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The Potential Science and Engineering Value of Samples Delivered to Earth by Mars Sample Return

International MSR Objectives and Samples Team (iMOST)

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Executive Summary

Return of samples from the surface of Mars has been a goal of the international Mars sample community for many years. Affirmation by NASA and ESA of the importance of Mars exploration led the agencies to establish the international MSR Objectives and Samples Team (iMOST). The purpose of the team is to re-evaluate and update the sample-related science and engineering <u>objectives</u> of a Mars Sample Return (MSR) programme. The iMOST team has also undertaken to define the <u>measurements</u> and the <u>types of samples</u> that can best address the objectives.

Seven objectives have been defined for MSR, traceable through two decades of previously published international priorities. The first two objectives are further divided into sub-objectives. Within the main part of the report, the importance to science and/or engineering of each objective is described, critical measurements that would address the objectives are specified, and the kinds of samples that would be most likely to carry key information are identified. These seven objectives define a framework for understanding that returned martian samples will establish the basis for future martian exploration. They also have implications for how analogous investigations might be conducted for samples returned by future missions from other solar system bodies, especially those that may harbor biologically relevant or sensitive material, such as Ocean Worlds (Europa, Enceladus, Titan) and others.

Summary of Objectives and Sub-Objectives for MSR identified by iMOST

Objective 1: Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.

Intent: To investigate the geologic environment(s) represented at the M-2020 landing site and provide definitive geologic context for collected samples and detail any characteristics that might relate to past biologic processes.

This objective is divided into five sub-objectives that would apply at different landing sites.

- 1.1. Understand the essential attributes of a martian sedimentary system.
 - Intent: To understand the preserved martian sedimentary record.
 - Samples: A suite of sedimentary rocks that span the range of variation.
 - Importance: Basic inputs into the history of water, climate change, and the possibility of life.
- **1.2.** Understand an ancient martian hydrothermal system through study of its mineralization products and morphological expression.

Intent: To evaluate at least one potentially life-bearing 'habitable' environment Samples: A suite of rocks formed and/or altered by hydrothermal fluids.

Importance: Identification of a potentially habitable geochemical environment with high preservation potential.

1.3. Understand the rocks and minerals representative of a deep subsurface groundwater environment.

Intent: To evaluate definitively the role of water in the subsurface.

- Samples: Suites of rocks/veins representing water/rock interaction in the subsurface. Importance: May constitute the longest-lived habitable environments and a key to the hydrologic cycle.
- **1.4.** Understand water/rock/atmosphere interactions at the martian surface and how they have changed with time.

Intent:To constrain time-variable factors necessary to preserve records of microbial life.Samples:Regolith, paleosols, and evaporites.

Importance: Subaerial near-surface processes could support and preserve microbial life.

1.5. Understand the essential attributes of a martian igneous system.

Intent: To provide definitive characterization of igneous rocks on Mars.

Samples: Diverse suites of ancient igneous rocks.

Importance: Thermochemical record of the planet and nature of the interior.

Objective 2: Assess and interpret the biological potential of Mars.

Intent: To inform our efforts to understand the nature and extent of martian habitability, the conditions and processes that supported or challenged life, the timescales, and how different environments might have influenced the preservation of biosignatures and created nonbiological 'mimics'.

This objective has three sub-objectives:

- **2.1** Assess and characterize carbon, including possible organic and pre-biotic chemistry. Samples: All samples collected as part of Objective 1.
- Importance: Any biologic molecular scaffolding on Mars would likely be carbon-based.
- 2.2 Assay for the presence of biosignatures of past life at sites that hosted habitable environments and could have preserved any biosignatures.

Samples: All samples collected as part of Objective 1.

Importance: Provides the means of discovering ancient life.

2.3 Assess the possibility that any life forms detected are alive, or were recently alive.
 Samples: All samples collected as part of Objective 1.
 Importance: Planetary protection, and arguably the most important scientific discovery possible.

Objective 3: Quantitatively determine the evolutionary timeline of Mars.

- Intent: To provide a radioisotope-based time scale for major events, including magmatic, tectonic, fluvial, and impact events, and the formation of major sedimentary deposits and geomorphological features.
- Samples: Ancient igneous rocks that bound critical stratigraphic intervals or correlate with crater-dated surfaces.

Importance: Quantification of martian geologic history.

- Objective 4: Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system.
 - Intent: To recognize and quantify the major roles that volatiles (in the atmosphere and in the hydrosphere) play in martian geologic and possibly biologic evolution
 - Samples: Current atmospheric gas, ancient atmospheric gas trapped in older rocks, and minerals that equilibrated with the ancient atmosphere.

Importance: Key to understanding climate and environmental evolution.

- Objective 5: Reconstruct the processes that have affected the origin and modification of the interior, including the crust, mantle, core and the evolution of the martian dynamo.
 - Intent: To quantify processes that have shaped the planet's crust and underlying structure, including planetary differentiation, core segregation and state of the magnetic dynamo, and cratering.

Samples: Igneous, potentially magnetized rocks (both igneous and sedimentary) and impact-generated samples.

Importance: Elucidate fundamental processes for comparative planetology.

Objective 6: Understand and quantify the potential martian environmental hazards to future human exploration and the terrestrial biosphere.

Intent:To define and mitigate an array of health risks related to the martian
environment associated with the potential future human exploration of Mars.Samples:Fine-grained dust and regolith samples.

Importance: Key input to planetary protection planning and astronaut health.

Objective 7: Evaluate the type and distribution of *in-situ* resources to support potential future Mars exploration.

Intent: To quantify the potential for obtaining martian resources, including use of martian materials as a source of water for human consumption, fuel production, building fabrication, and agriculture.

Samples: Regolith.

Importance: Production of simulants that will facilitate long-term human presence on Mars.

Summary of iMOST findings

Several specific findings were identified during the iMOST study. Whilst they are not explicit recommendations, we hope that they will act as guidelines for future decision-making regarding planning of future MSR missions.

- 1 The samples to be collected by the Mars-2020 rover will be of sufficient size and quality to address and solve a wide variety of scientific questions.
- 2 Samples, by definition, are a statistical representation of a larger entity. Our ability to interpret the source geologic units and processes by studying sample sub-sets is highly dependent on the quality of the sample context. In the case of the M-2020 samples, the context is expected to be excellent, and at multiple scales: A). Regional and planetary context will be established by the on-going work of the multi-agency fleet of Mars orbiters; B). Local context will be established at field area- to outcrop- to hand sample- to hand lens scale using the instruments carried by M-2020.
- 3 A significant fraction of the value of the MSR sample collection would come from its organization into sample suites, which are small groupings of samples designed to represent key aspects of geologic or geochemical variation.
- 4 If the Mars 2020 rover acquires a scientifically well-chosen set of samples, with sufficient geological diversity, and if those samples were returned to Earth, then major progress can be expected on all seven of the objectives proposed in this study, regardless of the final choice of landing site. The specifics of which parts of Objective 1 could be achieved would be different at each of the final three candidate landing sites, but some combination of critically important progress could be made at any of them.
- 5 The retrieval missions of the MSR Campaign should (1) minimize stray magnetic fields to which the samples will be exposed and carry a magnetic witness plate to record exposure, (2) collect and return atmospheric gas sample(s), and (3) collect additional dust and/or regolith sample mass if possible.

i. Introduction

Return of samples from the surface of Mars has been a goal of the international Mars sample community for many years. Strategies for collection of such samples has ranged from 'grab and go' acquisition from the surface, to dust collection in the atmosphere. As comprehension of the complexity and potential habitability of Mars has increased, so has the realization that a randomlycollected sample, whilst interesting of itself, would not be sufficient to answer questions that could not otherwise be addressed in situ by rover instrumentation. Affirmation by NASA and ESA of the importance of Mars exploration led the agencies to establish the international MSR Objectives and Samples Team (iMOST) in November 2017. The purpose of the team is to re-evaluate and update the sample-related science and engineering objectives of a Mars Sample Return (MSR) programme in the light of current knowledge. The work draws on previous MSR planning efforts, but also considers advances in Mars science made following results from recent space missions (NASA's Curiosity and MAVEN). The data from ESA-Roscosmos' ExoMars Trace Gas Orbiter is eagerly anticipated, but it was not available in time to use in this analysis. The iMOST team has also undertaken to define the measurements and the types of samples that can best address the objectives. It is essential that samples are collected following application of carefully informed selection criteria so that their geological context is maintained and understood. The results of analyses of the collected material will catalyze a definitive understanding of the key systems at work on Mars in terms of its geologic evolution, habitability, and prospects for life.

The first stage required for an MSR campaign is deployment of NASA's Mars 2020 (M-2020) rover. It will collect and cache geological samples for possible eventual return to Earth by a sample-fetch mission, which could also collect atmospheric samples, and an Earth return mission.

Involvement of the international community in these missions would allow the long-prioritized goal of Mars sample return to be met in the following decade. This iMOST study considers the presently-known constraints on sample size and quality that will be imposed by the M-2020 sample acquisition and caching processes. Based on these constraints, we advocate a strategy that would determine the required context of cached samples so that the greatest number of sample science objectives could be achieved. This strategy recognizes the scientific value of suites of related samples, and that no single landing site would include samples that could address all objectives.

i.1. Purpose, and Intended Uses of This Report

In preparing this report, we intend to develop an understanding of the multiple dimensions of the potential scientific value of Mars samples returned to Earth. We convey information in support of the following:

- 1. <u>Planning</u>: The planning processes for the MSR retrieval and transportation missions. We have attempted to update as specifically as possible our understanding of the scientific and engineering value of the M-2020 samples if they were returned to Earth, to emphasize that the value justifies the cost. The Mars 2020 sample-caching rover mission is the first essential component of the Mars Sample Return campaign; its existence constitutes a critical opportunity—MSR is more real now than it has ever been.
- <u>Acquisition</u>: Some of the scientific objectives of MSR require types of sample, or sample suites that are designed in a specific way. Our intent is to convey the relationships between samples and objectives to the science team operating the M-2020 rover, for their use as they plan the operations and select the samples to be collected by this incredibly important asset.
- 3. <u>Return</u>: The M-2020 rover has more sample tubes than can be returned, so it is possible that not all the samples collected will be transported to Earth. If so, some future team associated with the retrieval missions will make decisions about which samples to return. We intend this report to provide rationale for those decisions. We also would like future teams to understand the relationships between samples and scientific objectives.
- 4. <u>Curation and Sample Analysis</u>: Our report is aimed at supporting planning for the curation and laboratory facilities and processes needed to make the measurements associated with achieving the objectives of MSR.

i.2. Perspectives on Mars Sample Return

Scientific exploration of Mars has been, and remains, a key component of the space programs of nations of the world. Of the planets in our solar system, Mars is the most accessible by spacecraft, the most Earth-like in terms of geologic history and environment, and the planet in our solar system perhaps most likely to have hosted an independent origin and evolution of life. The return to Earth of geological and atmospheric samples collected from the martian surface has long been an important goal of Mars exploration. Analysis in terrestrial laboratories of such samples is of extremely high interest to the international Mars exploration community as well as to other scientists and the public.

Although planning for sample return has a very long history, the recent successes of various orbital and landed missions to Mars have enhanced the rationale and renewed the impetus to pursue Mars sample return (MSR). As part of this development, in 2017, the space exploration programs associated with the International Mars Exploration Working Group (IMEWG) began discussion of a formal program of cooperation and collaboration related to MSR. A key programmatic consideration is that NASA is well on its way towards the launch in 2020 of a Mars sample-caching rover. The next crucial question is whether the space-faring nations can form a partnership to fly the missions needed to retrieve the samples, to transport them back to Earth, and

to set in motion the planning processes associated with the curation and study of the samples once they arrive.

i.2.1 This Study

The International MSR Objectives and Samples Team (iMOST) was chartered (Appendix 1) in November 2017 by the International Mars Exploration Working Group (IMEWG). It was established to update the community's planning related to the sample-related objectives of MSR, given what might reasonably be expected to be achieved by samples collected by the M-2020 rover. Included was a request to map out the types of samples that would be desired/required to achieve each of the objectives, and the measurements on the returned samples implied by the objective statements. We recognize that for some objectives, if specific samples are not in the MSR collection, the objective cannot be achieved.

i.2.2 Historical Perception of the Value of MSR

The potential scientific value of samples that could be returned from Mars has been seriously discussed in the literature for four decades, beginning with the National Research Council's Strategy for the Exploration of the Inner Planets (1978). Within the United States, this has then been extended through successor work by the National Research Council (NRC, 1978, 1990a, 1990b, 1994, 1996, 1997, 2003, 2006, 2007a), by MEPAG (McLennan et al., 2012; MEPAG, 2002, 2008, 2010). Two recent, and very influential documents, are the U.S. Decadal Survey report (NRC, 2011), which endorsed the concept of a sample-collecting rover as its highest priority in the flagship class for the decade 2013-2022, and the Mars-2020 Science Definition Team report (J. Mustard et al., 2013), which established the specific scientific foundation for that rover. These latter two documents formed the basis for the development of the Mars-2020 rover, which is designed to collect and cache a high-quality, "returnable" set of martian samples. As of this writing, this mission is well along in its design and build. Within Europe, Mars Sample Return has remained a fundamental and high priority (Horneck et al., 2016). It was envisioned as a part of the European Space Agency's Aurora Programme in the 2025-2030 horizon. The ExoMars mission series is the key legacy of Aurora, and MSR is an important part of ESA's current Exploration Programme. ESA and its partners have sustained interest in studying various elements of a possible MSR campaign, including a Sample Fetch Rover (e.g., Duvet et al., 2018; Picard et al., 2018) and Earth Return Orbiter (e.g., Vijendran et al., 2018). Finally, the International Mars Exploration Working Group (IMEWG) has sponsored several analyses relating to the internationalization of MSR (Beaty et al., 2008; Haltigin et al., 2018; this report).

Although MSR in general has been consistently and strongly endorsed, the specific scientific rationale for returning martian samples has evolved over time as our understandings of Mars have improved. The NRC (1978) report was written on the heels of the very successful *Viking* missions (launched in 1976). Following that, there was a hiatus in Mars mission activity until the missions of the Mars Surveyor Program (Mars Global Surveyor —1996; Mars Pathfinder—1996; Mars Odyssey—2001) and the Mars Exploration Program (Mars Exploration Rovers —2003; Mars Reconnaissance Orbiter —2005; Phoenix—2007; Mars Science Laboratory —2011; MAVEN—2013). During this same period, there was a 10-fold increase in the number of Mars meteorites that were available for study, including new types of sample as well as the relatively young volcanic rocks that still dominate the collection. Coupled to all of this was the rapid growth of the field of astrobiology, catalyzed by McKay et al.'s 1996 announcement of the possible discovery of evidence of ancient life in the martian meteorite ALH 84001. As a result, the scientific value of returned martian samples has shifted from first-order planetary-scale questions such as differentiation, to more specific questions related to understanding martian geologic processes and conditions and determining whether Mars has, or ever did have, life.

As well as increasing understanding of Mars and martian processes, returned samples could also assist in increasing comprehension of Earth's earliest history. The oldest well-preserved (i.e., low-grade metamorphic) rocks in the Earth's crust are the 3.4 Ga rocks of the Pilbara craton in Australia and Barberton craton in South Africa, although older rocks exists (e.g., the 4.0 Ga Acasta gneiss in Canada). Because the age of the Earth is 4.56 Ga, there are more than a billion years of Earth history that is not representatively recorded in its geologic record. Several significant events occurred on Earth during this period, probably including the origin of life. Mars has a beautifully preserved geologic record of a large fraction of this missing time interval. Thus, studying Mars may be our best strategy for understanding the early history of the Earth, and sample studies will play a key role.

i.3. What has changed recently that affects the expected value of the samples?

In general terms, the samples are valuable because they would allow us to achieve certain high-priority scientific objectives. A working list of these objectives was prepared by MEPAG E2EiSAG (McLennan et al., 2012), which did its analysis in 2010-11 (and published its findings in early 2012). Although the E2E objective taxonomy has proved very useful in guiding MSR planning in the intervening years, there have been recent advances on several different fronts that need to be accommodated into a systematic update to these objectives.

i.3.1 Martian meteorites

What has changed from our investigations into this set of samples? The number of Mars meteorites in our collections has now grown to over 100 (from 55 in 2011). Key new specimens include: (1) Northwest Africa (NWA) 7034: the first discovery of a martian breccia with an ancient age and containing clasts with a range of alkaline compositions; (2) Tissint was the first observed fall of a martian meteorite in ~50 years and was recovered before significant contamination; (3) several basaltic meteorites have more diverse ages from the Early Amazonian period of martian history than those already recognised, and new geochemical analyses of all the meteorites have revealed multiple mantle source regions. These meteorites are presumably representative of different regions of Mars.

i.3.2 New mission results from Mars

<u>Spacecraft</u>. The *Curiosity* rover landed on Mars (August 2012) after E2E-iSAG completed its work and has since operated successfully for more than 5 years. It has analyzed many solid samples (both igneous and sedimentary rocks and regolith) from an early Hesperian lacustrine environment, as well as the martian atmosphere. The probability for MSR to find chemical biosignatures has grown stronger with *Curiosity*'s discovery of complex organic molecules; prior to the mission, it was unclear if organic compounds could be preserved in near-surface materials. The *Opportunity* rover has continued to operate far beyond its expected lifetime, for the first time exploring Noachian rocks exposed in a huge impact crater. In addition, scientific output from the wealth of data returned by orbiter missions since 2011, such as NASA's Mars Reconnaissance Orbiter and Mars Odyssey, as well as ESA's Mars Express, has been fundamentally important in shaping and improving our understanding of the martian surface and its history.

