarrow Mn^{4+}$ $U^{2+} \rightarrow U^{4+}$ $As^{3+} \rightarrow As^{5+}$		jarosite, large kaolinite conc., alunite vs. carb.	

TABLE 12. SUMMARY OF MINERALOGICAL FEATURES RELEVANT TO BIOSIGNATURE PRESERVATION IN SEDIMENTARY
ENVIRONMENTS ON EARLY MARS

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		
Biomineral interactions	Biomagnetite, biocarbonate, biosulfides, oxides, phosphate precipitation; bioleaching and dissolution products		

butions (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 ($<120°C$). Elevated temperatures have been inferred by using sulfur ($>150°C$) and carbon ($>300°C$) 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.

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 and 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 iso-

late and preserve biosignatures (listed in order of increasing crustal residence times on Earth): ice, halite, sulfates (*e.g.,* Aubrey *et al.,* 2006; Panieri *et al.,* 2010), carbonates (*e.g.,* Birgel *et al.,* 2008), phyllosilicates (*e.g.,* Butterfield, 1990; Hedges and Keil, 1995), silica (*e.g.,* Knoll, 1985), hematite (Fernández-Remolar and Knoll, 2008), and phosphates (*e.g.,* Farmer and Des Marais, 1999; Xiao and Knoll, 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, 1985; Trewin, 1996). In fact, Walter (1996) 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 magnesium sulfates, require low temperatures or substantial humidity, or both, 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
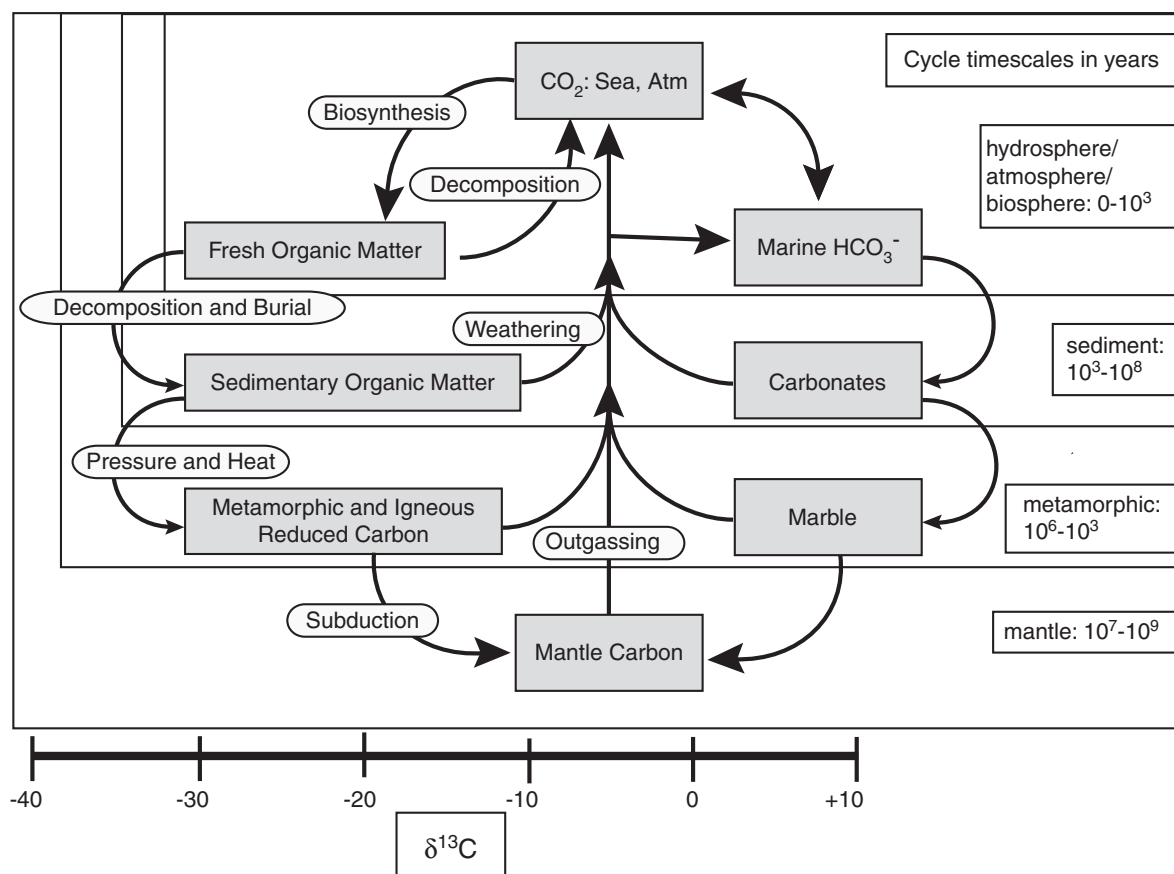
FIG 1. Earth's biogeochemical carbon cycle, showing principal carbon reservoirs (boxes) in the mantle, crust, oceans and atmosphere, and showing the processes (arrows) that unite these reservoirs. The range of each of these reservoir boxes along the horizontal axis gives a visual estimate of typical $\delta^{13}C$ values for each reservoir. The vertical bars at right indicate the timeframes within which C typically completely traverses each of the four subcycles. For example, carbon can traverse the hydrosphere-atmosphere-biosphere subcycle typically in the timescale between 0 and 1000 years. See Des Marais, 2001 for detailed discussion.

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 and 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, for example, types of flows. These can be used to interpret processes in the depositional environment, which would provide invaluable constraints on habitability and guide the search for biosignatures. There are some non-negligible dif-

ferences due to the lower gravity 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.