<u>Human Exploration</u>. We have an improved understanding of the specific ways in which returned sample studies would reduce the risk of a future human mission to Mars, and the priority of that activity (see MEPAG Goal IV, 2015). The most important study is to determine whether the martian regolith and airfall dust contain biohazards that would unavoidably be ingested by the astronauts—this risk can only be evaluated by MSR.

<u>Astrobiology</u>. We have made significant improvements in our understandings of the potential for the preservation of the signs of life in the geologic record. A key is that we now know that the martian environment has systematically evolved with time on a planetary scale. There were specific times, and specific places during those times, when the potential for habitability was greatly enhanced. Moreover, the study of terrestrial analog systems has given us a better understanding of

the factors that affect preservation of life's signals. Together, these give us a far more effective search strategy.

Instrument developments. There have been substantial improvements in our ability to prepare and analyze very small samples in Earth laboratories. Highly visible examples are the work that has been done on the Hayabusa asteroid samples (JAXA) and Stardust comet samples (NASA). Much instrumentation development around the world continue to add to our arsenal of new techniques and approaches.

<u>Knowledge of the expected nature of the samples</u>. Because of the engineering development work on the M-2020 sampling system, and associated planning work on the retrieval missions, we have now a more advanced understanding of the quantity, size, and physical state of the samples which could be retrieved. These parameters must be considered in evaluating the spectrum of returned sample science that is possible.

i.4. The Mars Sample Return Campaign and Mars-2020

i.4.1 The Mars Sample Return Campaign

The notional MSR architecture consists of three flight missions and one ground element (see Zurbuchen, 2017). The three flight missions would be 1) the M-2020 sample-collecting rover; 2) a retrieval mission that would include a fetch rover and a Mars Ascent Vehicle, and have the capability of lifting the samples from the surface into martian orbit; and 3) A rendezvous mission that could transport the samples from martian orbit to either Earth orbit or the Earth's surface. The ground element on Earth would consist of the facilities and processes needed after the samples arrive at Earth, including at least one Sample Receiving Facility and one or more sample curation facilities.

The design of the sample retrieval architecture has not been finalized as of this writing. However, the nominal design as of 2017 was to return 31 of the M-2020 sample tubes (Edwards, 2017). The intent is that there would also be an opportunity for the retrieval mission to collect 1 to 2 atmospheric gas samples (Edwards, 2017), in containers significantly larger than the rock sample tubes. The scientific value of these gas samples is discussed as part of Objective 4 of this report. The expected size and quality of the rock and regolith samples to be collected by M-2020 are discussed in Appendix 3. Two particular notes: 1). The sampling system has been sized so that the samples are expected to be 10-15 g each for rock samples, and 8 cm³ for regolith samples—this responds to community-sourced recommendations made by E2E-iSAG (2012); 2). The sampling system has been designed to be responsive to a number of sample quality requirements (listed in Appendix 3); These requirements have been carefully constructed by interaction between the science and engineering communities. Although this study did not explicitly re-open and redebate the issues of sample size and quality, we conclude that the sampling system design is responsive to long-articulated science requests.

Finding 1: The samples to be collected by the Mars-2020 rover will be of sufficient size and quality to address and solve a wide variety of scientific questions.

i.4.2 The Importance of Sample Context

The scientific objectives, investigations, and measurements listed below are intended to describe what can be achieved by geological and atmospheric samples returned from Mars. However, as observed by multiple prior works (e.g., McLennan et al., 2012; MEPAG, 2010; Mustard et al., 2013) the value of samples is in part dependent on understanding their context. After all, a sample, by definition, is representative of something larger, and the purpose of sample study is to understand that larger entity, or process, and to answer questions that apply to more than just the sample. In order to use our detailed understanding of a sample effectively, we need to have some understanding of the geology around it. Note that context has multiple scales, from planetary, to regional, to local, and these are relevant in different ways, depending on the scale of the question being answered.

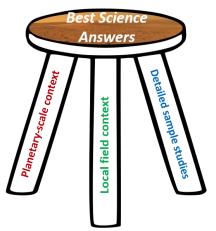


Figure i.1: Our strategy for optimizing our scientific exploration of Mars is based on three legs: 1) Understand planetary-scale context through orbital imaging, 2) Establish local field context through the operation of instrumented rovers and 3) Detailed returned sample studies. All three of these are mutually supportive—we need them all.

<u>Orbital:</u> The geological framework of all past (*Pathfinder, Spirit, Opportunity, Phoenix, Curiosity*) and future (*Insight,* M-2020, *ExoMars*) landed spacecraft was/is made from orbital data. Site analysis also includes a significant component of landing site safety and trafficability following landing, and morphologic and compositional data obtained from orbit are needed to meet operational requirements. Recent community landing site science assessments have been driven by morphologic and mineralogical evidence of aqueous activity. One without the other was considered insufficient justification for further consideration. To achieve the full scientific potential of samples returned from Mars, in-depth analysis of orbital data is required to provide baseline products for analysis and operations. These products include geological maps of the site, high-resolution imaging, digital elevation models, geomorphic maps of terrain texture for rover trafficability and compositional maps of minerals identified from visible through infrared spectral data.

Landed: Local geologic context is of paramount importance in making decisions for sample selection. While orbital data provide the context for selecting a landing site 10s of km² in size, selection of samples requires knowledge of the exact geologic setting at the meter to sub-meter scale. This begins with 3-dimensional surveys of outcrops to determine the stratigraphy of the geologic units followed by assessments of the mineralogy and chemistry of the geologic units. The context mineralogy and chemistry (mm to cm scale) is determined through laser, emission, Raman and infrared remote sensing techniques and fine-scale (micron to mm scale) texture, chemistry and mineralogy with imaging, APXS, X-ray fluorescence, and laser sensors. The combination of orbital context with detailed local morphology, mineralogy and chemistry are the data needed to drive a rover to a positon to use fine-scale morphology, texture and composition sensors. At this point, the pieces are in place to make the critical sampling decisions. It is only with this nested set of quantitative data that the value of the samples can be established.

Synergy: The synergy between orbital data and *in situ* investigations is critically important to generate new insights that have regional and global implications. *In situ* investigations provide more in-depth, ground-truth analysis than orbital investigations, such as detailed mineralogy and chemistry, especially in locations covered by dust, and thus devoid of orbital signatures of minerals. It is the integration of field (planetary, regional, local) data with sample data that is scientifically so powerful. This is being managed in other parts of the general Mars exploration enterprise and is not discussed further in this report.

<u>Synergies with the ExoMars mission</u>: There are many synergies between the Mars 2020 and the European/Russian *ExoMars* 2016/2020 missions (the 2016 *Trace Gas Orbiter* (TGO) and the 2020 lander/rover mission, Vago et al., 2017). In the first place, mapping of trace gas distribution and concentration in time and space around Mars (e.g., Webster at al., 2018) by the TGO will be a critically important input into choosing the timing of collecting the surface gas samples described

above under Objective 4. The planetary-scale surveys of trace gas concentration, especially methane, will establish the context for interpreting the analytic data collected on these samples. More importantly, the data collected by the *ExoMars 2020* rover will play an important role in selecting and optimizing the samples to be collected by M-2020. ExoMars will not have the capacity to cache samples for return to Earth, so there is no scenario in which it can contribute physical samples to MSR. However, this mission will carry an extremely powerful organics detector (the MOMA instrument), and it is expected to generate critical data regarding the variations in organic geochemistry in different kinds of martian materials. ExoMars will also carry an IR spectrometer (micro-Omega) that will generate information about hydrated minerals that will not be possible for M-2020. Finally, *ExoMars* will have the ability to take its own samples down to a depth of 2 m, and thereby to understand the relationship of organic geochemistry and mineralogy to surface oxidative and radiolysis processes. This information, which will be generated at the same time as the M-2020 rover is carrying out its sampling operations at a different landing site, can be key to optimizing the sample selection decisions by the latter. Both M-2020 and the ExoMars rover will be operating in ancient geologic terrane, and by sharing their scientific understandings of the rock-forming and rockmodifying processes in early martian geological history, they will be able to support each other. ExoMars' data on subsurface relationships will be valuable for helping the M-2020 team to benefit from natural geological advantages such as unconformities, differential erosion, scarps, etc. The ExoMars data will establish essential context for interpreting the far more precise data that would come from returned sample analysis.

Finding 2: Samples, by definition, are a statistical representation of a larger entity. Our ability to interpret the source geologic units and processes by studying sample sub-sets is highly dependent on the quality of the sample context. In the case of the M-2020 samples, the context is expected to be excellent, and at multiple scales: A). Regional and planetary context will be established by the on-going work of the multi-agency fleet of Mars orbiters; B). Local context will be established at field area- to outcrop- to hand sample- to hand lens scale using the instruments carried by M-2020.

i.4.3 The Importance of Sample Suites

In order to achieve the full scientific potential of samples returned from Mars, it will be necessary to go far beyond that which can be gleaned from individual, geologically unrelated, samples, which is one of the challenges faced by studying meteorites. Virtually all of the geological settings targeted by the MSR campaign to answer the most important outstanding astrobiological and geological questions are geologically complex. Within such settings, many of the most relevant processes that were operating can only be understood by examining variability among geologically and petrogenetically related samples (i.e., unraveling spatial, compositional, and temporal gradients). For example, in sedimentary settings, interpretations of depositional settings and paleoclimate/climate change rely on evaluating both spatial and temporal (stratigraphic and sedimentological) relationships. In hydrothermal settings, constraining fluid pathways and alteration history (and thus identifying the most habitable niches) requires the mapping of mineralogical and geochemical gradients, often over significant distances. And in volcanic settings, it is often necessary to define liquid lines of decent (associated with fractional crystallization) with multiple petrogenetically related samples to thoroughly evaluate magmatic processes and source characteristics. An individual sample taken from such complex geological settings, while no doubt extremely informative and valuable, would only sample single points in multi-dimensional (spatial, temporal, composition, temperature, etc.) complex systems, and thus would be inadequate for evaluating many of the most important processes.

Accordingly, this analysis is in agreement with other recent studies of the types and numbers of samples that should be returned by a MSR campaign, that concluded that most samples should be

collected as distinct "sample suites" (McLennan et al., 2012; MEPAG, 2008). A "sample suite" can be defined as a set of genetically related samples required to interpret the key geological processes that formed them. The optimum size of such suites is a complex issue that must balance the need for covering likely variability with the reality of limited mission resources. On Earth, it is not uncommon for such sample suites to number in the many dozens to many hundreds. For a MSR campaign, the ND-SAG (MEPAG, 2008) concluded that, for the most important geological settings, sample numbers in the range of 5-8 were about the right balance. In practice, while such sample numbers certainly are reasonable, conditions on the ground – based on both science and resources – will dictate the final number of samples in these suites.

Finding 3: A significant fraction of the value of the MSR sample collection would come from its organization into sample suites, which are small groupings of samples designed to represent key aspects of geologic or geochemical variation.

i.4.4 Attributes of the Candidate Landing Sites

For the M-2020 rover, NASA is currently evaluating three final candidate landing sites (colloquiually known as Columbia Hills, NE Syrtis, and Jezero crater), which have fundamentally different geology from each other. We already know that none of these sites (and no single place on Mars) covers terrane that would generate all of the samples that would be required to address all of the objectives described in this report. However, we also know that there are limits to the use of orbital data in predicting what is on the ground. A good rule of thumb is that if we can see it from orbit, it is there, but if we don't see it from orbit, it does not mean it is absent. Thus, the way to think about this report is that it is the documentation of the samples and measurements needed to achieve the scientific objectives as perfectly as possible (i.e., a wish list). What will be collected by M-2020 will almost certainly be something less than this and will depend on what is physically accessible to the rover, the nature of the discoveries it makes, how the rover's timeline plays out, where within the landing ellipse the rover touches down, and many other factors. However, a case can be made that for the kinds of samples required or desired, it is reasonable to expect that M-2020 will be able to assemble a collection that can be used to achieve at least a part of each of the scientific objectives proposed. Aspects of the scientific objectives not covered by material collected by M-2020 or not returned to Earth in the first MSR will constitute a demand for future MSR.

<u>Columbia Hills</u> (175.6°E 14.5°S) is located within Gusev crater and was previously explored by the Sprit rover during the Mars Exploration Rover mission (Squyres et al., 2004). The Columbia Hills are hypothesized to be a "kipuka" of ancient (likely Noachian or Hesperian) volcanic and/or lacustrine sediments that were embayed by the lava flows that formed the Gusev plains (e.g., McCoy et al., 2008). Within the Hills, *Spirit* discovered nearly pure silica deposits with unique digitate morphologies that have been proposed to be hydrothermal spring deposits (Ruff et al., 2011; Ruff & Farmer, 2016). The Columbia Hills and surrounding basalt plains also contain a geochemically diverse suite of igneous units (McSween et al., 2006) as well as evidence for various types of aqueous alteration, including phyllosilicates (Clark et al., 2007) and an altered tephra unit containing carbonate that could be related to past lacustrine activity (Ruff et al., 2014).

Northeast (NE) Syrtis (77.1°E 17.9°N) is located in the plains on the rim of the Isidis impact basin where erosion has exposed pre-Noachian and Noachian crustal units (Ehlmann et al., 2009). The basement unit contains primitive crust, Isidis megabreccia, large fractures, and is frequently altered to phyllosilicates (Bramble et al., 2017), which together suggests the past presence of habitable deep crustal aqueous environments (e.g., Ehlmann et al., 2011a). A regionally extensive olivine- and carbonate-bearing unit mantles the basement and has been variously hypothesized to have been emplaced as impact melt, ultramafic lavas, tephra, or impact ejecta (Bramble et al., 2017; Kremer et al., 2018; Mustard et al., 2009). The carbonates may have been produced through alteration in a surface or subsurface aqueous environment (e.g., Edwards & Ehlmann, 2015). The sequence is capped by a mafic unit of possible igneous origin (e.g., Bramble et al., 2017).

<u>Jezero</u> (77.5°E 18.4°N) is a 45 km diameter crater just north of NE Syrtis that has been interpreted as a Noachian open-basin paleolake (Goudge et al., 2012). Jezero contains several lacustrine deltas and fans (Goudge et al., 2017, 2018)) fed by a large watershed interpreted to have been active in the late Noachian (Fassett & Head, 2005). The crater rim is composed of the regional altered basement and is partially mantled by the same regional carbonate- and olivine-bearing unit as at NE Syrtis, (Goudge et al., 2015). The stratigraphically lowest unit within the basin is the light toned floor, which is also olivine- and carbonate-bearing (Ehlmann et al., 2008). This unit is overlain by a large delta with diverse alteration mineralogies (Goudge et al., 2017), as well as a mafic capping unit that could be consistent with either volcanic sediments or a lava flow (Goudge et al., 2015; Ruff, 2017). Additional strong carbonate spectral signatures are present along the margin of the crater and may be consistent with lacustrine deposits (Horgan & Anderson, 2018).

Finding 4: If the Mars 2020 rover acquires a scientifically well-chosen set of samples, with sufficient geological diversity, and if those samples were returned to Earth, then major progress can be expected on all seven of the objectives proposed in this study, regardless of the final choice of landing site. The specifics of which parts of Objective 1 could be achieved would be different at each of the final three candidate landing sites, but some combination of critically important progress could be made at any of them.

i.5. The Proposed iMOST Objectives for Mars Sample Return

i.5.1 Introduction

When E2E-iSAG (McLennan et al., 2012) formulated their version of the specific samplerelated objectives of Mars Sample Return, they presented a taxonomy of 8 objectives, along with a ninth objective related to extant life that was book-kept separately (Figure i.2). We carefully considered the E2E-iSAG objectives, and after extensive iteration, we propose that E2E's structure can be rationalized into 7 objectives. The first two of the iMOST objectives are then sub-divided into sub-objectives. Our refined objective structure for Mars Sample Return is compared with that of E2E-iSAG in Figure i.2; Table i.1 shows the full set of iMOST objectives and sub-objectives.

i.5.2 How Does the iMOST Objective Set Represent a Change from Previous Versions?

In summary, we have proposed a simplification of E2E's structure of nine objectives to one with only seven objectives. Primary differences between the objectives proposed by E2E-iSAG (McLennan et al., 2012) and this work, and the reasons why we have made changes, are as follows:

Pre-decisional – For planning and discussion purposes only.

Scientific Objectives for MSR

	From E2E-iSAG (2011) Objective Description (in priority order)			E2E ntecedent or iMOST
A1	Critically assess any evidence for past life or its chemical precursors, and place detailed constraints on the past habitability and the potential for preservation of the signs of life	1	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.	
С1	Quantitatively constrain the age, context and processes of accretion, early differentiation and magmatic and magnetic history of Mars.	2	Assess and interpret the biological potential o Mars.	of A1, A2
B1	Reconstruct the history of surface and near- surface processes involving water.	3	Quantitatively etermine the evolutionary timeline of Mars.	C1
B2	Constrain the magnitude, nature, timing, and origin of past planet-wide climate change.	4	Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system.	B1, B2,
D1	Assess potential environmental hazards to future human exploration.	5	Reconstruct the processes that have affected the origin and modification of the interior, including the crust, mantle, core and the evolution of the martian dynamo.	C1, C2
В3	Assess the history and significance of surface modifying processes, including, but not limited to: impact, photochemical, volcanic, and aeolian.	6	Understand and quantify the potential martia environmental hazards to future human exploration and the terrestrial biosphere.	n D1
C2	Constrain the origin and evolution of the martian atmosphere, accounting for its elemental and isotopic composition with all inert species.	7	Evaluate the type and distribution of <i>in situ</i> resources to support potential future Mars exploration.	D2
D2	Evaluate potential critical resources for future human explorers.			
A2	Determine if the surface and near-surface			

materials contain evidence of extant life

Figure i.2: Comparison of the scientific objectives and priorities for Mars returned sample science as organized by E2E-iSAG and by this work. The primary differences between the two schemes are that (1) for objective #1, the critical sub-objectives of establishing geologic context, evaluating habitability or preservation potential, and assessing biosignatures assemblages have been called out; (2) the content of objectives B1 and B2 which relate to water, have been repackaged into objective #4 on the right; (3) objectives B1, C1 and C2 have been divided

• We conclude that E2E's objective A1 (the life objective) and their objective C2 (the atmosphere objective) overlap with their three B objectives (B1, B2, and B3, all of which relate to water) in a way that is overly complex. The previous three water-related objectives (B1, B2, B3) all related to habitability potential, which is an intimate part of the life objective. In addition, the extant life objective, which E2E noted, but did not formally include because of the implications for planetary protection (PP). However, this should not preclude the fact that science has its own independent reasons for being interested in the possibility of extant life. With regards to the atmospheric objective (C2), it does not make much sense to separate the volatile components of B1, B2, and B3. We find that all of this content this can be described more simply and effectively with two objectives, life and volatiles, that are somewhat more broadly phrased than the E2E originals.

- Missing from the E2E list is an objective related to understanding martian geologic processes at a local scale. This relies on both field data (that will be collected by the M-2020 rover) and on sample data. We know that several of the other objectives are quite dependent on the outcome of these investigations, including the critical life and geochronology objectives. However, in addition to enabling other objectives, this knowledge is important on its own; it is therefore both a means and an end. We have inserted this as Objective #1.
- The E2E objective C1 (Quantitatively constrain the age, context and processes of accretion, early differentiation and magmatic and magnetic history of Mars) combines two different phenomena, albeit they are related topics—geochronology and planetary-scale geologic processes. The samples and context needed to achieve these two objectives are quite different, so we have found it more useful to split C1 into two separate objectives (our new Objectives 3 and 5).
- The two human-related objectives (Objective 6: hazards, and Objective 7: ISRU) are carried forward essentially unchanged from the previous D1 and D2.

As well as the above re-organisation and re-grouping of the objectives, we have dropped the attempt to list them in specific priority order. Although the E2E team presented their objectives in priority order, we found that because there are some key inter-dependencies, sequential prioritization is difficult. For example, organic geochemistry (Sub-Objective 2.1) is one of the six classes of biosignature listed under Sub-Objective 2.2. However, there is more to organic geochemistry than biosignatures; for example, carbon cycling is a general crustal, or even planetary, process that needs to be understood independent of biology. There is no logical way to put 2.1 and 2.2 into a sequential prioritization system, since to some extent they are each subsets of each other.

i.5.3 Structure of this Report

The seven proposed objectives for Mars Sample Return are listed in Table i.1. The following seven chapters discuss each of the objectives (and, for #1 and #2, each of the associated subobjectives) in detail. For each, we have presented an introduction and current state of knowledge, an analysis of key open questions, and discussion of why returned sample analysis is important to addressing these open questions. Each proposed objective has been decomposed into a set of component investigation strategies, and for each of those the samples needed to carry out the strategy are identified, as well as the measurements that would logically need to be made on those samples. Prioritization only exists in these sections where explicitly stated. The Discussion section compiles the diversity of sample types described in the technical sections of the report, and discusses some possibilities for follow-up studies. Appendices include the Terms of Reference for this study, a glossary of key technical terms, a glossary of acronyms, an affiliation table for the authors of this report, and a description of the expected size and quality of the samples to be collected by Mars-2020.

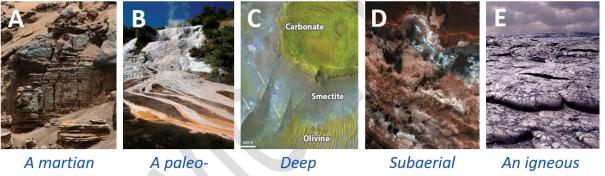
Proposed Objectives				
	Shorthand	Full Statement of Objective		
Objective 1	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record		
Sub-Obj. 1.1	Sedimentary System	Understand the essential attributes of a martian sedimentary system		
Sub-Obj. 1.2	Hydrothermal	Understand an ancient martian hydrothermal system through study of its mineralization products and morphological expression		
Sub-Obj. 1.3	Deep sub- surface groundwater	Understand the rocks and minerals representative of a deep sub- surface groundwater environment		
Sub-Obj. 1.4	Subaerial	Understand water/rock/atmosphere interactions at the martian surface and how they have changed with time		
Sub-Obj. 1.5	Igneous terrane	Understand the essential attributes of a martian igneous system		
Objective 2	Life	Assess and interpret the biological potential of Mars.		
Sub-Obj. 2.1	Carbon chemistry	Assess and characterize carbon, including possible organic and pre- biotic chemistry.		
Sub-Obj. 2.2	Biosignatures- ancient	Assay for the presence of biosignatures of past life at sites that hosted habitable environments and could have preserved any biosignatures.		
Sub-Obj. 2.3	Biosignatures- modern	Assess the possibility that any life forms detected are still alive, or were recently alive.		
Objective 3	Geochronology	Determine the evolutionary timeline of Mars		
Objective 4	Volatiles	Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system.		
Objective 5	Planetary- scale geology	Reconstruct the history of Mars as a planet, elucidating those processes that have affected the origin and modification of the crust, mantle and core.		
Objective 6	Environmental hazards	Understand and quantify the potential martian environmental hazards to future human exploration and the terrestrial biosphere.		
Objective 7ISRUEvaluate the type and distribution of in situ repotential future Mars Exploration		Evaluate the type and distribution of <i>in situ</i> resources to support potential future Mars Exploration		

1 Objective 1: Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.

The geology of Mars encompasses many geological environments that have formed and been modified by a variety of geologic processes over the course of martian geological time. However, 1). These geologic environments are not equally relevant to the high-level primary open questions associated with the current exploration of Mars (MEPAG, 2015; NRC, 2011), and 2). There are no places on Mars where all of these geologic environments exist together. Therefore, it is necessary to prioritize. For the past two decades or so, Mars exploration has been dominated by the life question.

In this context, a key input into which martian geologic environments are most relevant was the workshop "Biosignature Preservation and Detection in Mars Analog Environments" (documented by Hays et al., 2017). That group concluded that on Earth, signs of ancient life are best recorded in five geologic environments: sedimentary systems, hydrothermal systems, rocks that have experienced deep groundwater, environments that have experienced water/rock/atmosphere interaction, and ancient iron-rich springs. The first four of these environments are known to exist on Mars, where they are relatively widespread (see Table 1.1 and Figure 1.1). We are not able to put them in a generic priority order, since they ALL contain evidence of life. This is not to say that we know that Mars life is exactly like Earth life, and we know where to look, but that this gives us a logical strategy to start the search. As part of the landing site selection process for the M-2020 sample-caching rover, all of the sites proposed over the last several years have involved one or more of these four ancient environments. As described above (see Section 2.4.4), as of this writing the M-2020 landing site process has winnowed this down to three final candidate sites. From each it would be possible to sample rocks from at least one (and in many cases, more than one) of these four key geological environments. Clearly, a key priority for returned sample analysis is to understand the ncesses, timing, geochemistry, and biological potential in these four ancient geologic environments on Mars.

In addition, a fifth geologic environment (Table 1.1 and Figure 1.1) is of general interest to MSR—the igneous environment. Igneous rocks constitute probes of a planet's interior and are uniquely amenable to geochronology studies. They have played a crucial role on the Earth, the Moon, and Mars (through meteorite studies) in understanding planetary-scale geologic evolution.



sedimentary system

hydrothermal system

subsurface system

water/rock/ atmosphere interaction

system

Figure 1.1: The five target geologic environments for Objective 1. The five geologic environments of primary interest for Objective 1. Understanding these geologic environments is both an end in itself and a means to understanding the context of the samples for other objectives. A). Parallel, few centimeters thick laminations in fine-grained sedimentary rocks interpreted as lacustrine deposits at Gale crater (Mastcam image, Hidden Valley area, Curiosity rover) B). Hydrothermal discharge with colorful microbial communities distributed in a temperature gradient, and build-up of white siliceous sinter, Orakei Korako geothermal field, New Zealand; C). Carbonated olivine-bearing rock resting on clay-rich Noachian basement crossed by mineralized fractures (white arrows) in Nili Fossae (HiRISE colored by CRISM); D). Layered, phyllosilicate-rich rocks at Mawrth Vallis, Mars; bluer Al-clays overlying Fe/Mg-clays, indicating downward leaching due to surface weathering (HiRISE image); E. Basaltic lava, Hawaii.

Since the strategies for the optimal design of the sample suites, how those samples would be investigated, and the current state of our knowledge are quite different for the different geological environments shown in Figure 1.1, we have chosen to designate them as five sub-objectives within Objective 1 (Table 1.1). It is our expectation that at least one of the first four of these sub-objectives can be achieved using M-2020 samples, in order to make progress towards our life objectives, as

well as at least some progress towards the fifth (igneous) objective. (We assume for planning purposes that it will be impossible to characterize them all at any individual site on Mars.)

Establishing the detailed geologic context of a paleoenvironment specifically involves interpretation of geologic history, determining spatio-temporal relationships of different lithologies, and understanding the physico-chemical conditions of rock formation/modification. The incorporation of field data obtained by the sample-collecting rover is essential.

The samples for MSR would come from one of the three candidate landing sites currently being considered for the M-2020 rover (see Section i.4.4). These three candidate sites each feature at least one, and in some cases more than one, of the high-priority life-related geological environments. In advance of the completion of the M-2020 landing site selection process, it is not possible to know which of these high-priority geological environments will be samplable by the M-2020 rover. However, the landing site selection process is designed to put these candidates in priority order, and regardless of how it comes out, returned sample studies will play a critically important role.

 Table 1.1: Division of Objective 1 into Sub-Objectives.

Objective 1	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record	
Achieve at lea geology	Achieve at least one of the following sub-objectives, and as many more as possible given the local geology		
Sub-Obj. 1.1	Sedimentary System	Understand the essential attributes of a martian sedimentary system	
Sub-Obj. 1.2	Hydrothermal	Understand an ancient martian hydrothermal system through study of its mineralization products and morphological expression	
Sub-Obj. 1.3	Deep sub- surface groundwater	Understand the rocks and minerals representative of a deep sub-surface groundwater environment	
Sub-Obj. 1.4	Subaerial	Understand water/rock/atmosphere interactions at the martian surface and how they have changed with time	
Sub-Obj. 1.5	Igneous terrane	Understand the essential attributes of a martian igneous system	

1.1 Sub-Objective 1.1: Understand the essential attributes of a martian sedimentary system

UNDERSTAND A MARTIAN SEDIMENTARY SYSTEM		
Why is this objective	A key input into interpreting the history of water on	
critical?	Mars; search for life.	
	One or more suites of sedimentary rocks	
Which are the most	representative of the stratigraphic section, different	
important samples?	lithification intensity and style, and coarse-grained	
	rocks with grain diversity.	

1.1.1 Introduction and Current State of Knowledge

Sedimentary systems on Earth and Mars consist of a source, a transport mechanism, a sink, and any post-depositional modification, thus constituting the "source–to–sink" paradigm (e.g., Allen, 2008) in the study of sedimentary rocks (Figure 1.2). While interpreting the geologic record of a sedimentary system, it is important to understand how the above parameters varied in both time and space in order to understand how the surface environment, including the climate, evolved.

A key point in understanding Mars is to unravel the evolution of its climate through time. Lacustrine basins (and marine basins if they ever existed) are especially important repositories of paleoenvironmental and paleoclimatic data (e.g., Renaut & Last, 1994; Smoot & Lowenstein, 1991) mainly because of their relatively continuous stratigraphic records. In lacustrine systems, variables that shape lithologies and facies are basically related to the surrounding environments. Thus, **climates, hydrology, tectonic and ground water history** are all co-existing elements in the formation of chemical authigenic deposits, the shape of the basins, the geometries of sedimentary bodies and internal facies, and so forth. Lacustrine sedimentary basins can provide this wealth of information whether they are hydrologically "closed" or "open". Closed basins are somewhat more sensitive to variations in external influences but even basins with out- and in-flowing rivers retain numerous climate and other proxies.

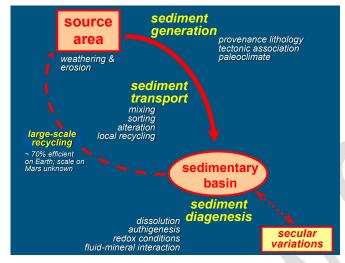


Figure 1.2: Schematic diagram showing "source to sink" history of sedimentary rocks and selected examples of the types of information (white type) that can be obtained from samples. Comparisons of sedimentary rocks of differing age provide constraints on processes such as paleoclimate evolution and crustal evolution. Such approaches are known to be applicable to the martian sedimentary record (Grotzinger et al., 2011; Grotzinger et al., 2013; McLennan & Grotzinger, 2008). Adapted from (Johnsson, 1993 and Weltje & von Eynatten, 2004).

Paleolakes on Mars have been identified through the presence of delta fans in more than 100 locations, predominantly in ancient impact craters and basins(Cabrol et al., 2010; Cabrol & Grin, 1999; Goudge et al., 2012). Most are connected to fluvial valleys at the most distal location of a regional watershed. Delta fans are found in Noachian highlands, where they locally reach 2 km thickness at Terby crater (Ansan et al., 2011), indicating substantial aqueous activity, while more recent, fresh stepped-deltas may have formed by ephemeral ponding (Kraal et al., 2008). The question of an "ocean" in the broader northern plains area has been debated for decades on the basis of geomorphic and topographic analysis of putative shorelines (Parker et al., 1993) and is still unresolved.

Martian lacustrine basins are similar to their terrestrial counterparts and can be dominated by chemical processes or by mechanical sedimentation with high to low sedimentation rates. One important difference is that sedimentation is not matched on Mars with subsidence (e.g., Grotzinger & Milliken, 2012). Sedimentary accommodation on Mars is interpreted to have been largely (if not totally) provided by the water depth; subsidence has been absent or negligible. The consequence is that the stratigraphic record is discontinuous and dominated by erosional processes that create large amount of sediments. Reconstructing the geological history of lacustrine basins is therefore a complicated puzzle where the missing parts may overwhelm the preserved stratigraphy.

While the climate and duration over which paleolakes formed on Mars is a matter of debate, sedimentary deposits on the floors of paleolakes are unambiguous evidence for subaqueous deposits: these are the best locations for organic material preservation (lake basins on Earth bury more carbon per unit time than marine basins; (Kelts, 1988)) and therefore top priority locations for searching for life on Mars. On Earth, modern lakes in Antarctica with frozen cover, as well as hypersaline lakes in more temperate regions, display evidence of stromatolites whose formation is influenced by bacteria (Andersen et al., 2011; Bosak et al., 2013), and deposit organic matter in extreme environmental conditions that could have occurred on Mars. Indeed, organic material

preserved across the full paleo-environmental and depositional spectrum in marine and lacustrine environments on Earth chronicles a detailed genetic history accessible through biomarker analysis (Summons & Hallmann, 2014). This remains an important priority for returned sedimentary samples from Mars.