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 biosignatures, including concentrations of organics and spatial arrangements of minerals that reflect mats, stromatolites, roll-ups, biofilms, streamers, and so on (Tables 9 and 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 organic biomarkers and promote recrystallization. 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, which makes 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).

AU6 ▶ 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 and 12). Biomass accumulation in terrestrial systems is reflected in mats, stromatolites, roll-ups, wrinkle structures, and so on. 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 biosignatures. Thus, for biosignature 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 multifaceted approaches, the role of biology can often be assessed.

If life emerged on Mars and prospered in hydrothermal systems, these alteration processes would likely include biotic and abiotic components (Tables 9 and 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 micrometers to kilometers (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 tem-

peratures, 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 noncrystalline 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 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.

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 organic matter due to strong absorption capacity, low reactivity, and low permeability when compacted (Meyers and Ishiwatari, 1995; Farmer and Des Marais, 1999).

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 is pervasively concentrated at the margins of continents. Only a relatively small percentage of all primary productivity ($\sim 0.1\%$) survives remineralization and becomes preserved in sediments. If life colonized Mars, its global primary productivity would be 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 may have been 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 has its later counterpart. The size distribution of impactors may also have been different. Radiometrically dated samples from the Moon have made it possible to associate an absolute age with a certain crater density. The relation is nonlinear 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 billion years). 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 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 exhumed 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, although 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 hydrologic cycles of Mars and Earth would have affected any potential concentration of 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 has a total organic carbon content that exceeds 1% by weight; it would be expected that such deposits on Mars, should they exist, would have a similar carbon content.

Eolian 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. The production, concentration and preservation of organics, however, 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, that is, 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, which 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, for example, 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 that leads 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 that occur in hydrothermal vents in the oceans, 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 and 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) (Brazelton *et al.,* 2006; Bradley *et al.,* 2009). 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 have shown that Lost City-type vent fluids mixed with seawater are energetically favorable for biomass synthesis (Amend and 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 or isotopic record, or both, of its prior existence (*e.g.,* Kelley *et al.,* 2005; Bradley *et al.,* 2009). ◄AU7

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 that rely 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 SRB in a *ca.* 3 km deep saline aquifer in Archean metabasalt seems to require that the bacteria 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 early Earth. This would have included organic matter delivered by meteorites and interplanetary dust (Smith and Kaplan, 1970; Anders *et al.,*1973; 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 and 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 (Sherwood Lollar *et al.,* 2006; Proskurowski *et al.,* 2008). Hydrogen produced in high concentration by serpentinization chemistry leads to a thermodynamic drive for CO_2 reduction (Shock and Schulte, 1998). Methane and higher hydrocarbons may thus be produced abiotically in ultramafic hydrothermal systems by Fischer-Tropsch–type processes that comprise polymerization reactions leading to methane and higher hydrocarbons (Horita and Berndt, 1999; McCollom and Seewald, 2006, 2007).

Steele and coworkers (2007) 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 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 early Earth and, potentially, on Mars, chondritic meteorites and interplanetary dust particles (IDPs) have delivered abiotic organic matter to the martian surface. Carbonaceous chondritic 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 carbonaceous chondrites (CCs) contain relatively high abundances of small, polar organic molecules, for example, 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 and Alexander 2005) that is by definition insoluble in any solvent and is in many cases 99% of the organic matter in a given chondrite (Sephton, 2002; Sephton *et al.,* 2004; Botta, 2005). 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 OCs 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, which yielded 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, 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 IDPs that, in the case of 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 carbonaceous chondritic IOM, it appears likely that IDPs will be subjected to more degradation than carbonaceous chondritic IOM on the martian surface. Under ideal conditions, however, IDPs could survive on Mars and be detectable via py-

rolysis gas chromatography–mass spectrometry. 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 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 timescales. 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 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 sheetlike 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 and Hare, 1987) and polysaccharides (Dontsova and Bigham, 2005) as well as higher-molecular-weight material (Mayer, 1994a, 1994b; Kennedy *et al.,* 2002). Organic molecules compete with other polar species in the environment (*e.g.,* water, cations) 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 and Keil, 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 in the rock record.

On Earth, most sedimentary and hydrothermal organic matter is macromolecular. In these terrestrial settings, poly-

merization 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 that give 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 and Santschi, 1997), such as phyllosilicates (Ohashi and 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, which would potentially leave 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 and 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 sys-

tems as well as for evaporitic environments. Three columns toward the right of the table rank the potential to recognize such environments by 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 that would identify 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°C) subsurface + surface environments are considered for the hydrothermal category. ◀AU8

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 might 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 that reflect 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, by using Earth as a model, a MSL landing site in a sedimentary basin that contains 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 Earth's earliest sedimentary record. 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.

Abbreviations

APXS, Alpha Particle X-ray Spectrometer; CCs, carbonaceous chondrites; ChemCam, Chemistry & Camera; CheMin, Chemistry & Mineralogy; CHIMRA, Collection and Handling for Interior Martian Rock Analysis; EGA, evolved gas analysis; GC, gas chromatograph; GC-MS, gas chromatograph–mass spectrometer; IDPs, interplanetary dust particles; IOM, insoluble organic matter; LIBS, laser-induced breakdown spectroscopy; MAHLI, Mars Hand Lens Imager; MARDI, Mars Descent Imager; MastCam, Mast Camera; MSL, Mars Science Laboratory; OCs, ordinary chondrites; PADS, Powder Acquisition Drill System; PE, payload elements; QMS, quad-rupole mass spectrometer; RMI, Remote Micro-Imager; SAM, Sample Analysis at Mars; SRB, sulfate-reducing bacteria; TLS, tunable laser spectrometer; XRD, X-ray diffraction.

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