1.1.2 Key Open Questions for Sub-Objective 1.1

Figure 1.2 essentially provides the roadmap for the major issues that are involved with fully understanding sedimentary systems on Earth. As we gain a more sophisticated understanding of other planetary bodies with atmospheres, including Mars, it is also clear that this same paradigm, at some fundamental level, applies to all such systems (Grotzinger et al., 2013; McLennan & Grotzinger, 2008). Beyond Earth, an overriding additional question is whether or not life ever took hold. Consequently, in characterizing any martian sedimentary system, it will also be crucial to understand how any evidence for life (or its pre-biotic chemistry) would be preserved and characterized. Accordingly, the major outstanding questions to be addressed to understand a martian sedimentary system are summarized In Table 1.2, approximately in order from "source" to "sink" (which is not the same as priority order, which is provided below).

 Table 1.2: Key open questions for Sub-Objective 1.1: Understanding martian sedimentary systems

KEY OPEN QUESTIONS: SUB-OBJECTIVE 1.1

What was the character, diversity, geological history and age of the provenance region for the sediment that accumulated in any given martian depositional basin?

How was sediment generated on Mars and has that changed over geological time?

What was the history, including timing, quantity, and chemistry, of widespread surface and near-surface water on Mars and how is the ancient climate of Mars preserved in the resultant sediments?

What was the nature of water-related sediment transport regimes?

How did the many possible processes of sediment diagenesis on Mars operate?

What is the nature of martian aeolian processes, both in the past and at present?

Do martian sedimentary rocks record the evidence of ancient martian life and/or its pre-biotic chemistry?

1.1.3 Why Returned Sample Studies are Important to Sub-Objective 1.1

Orbiter, lander and rover investigations have provided, and will continue to provide, crucial geological, stratigraphic, sedimentological, mineralogical and geochemical information and context for source–to–sink sedimentary systems on Mars at scales ranging from $\ge 10^3$ km to $\le 100 \ \mu$ m. For example, using imagery at many scales, it has been possible to build stratigraphic/sedimentological models at Gale crater and at Meridiani Planum with remarkable fidelity and confidence and comparable results would be crucial context for any sampling campaign. We also have a large database of *in situ* geochemical analyses at hand sample (i.e., APXS) and sub-mm (i.e., LIBS) scales, and for selected targets we have an impressive array of mineralogical (e.g., mini-TES, Mössbauer, CheMin) and isotopic (SAM) data. Future rovers are very likely to continue to extend and enhance such measurements.

Nevertheless, although many of the critical scientific questions for Mars listed in Table 1.2 can be addressed by these investigations, in many cases they simply do not provide sufficient detail (e.g., detection limits, analytical precision, spatial resolution, etc.) to answer the questions completely. For example, micrometer-scale geochemical and isotopic data have become a routine part of the cutting-edge toolbox for modern sedimentological studies, and, while techniques such as LIBS and PIXL have remarkable cababilities, they simply do not have the spatial resolution or analytical sensitivity available in terrestrial laboratories. Figure 1.3 illustrates the range of measurements required to investigate a clastic sedimentary rock – it is clear that such a comprehensive set of analyses could not be carried out with instrumentation at the martian surface.

Additionally, unexpected results have proven to be ambiguous without the possibility for follow-up investigations that might require different analytical capabilities. For example, the nature of the ubiquitous amorphous component found at Gale crater cannot be resolved with available rover measurements at Mars but could be readily characterized by a variety of modern synchrotron analyses (e.g., Michel et al., 2007). Finally, the ultimate resolution of many of the critical questions listed above may rely on cutting edge analytical methods and associated sample preparation (e.g., electron microscopes, ion microprobes, synchrotrons, laser ablation mass spectrometry, accelerator mass spectrometry) that either cannot be taken to Mars, or would not operate effectively there.

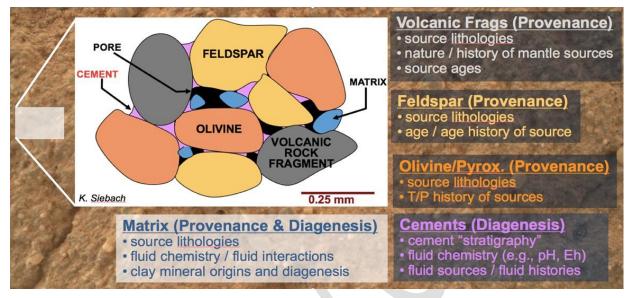


Figure 1.3: Schematic illustration of a microscopic view of a clastic sedimentary rock, illustrating types of information that can be obtained through study of various components (different grains, matrix material, ferent generations of cements) at a microscopic (sub-micron to millimeter) scale (adapted from p://slideplayer.com/slide/8858365/). Many of the analytical methods required to obtain the required mineralogical, textural, structural chemical and isotopic data, such as *in situ* high resolution microbeam techniques (e.g., ion microprobes, LA-MS) and other cutting-edge laboratory instruments (e.g., TIMS, GS-MS, AMS, STEM), must be carried out in Earth-based laboratories.

1.1.4 Sample Investigation Strategies to achieve Sub-Objective 1.1

The scale of sedimentary systems on Mars can be of the order of thousands of km across (e.g., Grotzinger & Milliken, 2012), whereas the scale of rover operations is expected to be of the order of, at most, tens of km. Thus it is not possible with current rover technology to visit and sample all the aspects of a sedimentary system that may be required to understand source-to-sink processes. On the other hand, Walther's Law (that conformable stratigraphic sequences of facies reflect laterally adjacent facies at the time of deposition) provides a very powerful indication that reasonably representative sampling of a sedimentary basin can be obtained at rover scales by sampling across the stratigraphy, as demonstrated at Gale crater (Grotzinger et al., 2015) and Meridiani Planum (Grotzinger et al., 2005).

At a well-chosen site in a martian sedimentary system, it should be possible to obtain appropriate samples to carry out many, if not most, of the proposed investigations required to meet the scientific objectives associated with returned sedimentary samples. Sedimentary systems offer a distinct tactical advantage during rover operations; experiences at Meridiani Planum and Gale Crater have shown that *in situ* data collection permits high-fidelity refinement of working facies models which, in turn, provide a framework to guide hypothesis testing and the prioritization of subsequent analytical (including sampling) targets. Finally, because of their frequent association with water and aqueous processes and their well-preserved nature on Mars, sedimentary systems also provide the highest chance for finding potential traces of life. The investigation strategy hence includes the complete characterization of a sedimentary system at highly different scales of observation, from macroscopic to microscopic, with samples taken from key stratigraphic units that are most appropriate for the investigations described below and that best address the largest number of high priority questions.

We propose six specific investigation strategies and 21 sets of measurements on samples returned from a martian sedimentary system (Table 1.3). The investigation strategies are listed in approximate priority order.

Table 1.3: Summary of sample-related investigation strategies to understand a martian sedimentary system

Investigation Strategies (IS) for Objective 1 Sub-Objective 1.1				
1	-	Interpret in detail the primary geologic processes that formed an modified the pre-Amazonian geologic record.		
1.1 Sedimentary System Understand the essential attributes of a martian sedimentary system				
IS 1.1A	Investigate physical and chemical sedimentary processes in standing or ponded water to understand more completely the occurrence of sustained, widespread liquid surface water on Mars, including the examination of evaporites resulting from such processes.			
IS 1.1B	Investigate sediment diagenesis, including the processes of cementation, dissolution, authigenesis, recrystallization, oxidation/reduction, and fluid-mineral interaction.			
IS 1.1C	Investigate the mechanisms by which sediment is/was generated on Mars, by understanding the weathering and erosional processes.			
IS 1.1D	IS 1.1D Investigate the provenance of the sediment in the sedimentary system, including variation in lithology, tectonic association, and paleoclimate.			
IS 1.1E	Investigate the nature of subaqueous (or subglacial) transport regimes that cut channels and valleys, including whether they were persistent or episodic, the size of discharge, and the climatic conditions and timescales of formation.			
IS 1.1F	1.1F Characterize the physical properties of aeolian materials to understand aspects of surface processes and climate history.			

<u>pestigation Strategy 1.1A</u>: Investigate physical and chemical sedimentary processes in standing or ponded water to understand more completely the occurrence of sustained, widespread liquid surface water on Mars, including the examination of evaporites resulting from such processes.

Although orbital observations have provided a wealth of information that constrains the nature of depositional basins and their sedimentary mineralogy, the reconstruction of the geological history of these basins cannot be performed satisfactorily without the analysis of samples. This is even more compelling in the presence of chemical deposits, such as evaporites, siliceous sediments or carbonates that may originate by precipitation directly from the water column, and therefore record chemical and other paleoenvironmental aspects of their parent waters through time.

Sedimentary deposition in standing or ponded water may chronicle the interface between surface water and groundwater on Mars (e.g., Hurowitz et al., 2010). This, in turn, permits a broader understanding of regional hydrological influences on sedimentation, and thus the spatial and temporal extent of sedimentary episodes driven by liquid water on Mars (Figure 1.4). For example, data collected by the Mars Exploration Rover *Opportunity* support a strong regional hydrological control on sedimentation and diagenesis (e.g., Grotzinger et al., 2005; Hurowitz et al., 2010; McLennan et al., 2005), and the importance of this influence was reinforced at Gale crater by *Curiosity* (Grotzinger et al., 2015; Hurowitz et al., 2017). These data contributed to a new understanding of the nature and extent of groundwater systems on Mars and their response to global climate change (e.g., Andrews-Hanna et al., 2007). In addition, lake basins receiving a significant groundwater influx on Mars (including Gale Crater; Horvath & Andrews-Hanna, 2017) have been recognized on the basis of volume to drainage area ratios (Fassett & Head, 2008), which increases the likelihood that a well-chosen lacustrine sedimentary site may record large-scale hydrological events expressed in multiple sedimentary basins. Moreover, visual observations from a rover can identify discontinuities such as unconformities and erosional surfaces because they are the most compelling expressions of erosional processes. Analysis of samples and identification of erosional events are the tools for the reconstruction of the histories of entire regions of Mars and the identification of large scale, even global, events.

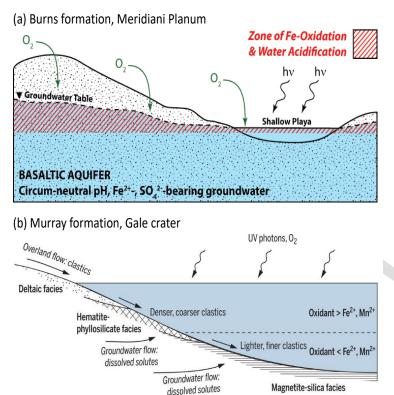


Figure 1.4: (a) Groundwateratmosphere interaction in the Burns formation, Meridiani Planum (Hurowitz et al., 2010). Reduced groundwaters from a basaltic aquifer become oxidized when in contact with the atmosphere near the top of the groundwater table or in ephemeral playa lakes, resulting in low pH aqueous conditions, evidence for which is preserved in diagenetic phases in Burns formation sediments. (b) Redox stratified lake model for mudstones of the Murray formation, Gale crater (Hurowitz et al., 2017). An ancient redox stratified lake in Gale crater is fed by surface flow and groundwater. Evidence for alternating redox conditions is preserved within the sediment mineralogy which changes from a relatively oxidized hematitephyllosilicate (HP) shallow water facies to a relatively reduced magnetite-silica (MS) deeper water facies.

Table 1.4 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1A and move towards understanding of a martian sedimentary system.

Table 1.4: Samples and measurements implied by Investigation Strategy 1.1A

Samples identified to advance Investigation Strategy 1.1A:

• A suite of sedimentary rocks representative of the stratigraphic section

Measurements identified to advance Investigation Strategy 1.1A:

- Provide geologic context by measuring stratigraphy and determining structure.
- Measure mineralogy and chemistry of both clastic and chemical sediments, capturing different stratigraphic positions.
- Perform provenance and geochronology studies of sediments.
- Measure texture, grain size, grain shape of sediments
- Evaluate subsidence and accommodation space as part of understanding basin-scale processes.

<u>Investigation Strategy 1.1B</u>: Investigate sediment diagenesis, including the processes of cementation, dissolution, authigenesis, recrystallization, oxidation/reduction, and fluid-mineral interaction.

Diagenetic processes include all changes in texture by fluid circulation, heat and pressure leading to the cementation of initially loose sediments, as well as any relatively low temperature

post-lithification changes (e.g., veins, concretions, secondary porosity, and pressure solution). These processes are fundamental in our understanding of the initial depositional environments, because early diagenetic processes (i.e., those occurring while diffusional contact with the overlying water column is maintained; or before lithification) reflect those that may be confined to sedimentary pore waters, but may influence the chemical budget of the overlying water column (i.e., microbial metabolic influences in marine or lacustrine sediments on Earth, or redox stratification at Gale Crater; (Hurowitz et al., 2017)). For example, experimental work suggests that authigenic or early diagenetic magnetite formation in Gale Crater mudstones may have been driven by groundwater infiltration into lacustrine sediments which also generated $H_2(g)$ (Tosca et al, in review). This implies that early diagenetic processes may have strongly impacted surface and perhaps atmospheric chemistry on early Mars, while at the same time offering uniquely favorable environments for metabolic processes known to be ancient on the Earth (i.e., methanogenesis *via* the acetyl-CoA pathway, which depends on the presence of H_2 and CO_2 ; (Braakman & Smith, 2012)).

Diagenetic processes also modify initial sedimentary compositions. For instance, many outcrops where clay minerals have been detected by orbital spectrometers are part of sedimentary deposits, but it is often impossible to determine unambiguously if the minerals were formed *in situ* (authigenic) or were transported from eroded ancient crust (allogenic). While this difference is fundamental to understand the conditions under which clay minerals formed, the mineral phases, taken independently, are rarely sufficient to discriminate between the two origins (e.g., Milliken & Bish, 2010). On Earth, microscopic observations of the texture of rocks are used to discriminate between these scenarios by distinguishing clastic grains from cements and authigenic phases.

Diagenetic processes are also important in understanding post-depositional environments and aqueous episodes occurring after sediment burial. At rover scales, veins and concretions observed by both Opportunity and Curiosity have led to fundamental insights into post-depositional environments. The association of authigenic minerals (jarosite) and hematite-rich concretions point towards acidic fluids at Meridiani Planum (e.g., Squyres & Knoll, 2005; Figure 1.5); the conditions may be relatively localized and related to groundwater redox processes (Hurowitz et al., 2010; Figure 1.4a). At Gale Crater, Curiosity identified a variety of phases, such as calcium sulfate veins, Mg-rich concretions, and halos of opaline silica (Figure 1.5b and c) that imply several episodes of fluid circulation that were not recognized from orbital data (e.g., Frydenvang et al., 2017; Nachon et al., 2014). However, rover observations are greatly limited by the size of features and the types of analyses possible. Microscopic observations (down to the sub-micron scale) would enable the determination of relative chronologies of different episodes of diagenesis by the identification of paragenetic sequences of diagenetic features. Stable isotopes on authigenic minerals would help determine conditions (e.g., temperatures, depth) of formation. A wide array of precise radiometric isotope dating of cementing agents or K-rich authigenic components (such as jarosite, goethite and hematite) would be best accomplished in terrestrial laboratories.

Diagenetic processes discussed above would modify the preservation of organic material potentially present in aqueous sediments, either by degrading the textures of microfossils, or replacing their initial composition by authigenic minerals in response to fluid episodes (e.g., Hernández-Sánchez et al., 2014). At the same time, some diagenetic processes may liberate chemicals that promote chemosynthetic pathways for C-fixation, which may in turn promote organic matter production. In either case, laboratory-based microscopic observations would enable a detailed assessment of the rock to determine whether the mineral phases are relevant to diagenetic episodes or formed prior to burial of the sediments. Thus, diagenetic processes are fundamental for making an in-depth assessment of the exobiological potential of a sedimentary rock. Acquiring such samples at various degrees of cementation would enable characterization of the diagenetic processes.

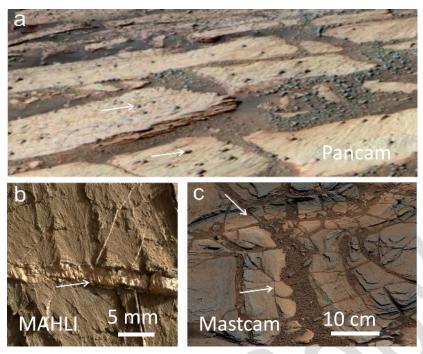


Figure 1.5: Images illustrating diagenetic features observed in sedimentary rocks on Mars that show the action of aqueous fluids and variable physico-chemical conditions (e.g., pH, Eh, temperature) linked to surface and/or subsurface environments. Diagenetic overprints may influence preservation of biological material or pre-biotic chemistry. (a) *Opportunity* Pancam observations of sedimentary rocks in the Burns formation at Meridiani Planum showing 5 mm diameter iron-rich (hematite) concretions (arrows) resulting from fluid circulation during diagenesis. (b) A 5 mm thick light-toned vein (arrow) observed at Gale crater by the MAHLI imager onboard the *Curiosity* rover. It is composed of sulfate minerals such as gypsum and bassanite resulting from precipitation of sulfur-rich fluids inside fractures formed by hydraulic fracturing after rock cementation. (c) Light-toned halo (arrows) observed by *Curiosity* at Gale crater formed around a fracture zone (partly filled by sand). The halo is made of silica predominantly (including opaline silica) and is a result of late-stage diagenesis.

Table 1.5 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1B and move towards understanding of a martian sedimentary system.

 Table 1.5: Samples and Measurements implied by Investigation Strategy 1.1B

Samples identified to advance Investigation Strategy 1.1B:
• A suite of sedimentary rocks showing a range of lithification intensity and style.
Measurements identified to advance Investigation Strategy 1.1B:
Determine the mineralogy of sedimentary rocks and evaluate the possibility of secondary

- Determine the mineralogy of sedimentary rocks and evaluate the possibility of secondary minerals that may have formed as cement in the pore network.
- Determine the paragenetic sequence, including both overgrowth relationships and mineral dissolution events.
- Measure the radiometric ages of the cement with permissible mineralogy (e.g., jarosite, calcite, etc.)
- Determine how diagenetic processes may either enhance or obscure possible taphonomy.

<u>Investigation Strategy 1.1C</u>: Investigate the mechanisms by which sediment is/was generated on Mars, by understanding the weathering and erosional processes (the interrogation of chemical weathering is also discussed further under Investigation Strategy 1.4A).

The initial process in the "source to sink" history of a sedimentary basin (Figure 1.2) is weathering, involving both the physical breakdown and chemical alteration of source rocks, processes occurring simultaneously and in a synergistic manner Johnsson, 1993). Orbital remote

sensing, *in situ* measurements of mineralogy and geochemistry, and experiments (see reviews in Grotzinger et al., 2013; McLennan, 2012; McLennan & Grotzinger, 2008) provide a growing body of evidence that a variety of chemical weathering processes have operated on Mars and that such processes, to the degree that *in situ* rover measurements permit, are recorded in martian sedimentary rocks (e.g., Mangold et al., 2017; McLennan et al., 2014). Chemical weathering involves changes, separation and redistribution of a wide variety of minerals, rock fragments, elements and stable and radiogenic isotopes (e.g., McLennan et al., 1993, 2003; Nesbitt, 2003). In detail, such processes may be very complex and occur within soil profiles in source terrains, during transport of sediment from source to sink, and during short-term episodes of deposition/re-erosion as sediment is transported through the sedimentary system from initial source to final depositional basin. As such, the mineralogical, chemical and isotopic compositions of sedimentary rocks and their constituents, that are influenced by chemical weathering and are deposited at any given time, provide a proxy for the penecontemporaneous climate integrated over the catchment region (e.g., Gislason et al., 2009; West et al., 2005). Accordingly, many stratigraphic profiles provide faithful records of climate change.

Table 1.6 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1C and move towards understanding of a martian sedimentary system.

 Table 1.6: Samples and Measurements implied by Investigation Strategy 1.1C

Samples identified to advance Investigation Strategy 1.1C:

- Rocks of any type that show a range of weathering styles and weathering intensity, including weathering rinds, if present.
- Sedimentary rocks with a variety of grain compositions.
- Modern regolith, especially if locally derived.

Measurements identified to advance Investigation Strategy 1.1C:

- Determine the minerals formed by the weathering process over a range of distinct parent lithologies.
- Determine the mineralogy and mineral chemistry of the sedimentary grains, and their relationship to the parent lithologies.
- Determine the proportion of grains derived from igneous, metamorphic, and sedimentary rocks (and associated geochronology measurements, since there are many weathering minerals that can now be dated, such as hematite, goethite, etc.)

<u>Investigation Strategy 1.1D</u>: Investigate the provenance of the sediment in the sedimentary system, including variation in lithology, tectonic association, and paleoclimate.

A fundamental control on the mineralogical, chemical and isotopic composition of sedimentary rocks is the original composition of igneous-metamorphic-sedimentary source rocks (the sediment provenance). A primary goal of sedimentary petrology is thus to constrain the nature of the provenance (e.g., Garzanti, 2016) and in turn interpret that provenance in terms of the geology (i.e., lithologies) of the hinterland, relationships to tectonic associations, role of sedimentary recycling, relationships to paleoclimate and implications for the ultimate magmatic history (i.e. crustmantle evolution) of the igneous sources (see reviews in McLennan et al., 1993, 2003; Veizer & Mackenzie, 2014). The study of sedimentary provenance has become increasingly sophisticated and bulk rock petrographic, geochemical and isotopic approaches (e.g Bhatia, 1983; Dickinson, 1970; McCulloch & Wasserburg, 1978) have given way to studies where provenance may be evaluated quantitatively, often on a "grain by grain" basis (e.g., Vermeesch, 2004; Figure 1.3). This approach applies a myriad of geochemical and isotopic methods to a variety of individual (typically sand-sized or larger) grain types (e.g., various detrital mineral chemical compositions), including, for example, U-Pb dating of individual zircon (often combined with O-isotope and Lu-Hf isotope characterization of the same grains), monazite, rutile and quartz grains, Pb isotope compositions of individual quartz,

feldspar and hornblende grains, ⁴⁰Ar/³⁹Ar ages of a variety of detrital minerals and so forth (see review in McLennan et al., 2003). Such approaches will be especially important for Mars sample return where bulk sample numbers will be limited, but where individual sand-sized grains within sediments and sedimentary rocks may effectively be treated as separate samples that can be evaluated petrographically, geochemically and isotopically.

Table 1.7 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1D and move towards understanding of a martian sedimentary system.

Table 1.7: Samples and Measurements implied by Investigation Strategy 1.1D

Samples identified to advance Investigation Strategy 1.1D:

• Relatively coarse-grained clastic sedimentary rocks. Most valuable would be rocks for which at least some of the sedimentary grains are multi-mineralic (i.e., small rocks), and which could be studied independently.

Measurements identified to advance Investigation Strategy 1.1D:

- Determine the mineralogy and mineral chemistry of lithic fragments and mono-mineralic grains.
- Determine the crystallization ages of lithic clasts, where possible (e.g., within coarse clasts) using radiometric dating.
- Determine an integrated surface exposure age of the source regions by measuring cosmogenic nuclides.

<u>Investigation Strategy 1.1E</u>: Investigate the nature of subaqueous (or subglacial) transport regimes that cut channels and valleys, including whether they were persistent or episodic, the size of discharge, and the climatic conditions and timescales of formation.

The exobiological potential of a sedimentary landing site depends on its relevance for past aqueous environments in relation with the context of deposition of sediments, and thus to the nature of transport regimes. For instance, high discharge rate channels, such as those found in catastrophic floods, involve highly turbulent flows moving large blocks disfavoring a good preservation of organics. Downstream, in lakebeds, variations of fluvial regimes are accessible through subtle observations, such as small changes in size of grains and laminations (e.g., crossbedding related to more dynamic environments). The Curiosity rover has analyzed locally fluvial conglomerates and sandstones having provided first-order analyses of fluvial sedimentary facies, flow rates and clast composition (Edgar et al., 2018; Mangold et al., 2016; Williams et al., 2013). Microscopic analyses of a series of sedimentary rocks from cross-bedded sandstones (sampling dynamic channels) to mudstones (quiet environment) would enable scientists to determine at enhanced level of detail the sorting effects related to transportation (variations in proportion of minerals due to their hardness, size or shape) and the degree of roundness of grains in order to provide information on distance and time of grain transportation (e.g., Le Roux & Rojas, 2007; McLaren & Bowles, 1985; Whalley, 1978). Facies analysis at microscopic scale can also provide information on the type of conditions during deposition, such as those due to desiccation or frost. For instance, sedimentary deposits in subglacial lakes in Antarctica show specific microstructures that are specific to this surface environment (Andersen et al., 1993; Hendy, 2000, Rivera-Hernandez, submitted).

Table 1.8 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1E and move towards understanding of a martian sedimentary system.

 Table 1.8: Samples and Measurements implied by Investigation Strategy 1.1E

Samples identified to advance Investigation Strategy 1.1E:

• A suite of sedimentary rocks representative of stratigraphy within an ancient stream channel. Measurements identified to advance Investigation Strategy 1.1E:

- Measure mineralogy and chemistry of both clastic and chemical sediments, capturing different stratigraphic positions.
- Perform provenance and geochronology studies of sediments.
- Measure texture, grain size, grain shape of sediments.
- Measure mineralogy and chemistry of both clastic and chemical sediments, capturing different stratigraphic positions.

<u>Investigation Strategy 1.1F</u>: Characterize the physical properties of aeolian materials to understand aspects of the surface processes and climate history

Orbital observations and surface missions demonstrate that aeolian processes have played a dominant role in the development of the martian planetary geomorphic surface and stratigraphic record. For example, recent studies of active dune fields in Gale crater demonstrate both the power and limitations of rover-based studies that are informed by and coordinated with orbital observations. Even within a largely fluvio-lacustrine basin, evidence for aeolian processes is likely to be encountered. For example, evidence for aeolian reworking occurs within the fluvial Shaler outcrops, as documented by the Curiosity rover within Gale crater (Edgar et al., 2018). Within a lacustrine stratigraphic record, the significance of wind-scoured surfaces and aeolian deposits is that these represent hiatuses in subaqueous deposition, and basin-scale examples are paleoenvironmental signals. Within Gale crater, a likely wind-scoured unconformity with tens of meters of relief (Watkins et al., 2016) scours into the lacustrine Murray formation (Grotzinger et al., 2015) and is overlain by the aeolian Stimson formation, thus signaling a major environmental change (Banham et al., 2017). Moreover, aeolian dunes have been interpreted as habitats that may carry a biological signature (Fisk et al., 2013). Aeolian samples may also advance our understanding of the martian volatile budget. For example, in the Bagnold Dune Field sands, H, S and Cl were depleted (probably because of martian dust being physically removed) but C and N-bearing phases are elevated. Whether this is related to organic matter from meteorites, modern products of interaction with the atmosphere or some other cause is not clear with currently available data (e.g., Bridges & Ehlmann, 2018).

Within a predominately lacustrine stratigraphic record, aeolian processes are likely to be manifested as: (1) erosional (deflationary) surfaces, (2) aeolian dry system accumulations, and (3) aeolian wet system accumulations. Even without overlying aeolian deposits, wind-scoured surfaces indicate a hiatus in subaqueous deposition of varying temporal and spatial extent. Where dry system dune strata occur overlying these surfaces, their preservation on Mars requires surface flooding or a rise in the water table. Wet aeolian systems occur where the water table is near the surface, and these are both most likely to occur associated with lacustrine strata and are the most intriguing for a biological signature. On Earth, aeolian wet system deposits typically represent an assemblage of sabkha, sand sheets, adhesion structures, and microbial mats. Examples of microbial mats within aeolian deposits have been identified in the rock record of early Earth (Simpson et al., 2013). The middle and upper units of the Burns formation, as studied by the *Opportunity* rover in Endurance crater, are interpreted as wet aeolian deposits (Grotzinger et al., 2005).

The advantages of a sample over orbital or rover data are many. Aeolian sediments may be derived from the reworking of local deposits or from multiple sources external to the basin, thus mixed provenance signals may be present. Moreover, grain mineralogy may be obscured by dust coatings. Orbital data (e.g., CRISM) is too coarse in resolution to make these fine distinctions, and *in situ* sampling (e.g., LIBS) has a limited compositional range and entire grain populations are not treated. Grain size range cannot be fully resolved from rover images, and it is unclear if dust is

transported as individual grains or as aggregates. Both issues are readily addressed in a laboratory *via* laser or image particle analyzers. Wet aeolian system deposits especially are likely to contain fine grains transported as suspended dust, whereas ripple and dune strata represent the traction (creep and saltation) load. Given an analysis of the full spectrum of grain sizes, the wind energy needed for transport can be derived. Finally, the diagenetic history of aeolian strata may be different from that of associated subaqueous deposits, and grain surface weathering products cannot be measured with current *in situ* bulk analyses. Both aspects are readily addressed in the lab. Modern aeolian sediment and lithified aeolian sedimentary rock in the same area may be widely separated in time, thus representing different environmental conditions, provenance and grain histories. Moreover, the texture (i.e., grain packing, alignment, porosity) of the aeolian deposits and diagenetic history will only be evident in a sedimentary rock. Samples should be collected both from modern aeolian sand on the surface, and from individual stratigraphic horizons where aeolian rock outcrops.

Table 1.9 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.1F and move towards understanding of a martian sedimentary system.

Table 1.9: Samples and Measurements implied by Investigation Strategy 1.1F

Samples identified to advance Investigation Strategy 1.1F:

• Sample of modern aeolian sediment from the surface.

• Sample(s) of lithified aeolian sedimentary rock (at different stratigraphic horizons). Measurements identified to advance Investigation Strategy 1.1F:

- Determine the mineralogy of sand and dust fractions in order to identify source areas.
- Determine the grain-size range, sediment sorting, and sand grain shape in order to reconstruct the wind transport.
- **1.2** Sub-Objective 1.2: Understand an ancient martian hydrothermal system through study of its mineralization products and morphoplogical expression

UNDERSTAND A MARTIAN HYDROTHERMAL SYSTEM		
Why is this objective <i>A key input into interpreting the history of water on</i>		
critical?	Mars; search for life.	
	One or more suites of hydrothermal samples and/or	
Which are the most	altered host rocks representing variations in position,	
important samples?	time, chemistry, and/or mineralogy (e.g., proximal to	
	distal) relative to the hydrothermal vent	

1.2.1 Introduction and Current State of Knowledge

Highly promising locales for exploring the ancient environment of Mars, including prospecting for preserved biosignatures, are places where heat from volcanism or impacts interacted with surface water, including ice, to form hydrothermal systems. Hydrothermal processes are fundamental phenomena that occurred and continue to occur as part of the fabric of the Solar System's evolution, from colliding bodies to water (or ice)-rock interactions within growing planetesimals and nascent planets that have built up their mineral inventories over time (Hazen et al., 2008). Hydrothermal systems link global atmospheric, hydrologic and lithospheric cycles, and create an important habitable environment in surface and shallow subsurface realms, on Earth and likely Mars. Hydrothermal minerals (e.g., jarosite, alunite) are useful for dating such events, and for extracting paleoclimate information and alteration history in these settings (Stoffregen et al., 2000.) They are known on Earth throughout the geological record (~3.5 Ga to present), and they not only host life – including "extreme" life adapted to conditions that may be present elsewhere in the Solar

System – but they also preserve robust mineralogical, textural and compositional evidence of ancient microbial biosignatures (e.g., Farmer, 2000; Konhauser et al., 2003; Trewin et al., 2003; Handley et al., 2008; Westall et al., 2015a; Djokic et al., 2017). Evidence for ancient hydrothermal systems on Mars (Figure 1.6) has been presented from several sites (e.g., Newsom, 1980; Schulze-Makuch et al., 2007; Allen and Oehler, 2008; Gulick, 1998; Rossi et al., 2008; Ehlmann et al., 2009; 2011b; Marzo et al., 2010; Skok et al., 2010; Mangold et al., 2012; Thollot et al., 2012; Osinski et al., 2013; Carrozzo et al., 2017; Michalski et al., 2017; Thomas et al., 2017), including at Gale Crater (Zn-and Ge-enrichment measured by Curiosity rover; Berger et al., 2017), and at two of the three finalist M-2020 candidate landing sites: Columbia Hills (Squyres et al., 2008; Ruff et al., 2011; Ruff & Farmer, 2016), and NE Syrtis Major (Mustard et al., 2007, 2008; Ehlmann & Mustard, 2012; Bramble et al., 2017 and references therein). Some inferred hydrothermal phenomena involved magmatic interactions with glaciers or valley networks (e.g., Ackiss et al., 2016; Bouley et al., 2016). Both early and late diagenetic hydrothermal signatures have been identified (e.g., Yen et al., 2008; Ruff et al., 2017; Berger et al., 2017).

Here we discuss hydrothermalism as related to groundwaters reaching the surface whereas Section 4.4 (Sub-Objective 1.3) deals with accessing the hydrothermal groundwaters.

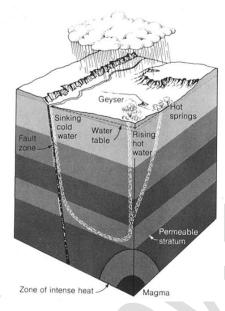


Figure 1.6: Hydrothermal circulation interacting with the lithosphere, atmosphere, hydrosphere and biosphere.

1.2.2 Key Open Questions for Sub-Objective 1.2

Hydrothermal deposits represent a category of an ancient geologic environment long recognized as an important target for astrobiological exploration of Mars (Walter & Des Marais, 1993; Farmer & Des Marais, 1999; Michalski et al., 2017), and now found to be at least locally present in the martian geologic record (Figure 1.6), for example at Columbia Hills (Squyres et al., 2008; Ruff et al., 2011; Ruff & Farmer, 2016). On Earth, hydrothermal environments are inhabited by extremophiles with deep phylogenetic roots in the three-domain "tree of life" (Woese & Fox, 1977; Reysenbach et al., 2001). Critically, all the known hot spring deposits on Earth, extending from the present day back to at least 3.5 billion years of the geological record, contain a variety of preserved biosignatures (e.g., Walter et al., 1996; Guido & Campbell, 2011; Djokic et al., 2017), even at the high temperatures recorded around vents (e.g., ~100 °C of continental hot springs; Campbell et al., 2015a).

Sources of hot water on early Mars would have melted ice, at least locally, by geothermal heat flow, igneous processes (e.g., subsurface magmatic and volcanic) and/or meteorite impacts. The climatic and bombardment history of Mars may have allowed only a short window for evolution and/or punctuated surface habitability (Westall et al., 2015a). If so, then life that may have

developed probably would have been subsurface and/or in subaqueous enclaves within subaerial settings, chemotrophic and anaerobic, as inferred for the early Earth, and potentially associated with hydrothermal systems (e.g., Gogarten-Boekels et al., 1995; Abramov & Mojzsis, 2009; Westall et al., 2015a, b, 2018; Djokic et al., 2017; Michalski et al., 2017). On Earth, hydrothermal environments include subaerial hot spring aprons, mounds and fumaroles, as well as shallow and deep-sea vents (black and white smokers), and subaqueous lacustrine spring-vents and hot-water fluvial systems (Figure 1.6). While not all these Earth-based hydrothermal systems have known direct analogs on Mars (e.g., large volumes of carbonate associated with the Lost City type vents of the mid-Atlantic Ridge), they illustrate a range of conditions and settings in which microbes dominate the base of the food chain at above-ambient temperatures. Most importantly, these are typically mineralizing systems where biological information is captured and preserved by rapid mineral precipitation (e.g., Walter & Des Marais, 1993; Farmer & Des Marais, 1999; Van Dover, 2000; Campbell et al., 2015a, b).

Table 1.10: Key open questions for Sub-Objective 1.2: Understanding martian hydrothermal systems

KEY OPEN QUESTIONS: SUB-OBJECTIVE 1.2

What is the spatiotemporal distribution of hydrothermal events throughout Mars' history, both magmatic and impact related? Has this collectively been geographically extensive enough over long enough intervals to sustain habitable environments with liquid water that were suitable for life?

How have hydrothermal processes affected Mars' climatic, hydrologic and lithospheric domains? In what manner do hydrothermal processes link these features of the planet through time?

Can models for recognition of hydrothermal edifices and deposits on Mars be refined in a nested hierarchy of observations, from orbital to outcrop to sample to micron-scale laboratory analyses?

Would martian hydrothermal processes and products be expected to be similar to or different from those on Earth? For example, sinter like deposits have been identified from Columbia Hills and compared to terrestrial hot spring deposits at El Tatio, Chile (Ruff and Farmer, 2016), while large fractures and extensive fracture-parallel ridge deposits have been found in Magaritifer Terra (Thomas et al., 2017). The latter may have no equivalent on Earth. What do these types of putative hydrothermal settings tell us about Mars' geologic history?

Do the ages of the hydrothermal systems overlap with the water-rich interval of Mars' evolution as a planet?

1.2.3 Why Returned Sample Studies are Important for Sub-Objective 1.2

Much has been learnt of martian hydrothermal systems from orbit, assuming that mineral assemblages produced by such systems on Mars are comparable with those of analogous systems on Earth. Similarly, data from rovers, particularly *Spirit* (Figure 1.7) have given us insight to chemical processes operational in a fossil hydrothermal system. Despite these advances, many questions are still outstanding and can only be addressed by detailed fine-scale analyses using complementary techniques. For example, hydrothermal systems on Earth host microbial communities, but detection of biosignatures in fossilized hydrothermal systems requires multiple lines of evidence taken from high resolution imagery matched with elemental and isotopic data. Even then, identification of ancient biosignatures is not straightforward, and generates much vigorous debate (e.g., Brasier et al., 2002, 2005; Schopf et al., 2002, 2012; Marshall et al., 2011; Nutman et al., 2016; Dodd et al., 2017). Another objective that requires returned samples is the need to determine highly precise ages of different layers or structures within the material. This would enable inferences to be made about the scale and rate of hydrothermal processes – measurements not possible *in situ* on Mars.

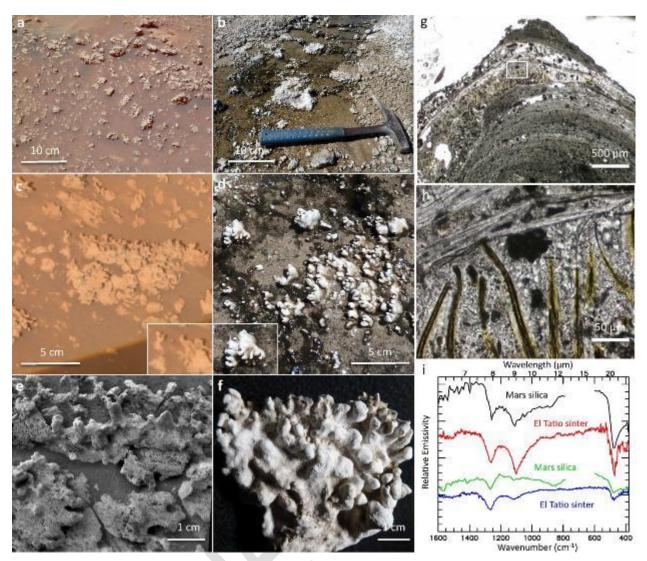


Figure 1.7: Scale-integrated comparison of opaline silica in the Columbia Hills of Gusev Crater, Mars vs. modern hot-spring silica deposits (sinter) produced in outflow channels of El Tatio, Chile. The nodular and digitate expression and distribution of martian silica (a, c, e) is comparable to that of the Chilean silica (b, d, f). Thin-section analysis of Chilean silica (g, h) shows filamentous microbes entombed during formation of digitate structures (microstromatolites). Thermal infrared spectra (i) reveal similarities at the molecular scale between martian and Chilean silica, with spectral variations attributable to the variability of a halite (NaCl) crust; more halite in green and blue spectra, less in black and red spectra. Modified from (Ruff & Farmer, 2016).

1.2.4 Sample Investigation Strategies to achieve Sub-Objective 1.2

The key investigation strategies and samples proposed below are intended to establish the geologic context of at least one martian hydrothermal environment, which will help to constrain past habitability and assess the potential for biosignature capture and preservation (see Objective 2). A key strategic element is to focus sampling from environments that represent the highest potential for delimiting both past habitability and state of preservation (e.g., conditions producing lagerstätte, or exceptional preservation and which protect original biosignatures from post-depositional obliteration by diagenetic and/or environmental processes) (Hays et al., 2017). Hydrothermal environments are advantageous targets because terrestrial examples are replete with biology at all scales and across many types of gradients (Figure 1.8). Their mineralization capability has the potential to shield biosignatures in a robust, *in situ* mineralogic tomb that could be amenable to both detection and long-term preservation. We propose 5 specific investigation strategies and 14 measurements on returned samples from martian hydrothermal deposits.

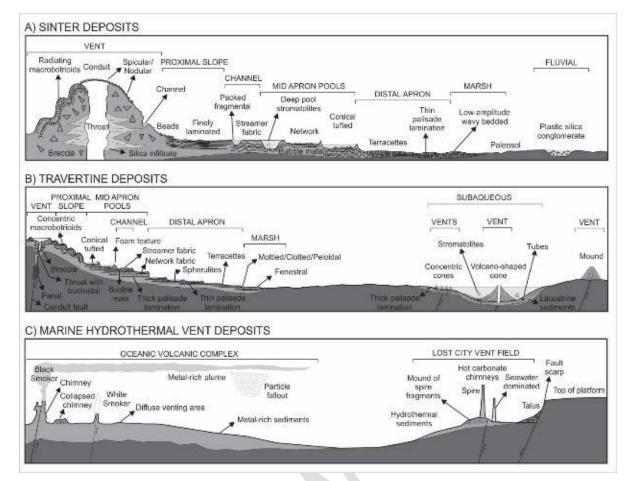


Figure 1.8: Schematic cross-sections of Earth-based, shallow, surface hydrothermal environments. (a) siliceous hot-spring deposits (sinter) of near neutral pH, alkali chloride fluid composition, and (b) calcareous hot-spring deposits (travertine)) (Guido & Campbell, 2011; Renaut & Jones, 2011). Textural biosignature distribution patterns occur along temperature gradients from proximal vent areas (~100 °C) to distal apron/flank settings (~25-30 °C). Marine hydrothermal vents (c) produce even steeper temperature gradients, from ~400 °C at black smoker vent emission points to ambient seawater temperatures short distances away from the vents (Van Dover, 2000).

The search for hydrothermal biosignatures would initiate with rover cataloging of spectral signatures in aqueous-influenced sedimentary rocks/minerals at the site, followed by selection of areas for targeted in situ observations that could produce spatially integrated maps of mineralogy and macro- and microtextures. Mapping the site of aqueous deposits would help test if facies (i.e., environmental) models of Earth's hydrothermal systems provide appropriate analogs for mineralized hydrothermal deposits on Mars. A recent example highlighting this approach is illustrated by study of the hydrothermal opaline silica deposit discovered by Spirit rover in Gusev crater interpreted as fumarole related or near-neutral pH alkali chloride sinter (Squyres et al., 2008). It contains unusual, knobby, digitate structures unlikely to have been formed by wind erosion (Ruff et al., 2018), and which have been inferred as a morphological PBS (Figure 1.7) (Ruff et al., 2011). Comparison with siliceous hot-spring deposits (sinter) at El Tatio geothermal field in Chile reveal close similarities with respect to textures (Figure 1.7 a-h) and mineral spectra (Figure 1.7 i) (Ruff & Farmer, 2016), thereby strengthening the environmental framework and interpretation of the possible biotic nature of the structures. In particular, the knobby silica features at El Tatio constitute microstromatolites, entombing bacterial filaments within spring-derived hydrothermal silica (Figure 1.7 g, h). In analogous features forming in New Zealand hot springs, even the fine siliceous laminae that alternate with similar filamentous horizons to microbially excreted EPS (exopolymeric substance) (Handley et al., 2005, 2008).

We propose five specific investigation strategies and 14 sets of measurements on samples returned from a martian hydrothermal system (Table 1.11).

Table 1.11: Summary of sample-related investigation strategies to understand an ancient martian
hydrothermal system.

Investigation Strategies (IS) for Objective 1 Sub-Objective 1.2		
.3	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.
1.2	Hydrothermal	Understand an ancient martian hydrothermal system through study of its mineralization products and morphological expression.
IS 1.2A	Identify hydrothermal facies that reflect primary differences in deposit formation temperature, due to cooling and degassing of fluid discharge along a gradient with respect to proximity to the vent source.	
IS 1.2B	 Reconstruct the character of the fluids of the paleo-hydrothermal system. Determine the primary environmental and geochemical parameters at the time the system was active. 	
IS 1.2C	Reconstruct how the depositional system changed over time, and as a function of position within the system.	
IS 1.2D	2D Determine the age of the hydrothermal system, and the duration and rate of water flow.	
IS 1.2E	Investigate the po processes.	ssibility of post-depositional modification/fluids, and interpret those

<u>Investigation Strategy 1.2A</u>: Identify hydrothermal facies that reflect primary differences in deposit formation temperature, due to cooling and degassing of fluid discharge along a gradient with respect to proximity to the vent source.

Terrestrial hydrothermal systems facies models (e.g., Figure 1.7) predict locales along temperature gradients from vent-to-peripheral hydrothermally influenced areas where signs of life are concentrated. Therefore, sampling along such gradients may be selective and targeted to maximize potential to locate potential biosignatures within a clear paleoenvironmental framework. In particular, microbial life adapted to terrestrial hydrothermal environments is limited by an optimum maximum growth temperature of 80 °C (Madigan & Martino, 2006), with survival at up to 122 °C (Takai et al., 2008). In continental hot springs, for example, ideal sites for sample collection would be in the middle to low temperature apron suites (~55 - 25 °C) of hydrothermal materials (Figure 1.8 a). Not only are the mineralized microbial deposits thickest there, but the microorganisms tend to become entombed more rapidly and completely, especially if mineralization was early in diagenesis (e.g., Campbell et al., 2015a, b and references therein). In fact, the Columbia Hills silica features are interpreted to have formed in this type of setting, in inferred-Noachian age, hot-spring discharge channels morphologically and mineralogically similar to high-elevation, saline, low-flow hot springs at El Tatio geothermal field, Chile (Ruff et al., 2011; Ruff & Farmer, 2016). Furthermore, shallow subsurface, lateral zones (i.e. within sediments infused with percolating hydrothermal fluids; Rasmussen, 2000; Westall et al., 2015a, 2018) could be important additional sampling targets. Thus, we may expect to see systematic trends in deposit thickness (as mounds and lateral thinning of beds away from vent point sources) and textural types, and/or systematic shifts in isotopic fractionation patterns in values for oxygen and silicon isotopes, and/or downslope changes in mineralogy, etc. Thus, returned samples would ideally – and as a priority – include suites that represent temperature gradients away from spring-vent sources (Figure 1.8), particularly in mid- to distal apron settings at moderate to tepid thermal fluid temperatures (~60-30 °C in Earth siliceous hot spring (sinter) analogs), where microbial mat development is also most prominent. Thus, target sample suites could be focused on this portion of a given paleo-hydrothermal deposit.

Table 1.12 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.2A and move towards understanding of a martian hydrothermal system.

 Table 1.12: Samples and measurements implied by Investigation Strategy 1.2A

Samples identified to advance Investigation Strategy 1.2A:

- A suite of hydrothermal samples and/or altered host rocks representing decreasing paleotemperature with distance (e.g., proximal to distal) from the hydrothermal vent. *Measurements identified to advance Investigation Strategy 1.2A:*
- Identify spatial and temporal variability in the mineralogy, chemistry, texture, grain size and grain shape of each defined facies formed, or modified, by hydrothermal activity. This will delineate the extent of the hydrothermal footprint in time and space.
- Measure the stable isotopic compositions of oxygen and silicon in primary rocks and minerals to look for systematic trends with respect to facies and minerals that may reflect thermal gradients.
- Raman spectroscopy/mapping of rock sample surfaces, which can be used for paleotemperature estimates.
- SEM/EMPA for detailed examination of mineral fabrics and compositions to evaluate consistency with low-temperature hydrothermal conditions at the martian surface.

<u>Investigation Strategy 1.2B</u>: Reconstruct the character of the fluids of the paleo-hydrothermal system. Determine the primary environmental and geochemical parameters at the time the system was active.

The often-changing nature of hydrothermal fluids in terrestrial environments reflects regional magmatic-crustal-hydrologic interactions and climate (e.g., Guido & Campbell, 2014; Sillitoe, 2015). Subsurface hydrothermal fluids feeding surface geothermal manifestations range from near-neutral alkali chloride waters tapping deep hot (>175°C) reservoirs of circulating heated groundwaters, to acidic steam condensates dissolved in groundwaters, to mixed acid-sulfate-chloride and bicarbonate fluids (Figure 1.9; Renaut & Jones, 2011). Commonly in Earth-analog hydrothermal paleoenvironments, textural variation in lithologies, along with particular mineral distributions, provide an important framework for identifying environmental parameters controlling microbial community composition and biogeochemical activity. Specifically, returned samples will allow a detailed assessment of microscale habitability based on contemporaneous evidence for 1) primary aqueous mineralogy, 2) rapid mineral precipitation, and 3) pervasive early cementation by a stable mineral phase. In terrestrial hot springs, fluid compositional and pH variations (e.g., alkali chloride, acid sulfate, bicarbonate, iron, acid-sulfate-chloride, hydrogen sulfide) can be extreme over short distances, providing important redox-potential gradients across which biogeochemical cycles operate (Van Dover, 2000; Jones & Renaut, 2012).

Thus, important biologically-relevant information on variable fluids of the hydrothermal system could be identified in the returned sample suite, potentially collected within a small area amenable to mission engineering parameters and objectives. A relevant returned sample suite could help constrain the stability and paragenesis of bioessential elements to determine if it would be reasonable for them to have existed in that environment at the time of deposition, whether their concentrations are significantly above average, and if associated minerals preserve evidence of biogeochemical cycling. The measurement of stable isotopic compositions (e.g., of C, H, N, O, S) in organic compounds or minerals in context with known isotopic pools enables the search for signatures that are inconsistent with abiotic processes. Stable isotope measurements should be coupled to distribution within samples (e.g., mapping in polished sections) at millimetric to nanoscale.

Pre-decisional – For planning and discussion purposes only.

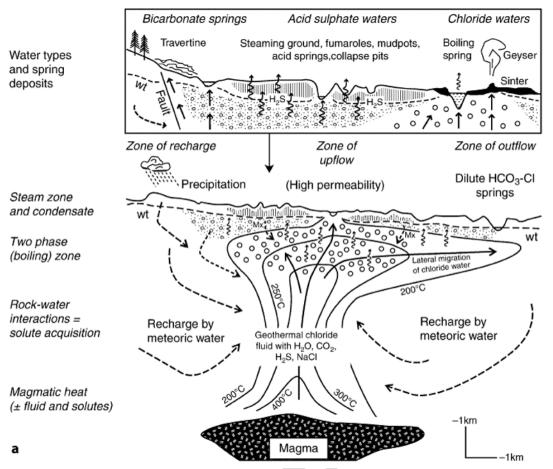


Figure 1.9: Continental terrestrial hot spring fluid types formed by magmatic heating and circulation of mainly meteoric waters that pick up solutes from water-rock interactions to form chloride reservoir-derived fluids (up to 400° C), with variable amounts of dissolved H₂S and CO₂, which may (1) rise directly to the surface in upflow zones to form near neutral alkali chloride geysers and hot springs; (2) undergo two-phase boiling during ascent and pressure release to form acidic steam condensate-fed mud pools and fumaroles; (3) feed bicarbonate springs with dissolved CO₂ at the margins of the geothermal field (from Renaut & Jones, 2011).

Table 1.13 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.2B and move towards understanding of a martian hydrothermal system.

Table 1.13: Samples and measurements implied by Investigation Strategy 1.2B

Samples identified to advance Investigation Strategy 1.28:

• A suite of hydrothermally generated deposits and/or hydrothermally altered host rocks representative of the range of chemistry and mineralogy within the potential hydrothermal system.

Pre-decisional – For planning and discussion purposes only.

Measurements identified to advance Investigation Strategy 1.2B:

- Measure geochemical proxies for salinity and the compositions of fluid inclusions in primary
 precipitates and secondary pore-filling cements that formed or were modified by
 hydrothermal processes.
- Measure the stable isotopic compositions (e.g., O, S, C, N, and Sr) of primary minerals and gasses (e.g., CO₂, SO₂, H₂S, CH₄, H₂, etc.) trapped in fluid inclusions.
- Measure bioessential elements (e.g., C, H, N, O, P, and S, other than compounds containing these elements in the atmosphere), as well as any bioessential trace elements (e.g., Fe, Zn, Co, Ni), and concentrations of potential electron donors in host rock or soil/paleosol samples associated with hydrothermal activity.
- Measure mineral suites to determine mixed valence states for redox energy and isotopic proxies of specific redox couples (e.g., δ^{34} S, δ^{56} Fe) expected in hydrothermal systems.

<u>Investigation Strategy 1.2C</u>: Reconstruct how the depositional system changed over time, and as a function of position within the system.

Stratigraphic analyses initiated with rover exploration and refined by petrologic and paragenetic analyses in returned sample suites would delineate the evolutionary history of the hydrothermal deposit and allow predictions to be made with respect to locating types of preserved biologic signatures, as well as confirming rover mapped distributions with microfacies analysis, and evaluating quality of preservation (Figure 1.10). Furthermore, hydrothermal systems are known to change compositional characteristics rather rapidly, e.g., reflecting a volcanic eruption (e.g., Simmons et al., 1993), or change in the hydrologic-climate cycle (e.g., Drake et al., 2014; Guido and Campbell, 2014, 2017). Thus, hydrothermal deposits could serve as paleoenvironmental dipsticks, reflecting fluctuating shifts in pH, Eh, water table, water-rock interactions, and PBS community composition. Important samples to target would be transitions in mineral and textural suites.

Table 1.14 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.2C and move towards understanding of a martian hydrothermal system.

Table 1.14: Samples and measurements implied by Investigation Strategy 1.2C

Samples identified to advance Investigation Strategy 1.2C:

- Hydrothermally generated/altered rocks sampling interbedding, cross-cutting and/or overgrowth relationships from different stratal positions within the hydrothermal system. *Measurements identified to advance Investigation Strategy 1.2C:*
- Use light microscopy, Raman, XRD, EMPA, FTIR and other methods to study hydrothermal deposits and host rocks to place minerals and microtextures into a broader stratigraphic context; determine the relative age and cross-cutting relationships of minerals, fabrics and structure, linking established outcrop scale to the microscale. Produce a paragenetic sequence of the complete history of the hydrothermal deposit.

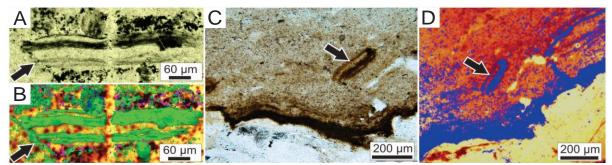


Figure 1.10: Mapping *via* petrographic thin section and *in situ*, high-resolution Raman spectroscopic analyses of hydrothermal minerals and fossilized microbial mat laminates in (A, B) a shallow marine hydrothermal paleoenvironment preserved in hydrothermal silica from early Archean chert in South Africa (3.3 Ga), and (C, D) Late Jurassic sinter from Argentina. Even if organic carbon has been lost, preferential mineralization of previously carbonaceous textures can still preserve evidence of biogenicity. Raman colors: green – carbon, yellow/orange/red – quartz, magenta – muscovite, blue – anatase (low temperature TiO₂ mineral). Modified from Westall et al., 2015b.

<u>Investigation Strategy 1.2D</u>: Determine the age of the hydrothermal system, and the duration and rate of water flow.

It is important to establish the age of the hydrothermal system and whether it overlaps with the water-rich interval of Mars' evolution as a planet, a time when life is predicted to have most likely been present. Returned samples would be subjected to quantitative geochronologic analysis, placing the hydrothermal system into Mars' climatic, igneous and paleohydrologic history. For example, alunite and jarosite are common hydrothermal alteration products in epithermal systems and may be suitable for K-Ar and/or ⁴⁰Ar-³⁹Ar dating and, in combination with stable isotopes, may provide information about paleoclimate (e.g., Stoffregen et al. 2000), aiding reconstruction of Mars' magmatic-hydrologic-climatic evolution. Furthermore, nested investigation of textures (physical sedimentary and preserved biologic structures) of hydrothermal deposits, their sedimentology, bedding geometries, and stratigraphic relationships would aid estimates of channel volumes, mound sizes, and the depth of hydrothermal ponds over the entire hydrothermal system – proxies for volume and duration of thermal fluid flow/accumulation (e.g., Guido & Campbell, 2014), and thus primary controlling factors on the character and distribution of PBSs. Key samples would be rocks with datable mineral suites and textural-mineral types reflecting relative amount of fluid flow in the paleo-hydrothermal system.

Table 1.15 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.2D and move towards understanding of a martian hydrothermal system.

Table 1.15: Samples and measurements implied by Investigation Strategy 1.2D

Samples identified to advance Investigation Strategy 1.2D

 A suite of hydrothermally generated/altered rocks representative of the range of rocks fitting hypothesized age model within the potential hydrothermal system. For exposure ages, use mineralogy to constrain burial depth and timing of exposure history of local outcrops.

Measurements identified to advance Investigation Strategy 1.2D:

- Assess system size, and relative fluid volume and duration of fluid flow.
- Measure the radiometric ages (Rb-Sr, K-Ar, and ⁴⁰Ar/³⁹Ar) of the minerals with permissible mineralogy (e.g., jarosite, calcite, alunite, etc.)
- Measure cosmogenic nuclides (for example, but not limited to, ³He, ¹⁰Be, ²¹Ne, ³⁸Ar) of surface samples to determine exposure age and erosion rate.

<u>Investigation Strategy 1.2E</u>: Investigate the possibility of post-depositional modification/fluids, and interpret those processes.

This investigative component addresses preservation quality of preserved biologic signatures. Besides post-depositional geological activity, the relative timing of hydrothermal alteration overprints and other late diagenetic events have significant impacts on whether biosignatures are expected to be pristine, or whether they have been modified and could still be distinguishable. For example, microbial macro-textures commonly are preserved in siliceous and calcareous hot-spring deposits on Earth. However, high quality, micro-scale preservation of biosignatures – producing convincing fossil biosignatures – depends on timing of mineralization (e.g., early silicification (Campbell et al., 2015a, b, and references therein; Djokic et al., 2017), type of overprinting (e.g., acidic fluids with drop in phreatic level, or regional late silicification), and whether late diagenetic processes have been local or regional in extent (e.g., Walter et al., 1996; Guido & Campbell, 2009, 2011, 2017; Campbell et al., in review). Mapping diagenetic stage (e.g., Lynne & Campbell, 2003; Jones & Renaut, 2007), textural quality, and geochemical concentrations of relevant minerals and elements – at the microbial scale (e.g., Westall et al., 2015a, 2018) – may be achieved with key returned samples.

Table 1.16 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.2E and move towards understanding of a martian hydrothermal system.

 Table 1.16:
 Samples and measurements implied by Investigation Strategy 1.2E

Samples identified to advance Investigation Strategy 1.2E
• Rocks, especially clays, that potentially show evidence of late-stage diagenetic processes such
as hydrothermal alteration, superimposed on the hydrothermal system.
Measurements identified to advance Investigation Strategy 1.2E:
• Evaluate evidence for paleo-water table fluctuations, and timing of fractures and history of
infilling of fractures to form veins and differential concentration of hydrated sulfate and clay

- Evaluate evidence for paleo-water table fluctuations, and timing of fractures and history of infilling of fractures to form veins and differential concentration of hydrated sulfate and clay minerals.
- In constructing a paragenetic sequence of the history of a given hydrothermal deposit (see also 1.1C), differentiate cements and other paragenetic events that are pore-filling (i.e., late diagenetic), search for evidence of dissolution and/or extensive replacement, or recrystallization of primary phases, and examine the mineral composition for evidence of suites of hydrothermal alteration minerals.
- **1.3** Sub-Objective 1.3: Understand the rocks and minerals representative of a deep subsurface groundwater environment

UNDERSTAND A DEEP SUB-SURFACE GROUNDWATER ENVIRONMENT		
Why is this	A key input into interpreting the history of water on	
objective critical?	Mars; search for life.	
Which are the most important samples?	One or more suites of rocks from all units in the stratigraphy with evidence of groundwater flow, including altered and veined zones, including samples that represent time-evolution or distance.	

1.3.1 Introduction and Current State of Knowledge

Groundwater aquifers on Mars, an important source and sink of surface waters, may represent some of the longest-lived, potentially habitable environments on the planet. Chemolithotrophs, organisms that depend not on sunlight energy, but on inorganic chemical reactions for energy, are uniquely suited to life in the subsurface. The subsurface as a habitat on Mars was postulated because of the potential for water to persist and the protection provided from inhospitable surface conditions (Figure 1.11) (Gold, 1992; Boston et al., 1992; Ehlmann et al. 2011a; Schulte et al., 2006; Michalski et al. 2013, 2017). On Earth, terrestrial mafic and ultramafic igneous aquifers and sedimentary aquifers have been found to be significant microbial habitats (e.g., Ghiorse & Wilson, 1988; Stevens & McKinley, 1995; Whitman et al., 1998; Onstott et al., 2009; Kallmeyer, et al., 2012; Schrenk et al., 2013; Osburn et al., 2014; Hug et al. 2015; Rempfert et al., 2017). On Mars, the rock record for past groundwater aquifers is found globally, traceable by spatial patterns in the type and distribution of hydrated minerals (e.g., Murchie et al., 2009; Ehlmann et al., 2011a; Carter et al., 2013) and found by missions *in situ* (Grotzinger et al., 2005; McLennan et al., 2014) as predicted by modeling (Andrews-Hanna & Lewis, 2011; Horvath & Andrews-Hanna, 2017). Exposed rocks from such deep groundwater aquifers on Mars are accessible to be explored, sampled and investigated to understand their geologic history and potential habitability. Some even postulate that such aquifers may continue to exist to the present (e.g., Grimm et al., 2017).

Evidence for deep subsurface groundwater on Mars is found from orbit, in situ (Figure 1.11) and in the meteorite record. The first indication of fluid reservoirs in Mars' subsurface came from the meteorite record. Meteorites record the interaction of erupted lavas with a hydrosphere through the presence of hydrated minerals present at minor to trace amounts (e.g., phyllosilicates, carbonates, sulfates) (e.g., J. C. Bridges et al., 2001). These phases are even present in the martian meteorites that crystalized at a time after ~1.3 Ga (Nyquist, 2001) during which the Mars surface environment was thought to be cold and arid. This was the first pointer to fluid reservoirs in the subsurface, and these relatively late reservoirs in Mars time are poorly understood. At the Meridiani Planum landing site, shallow playa lakes fed by Hesperian groundwaters were discovered by the Opportunity rover (e.g., Squyres et al., 2004; Grotzinger et al., 2005). Multiple episodes of groundwaters are indicated by petrological relationships between hematite concretions, sulfate crystals, empty crystal molds, and occluded pore space in sand-sized rocks (e.g., Figure 1.11d) (McLennan et al., 2005; Tosca et al., 2005), and the age is constrained to be Hesperian from geological relationships. The last stages of waters evaporating near the surface were likely not habitable due to acidity and low water activity (Tosca et al., 2008), though the groundwaters prior to oxidation and evaporation would have been habitable. Elsewhere from orbit, other basins host distinctly sedimentary sulfate deposits, hundreds of meters thick, with fracture fills indicative of extensive groundwater flow (e.g., Lichtenberg et al., 2010; Thollot et al., 2012; Quinn and Ehlmann, 2018). Like at Meridiani, the explorations of the Curiosity rover in Gale crater show multiple episodes of interaction with groundwater following initial deposition in a lake (Figure 1.11e, f) (e.g., Grotzinger et al., 2014; 2015; McLennan et al. 2014; Vaniman et al., 2014; Siebach et al., 2014). Unlike at Meridiani, the waters at Gale were mostly neutral to alkaline, forming Mg smectites, magnetite, gypsum, and other phases in multiple phases of water activity that may have represented habitable environments (Bristow et al., 2015; Stack et al., 2014; Siebach et al., 2015). The last stages of groundwater at Gale crater may have been quite recent, as indicated by dates of < 2 Ga in jarosite in sandstones (Martin et al., 2017). Finally, throughout the Noachian crust of Mars, mineralized ridges with phyllosilicates and Fe/Mg smectite-chlorite-zeolite mineral assemblages point to circulating groundwaters, exposed in numerous locations by faulting, erosion or impact (Figure 1.11a) (Ehlmann et al., 2011a, b; Thollot et al., 2012; Saper & Mustard, 2013; Kerber et al., 2017). Interrogation of rocks representative of subsurface aquifers will provide unique insights into the primary geologic process recorded by the rock record (Objective 1), the potential habitability of groundwater systems, and potential biosignatures from microorganisms inhabiting these aquifers.

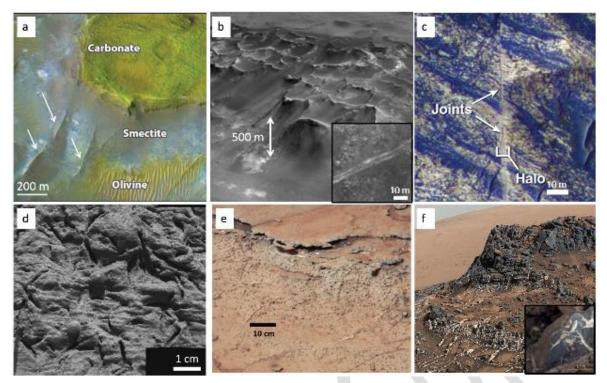


Figure 1.11: (a) groundwater-mineralized Fe/Mg phyllosilicate filled fractures in a > 300 m thick section (Saper and Mustard, 2013) beneath olivine-carbonate rich rocks formed in a shallow aquifer; (b) 500 m penetrative alteration of the NE Syrtis sedimentary sulfate deposits with isopacthus jarosite-bearing ridges (Quinn & Ehlmann, 2018); (c) haloes indicate groundwater flow through Valles Marineris sediments (Okubo et al., 2007); (d) microscopic imager data at Terra Meridiaini shows multiple generations of groundwater mineral precipitation and dissolution, indicated here by crystal vugs, (McLennan et al., 2005); (e) dark nodules and sulfate veins indicate multiple generations of groundwaters in rocks initially formed as Gale lake sediments (Siebach et al., 2014); (f) multiple generations of thick veins, including penetrative fractures indicate groundwaters in deeply buried rocks at Gale crater (Mastcam image from sol 938; Kronyak et al., 2017).

1.3.2 Key Open Questions for Sub-Objective 1.3

Groundwater aquifers were clearly a key component of Mars' hydrologic and climate cycle. Attributes of groundwater aquifers that can be further constrained by examination of rocks include the sources, timing, and persistence of groundwaters over different parts of the planet; the chemistry and temperatures of the groundwaters; their communication with the surface and/or with magmas; the evolution of the chemistry of groundwaters; the role of groundwaters in Mars' longterm geochemical cycling; the habitability of the subsurface; and groundwater aquifer rocks as a host for biosignatures of past life (Figure 1.12).

Are groundwaters part of a potentially globally connected hydrologic system (Figure 1.13) (e.g., Clifford et al., 1993; 2010; Andrews-Hanna & Lewis, 2011) or are groundwaters partitioned into smaller sub-basins? This is part of the larger question of the martian hydrological cycles, at the global scale was the system vertically integrated or horizontally stratified (Head, 2012). In contrast to Earth's oceans present continuously since > 4 Ga, Mars may have had an episodic northern ocean fed by outflow channels (e.g., Tanaka, 1997), but there is scant geologic evidence that Mars had a northern ocean in continuous existence for billions of years (e.g., Pan et al., 2017). Also, while mineralogic evidence for water-rock interaction was widespread, geochemical evidence does not show the leaching characteristic of open system water-rock reactions. This is a distinctly different situation from that of Earth where weathering driven by a surface hydrologic cycle has delivered sediments to ocean basins for all of Earth history. Instead, on Mars, surface runoff and groundwaters were crucial in periodically generating lakes, which in their later episodes were fed by groundwaters alone, facilitating diagenesis (Goudge et al., 2015; Michalski et al., 2015). Thus, investigations of

deep groundwaters naturally grade to those of sediments from surface waters in Investigation 1.1, where diagenesis of the sediments is by groundwaters, and surface hydrothermal systems in Investigation 1.2, which are the outflows of the warmest groundwaters.

Table 1.17: Key open questions for Sub-Objective 1.3: Understanding deep sub-surface groundwaters

KEY OPEN QUESTIONS: SUB-OBJECTIVE 1.3

What were the timing of and water sources sustaining the groundwaters of Mars?

What was the chemistry and temperatures of groundwaters on Mars and did these evolve with time?

Did groundwaters communicate with the atmosphere and with magmas and play a major role in Martian geochemical cycles?

Do Mars' groundwaters represent local water sources or a globally-connected hydrologic system?

What was the habitability of groundwater aquifers?

Do rocks from groundwater aquifers host biosignatures of past life?

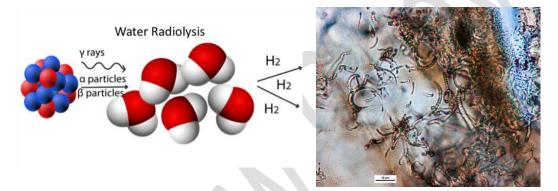


Figure 1.12: a) Cartoon depiction of the radiolysis of water to produce H₂ gas, a rich energy source for microorganisms that inhabit subsurface environments (source Jesse Tarnas, Brown University). b) Microbial trace fossils in 15 million-year-old impact glass from the Ries Impact Structure, Germany (Sapers et al., 2014)

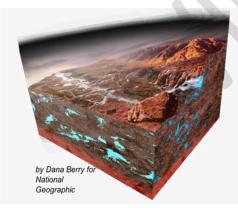


Figure 1.13: Concept of the surface and subsurface of Mars ~ 4 billion years ago, showing a surface hydrological system connect to subsurface groundwater systems

1.3.3 Why Returned Sample Studies are Important for Sub-Objective 1.3

From orbit, the record of groundwaters reveals more mineralogical diversity than has yet been interrogated by landed missions, which have not yet interrogated sections of intact Noachian rock. Chemically closed system alteration is indicated in most Noachian terrains with Fe/Mg smectites and chlorites, illite, zeolites, silica, and serpentine assemblages (Mustard et al., 2008; Ehlmann et al., 2010, 2011b; Carter et al., 2013), although it is not possible to discern from orbit whether these clay-bearing rocks were igneous or sedimentary (for discussion see Bandfield et al., 2013). The constituent minerals of these rocks from various places on Mars indicate groundwater alteration at conditions ranging from ambient to hydrothermal (Ehlmann et al., 2011a, b). The highest temperature phase detected to date is prehnite (formation temperatures constrained to ~200-400C; Frey & Robinson, 2009); amphiboles that would indicate higher temperatures are conspicuously absent (Carter et al., 2013). In several locations, mineralized veins indicate episodes of groundwater flow through sections of phyllosilicate-bearing rock that are 100s of meters thick (Saper & Mustard, 2013). Samples collected *in situ* with geological context at the meter scale and below to understand the chemistry, timing, episodicity, and longevity of groundwater availability are thus crucial to understanding martian climate and interpreting habitability.

1.3.4 Sample Investigation Strategies to achieve Sub-Objective 1.3

There are four main investigative strategies proposed to understand the geologic processes on Mars that have affected subsurface rocks in contact with groundwaters. To understand the extent of subsurface water/rock interaction we will investigate the morphologies and mineral assemblages suggestive of such processes. We will characterize the physio-chemical conditions of the fluids and the water/rock reactions to assess the potential habitability, determine the source of fluids and interpret the reactions governing mineral precipitation. We will examine the petrological relationships between phases to determine the evolution of the groundwater system and fluid chemistries with time.

We propose four specific investigation strategies and 16 sets of measurements on samples returned from a martian groundwater system (Table 1.18).

Investigation Strategies (IS) for Objective 1 Sub-Objective 1.3		
1	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.
1.3	Deep sub-surface groundwater	Understand the rocks and minerals representative of a deep sub- surface groundwater environment.
IS 1.3A	Interpret the morphologic features and minerals resulting from groundwaters in igneous and sedimentary host rocks to understand the extent of groundwaters, their transport, and their episodicity.	
IS 1.3B	Determine the physico-chemical conditions of water-rock interaction and assess habitability.	
IS 1.3C	Determine the source precipitation.	ce of fluids and abiotic or biotic reactions governing mineral
IS 1.3D	Determine the time	-evolution of the groundwater system and chemical reactions.

Table 1.18: Summary of sample-related investigation strategies to understand an ancient martian deep subsurface groundwater environment.

<u>Investigation Strategy 1.3A</u>: Interpret the morphologic features and minerals resulting from groundwaters in igneous and sedimentary host rocks to understand the extent of groundwaters, their transport, and their episodicity.

At the landing site, the stratigraphic context and host rock can only be discerned by measurements at meter-scale and lower. At present, for most minerals inferred from orbit to form from groundwaters, it is not known whether the host rock is igneous or sedimentary nor its local stratigraphy. The timing(s) of episodes of groundwater mineralization are thought to be ancient (> 3 Ga) but are constrained only by cross-cutting relationships with other stratigraphic units. Thus, basic first order questions about martian groundwater are the focus of the first investigation. These include the nature of the host rock, the extent of aqueous alteration/interaction with the host rock, the style of transport (pore space vs. fracture-confined), and episodicity.

Table 1.19 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.3A and move towards understanding of a martian sub-surface groundwater systems.

Table 1.19: Samples and measurements implied by Investigation Strategy 1.3A

Samples identified to advance Investigation Strategy 1.3A:

• A suite of rocks from all units in the stratigraphy with evidence of groundwater flow, including at depth and shallow. Features indicative of groundwater flow include mineralized fractures or ridges, diagenetic concretions, zones with color change indicating leaching and/or cements and should be sampled along with adjacent host rock.

Measurements identified to advance Investigation Strategy 1.3A:

- Analyze stratigraphy and petrography to determine the protolith of aquifer rocks (igneous or sedimentary and the local stratigraphy).
- Examine the mineralogy of host rock and veins/vugs/fractures to examine for evidence of chemical interaction with waters and the extent to which primary minerals have been altered by groundwater flow.
- Characterize the petrology to understand cross cutting relationships and the timing of groundwaters relative to other geological events.
- Evaluate the number of distinct episodes of groundwaters by examining rocks with crosscutting relationships between zones of distinct mineralogy or morphology.
- Use radiogenic isotopes to date formation ages of the groundwater host rock as well as the fluid-precipitated minerals (e.g., carbonate, jarosite, some phyllosilicates suitable for dating).

<u>Investigation Strategy 1.3B</u>: Determine the physico-chemical conditions of water-rock interaction and assess habitability.

Key water properties, including temperature, pH, Eh, aH₂O, and ion activities, can be derived by identification of mineral assemblages. On Earth, the currently recognized temperature limits for metabolic activity ranges from -20°C for microorganisms trapped in 8.5 to 25 meters deep Siberian permafrost (Rivkina et al., 2000) to 122°C for a methanogen isolated from a deep sea vent plume (Takai et al., 2008). Thus, understanding the temperature range of martian groundwaters is important. Understanding sources of heat – geothermal, magmatic, impact, or simple climate change – is also important for understanding the groundwater system. The minerals observed in fractures will change as the groundwater system evolves and multiple generations of minerals are precipitated. Patterns in mineralization will be observed in different parts of the aquifer, depending on gradients between surface and subsurface waters (e.g., Barnes & O'Neil, 1969; Plummer et al., 2003; Kühn, 2004). These observations can be used to track the geochemical evolution of the fluid, including the potential production of microbial energy sources (e.g., H₂ gas) and/or water/rock ratio (e.g., McCollom & Bach, 2009; Klein et al., 2013).

Table 1.20 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.3B and move towards understanding of a martian sub-surface groundwater systems.

 Table 1.20: Samples and measurements implied by Investigation Strategy Investigation Strategy 1.3B

Samples identified to advance Investigation Strategy 1.3B:

• Samples from cross sections of altered zones. Key phases include Fe and Mn oxides, phyllosilicates, silica, sulfates, carbonates, and other salts. Samples should be selected with knowledge of their position within the flow path to track fluid chemistry change with system time-evolution or distance.

Measurements identified to advance Investigation Strategy 1.3B:

- Determine all phases present in mineral assemblages in host rock and in groundwater-altered or -precipitated zones.
- Determine the crystal chemistry and valence of redox sensitive elements (Fe, Mn, Cr, S, etc.)
- Examine the petrologic relationships between primary and secondary minerals to determine the chemical reactions taking place in the ground water system and the fluid chemistry.
- Evaluate flow volumes, fluxes, and water-rock ratios from the mineral assemblages and their relative timings of formation.
- Establish the relative timing of each mineral formation to understand the evolution of the groundwater system and reactive flow transport.

<u>Investigation Strategy 1.3C:</u> Determine the source of fluids and abiotic or biotic reactions governing mineral precipitation.

Mineral phases and H, C, S, O and metal isotopes can be used to understand the relative contributions from different fluid sources (atmospheric, groundwater, magmatic). This is routinely done on earth by sampling systems from top to bottom through aquifer rocks because the isotopic signatures of the atmosphere are distinct from magmatic sources are distinct from host rocks. Thus, investigation of multiple samples helps determine flow path. Along with investigations in 1.3B, key measurements for this Investigation include:

Table 1.21 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.3C and move towards understanding of a martian sub-surface groundwater systems.

 Table 1.21: Samples and measurements implied by Investigation Strategy 1.3C

Samples identified to advance Investigation Strategy 1.3C:

- Sample as for IS 1.3A and 1.3B, but with an emphasis on sampling multiple positions in the inferred flow path through the host rocks and minerals from multiple episodes of interaction. *Measurements identified to advance Investigation Strategy 1.3C:*
- Measure H, C, S, O, and metal isotopes of mineral phases in the host rock and in groundwateraltered zones.
- Determine isotopic signatures from IS 1.3A as function of stratigraphic location and level to determine direction of water flow (top-down vs. bottom up).
- Measure atmospheric isotope values from coeval systems (e.g., glasses, quenched lavas).

<u>Investigation Strategy 1.3D</u>: Determine the absolute time-evolution of the groundwater system and chemical reactions.

We would like to know both the relative and absolute timing of when groundwater was present. Petrological relationships (overgrowths, cross-cutting relationships) can used to determine the time at which groundwaters were present and interacting with the rocks by time-ordering the formation and dissolution of phases. This will also lead to understanding changes in groundwater properties due to changing sources or fluid evolution. This has been done on Mars in a relative sense at the *Opportunity* (McLennan et al., 2005; Tosca et al., 2005) and Curiosity (Siebach et al., 2014) landing sites. The measurements are similar to those in Investigation Strategies 1.2B and 1.2C, but with emphasis on *in situ* data to understand the number of episodes of groundwater interactions to select the best samples to establish timing.

Table 1.22 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.3D and move towards understanding of a martian sub-surface groundwater systems.

 Table 1.22: Samples and measurements implied by Investigation Strategy 1.3D

Samples identified to advance Investigation Strategy 1.3D:

• The same as for IS 1.3C.

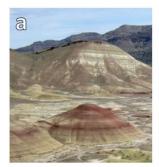
Measurements identified to advance Investigation Strategy 1.3D:

- Identify zones of mineral precipitation and dissolution.
- Determine the sequence of chemical events affecting the rock from petrology.
- Determine the stable isotopic values for all phases measured in IS 1.3A-C, sampling those from distinct episodes.
- Perform radiometric age dating of samples from the host rock and minerals precipitated during each episode.
- **1.4** Sub-Objective 1.4: Understand water/rock/atmosphere interactions at the martian surface and how they have changed with time

UNDERSTAND SURFACE WATER/ROCK/ATMOSPHERE INTERACTIONS	
Why is this	A key input into interpreting the history of water on
objective critical?	Mars; search for life.
	A suite of rocks or soils/paleosols representative of the
Which are the most	range of depth and weathering, from most-altered to
important samples?	least-altered/unaltered parent material; mineral
	deposits formed due to evaporation.

1.4.1 Introduction and Current State of Knowledge

The category of subaerial environments includes all environments at the surface or in the Pr-surface not covered by a body of water but where water is derived directly from precipitation, snow melt, or ambient-temperature groundwater, as described by Hays et al. (2017). This includes soils, wetlands, ephemeral ponds, cold springs, rock coatings and weathering rinds, glaciers, periglacial terrains, and snow packs, and these environments are often co-located both on modern Earth and in the terrestrial rock record (Figure 1.14). Subaerial alteration probably occurred primarily during the Noachian and Hesperian on Mars and probably contributed to many of the hydrous outcrops on the surface (e.g., Mustard et al., 2008; Bishop et al., 2008, 2018; Murchie et al., 2009; Ehlmann & Edwards, 2014) and thus investigating these materials on Mars will provide information about the aqueous geochemical environment and climate during their formation. These types of environments also represent potential habitable environments on early Mars. These environments are typically identified in the rock record by the presence of paleosol (lithified soil) profiles that can be topped by aqueously deposited sediments and precipitates from wetlands, ephemeral ponds, and springs. Thus, on Mars, these diverse environments are likely to be found in the rock record at the same landing site (Figure 1.14). Pre-decisional – For planning and discussion purposes only.



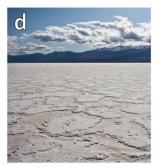
Stacks of volcanic paleosols produced via long term surface weathering



Wetlands formed in a persistent elevated groundwater table



Cold springs formed from localized emergence of groundwater



Playa formed from evaporation of a lake shore or groundwater table

Figure 1.14: Images of subaerial environments, which are linked by their common interactions with the atmosphere and water at the near surface. (a) Paleosol sequence formed on volcanic material, John Day Fossil Beds National Monument, OR. (b) Wetlands in a post-glacial environment, Alberta, CA. (c) Circumneutral cold spring near Green River, Utah (photo: S. Potter-McIntyre). (d) Playa environment in Death Valley, CA.

Terrestrial soils, also termed the "Critical Zone" for their importance in hosting terrestrial life (Brantley et al., 2006), can preserve extensive evidence for habitable environments, aqueous conditions, and life. The processes that form a soil - transformation from one component to another, translocations or transport within the soil, additions and losses - all cause changes in the soil which are essential to understanding the chemistry and aqueous processes that support these habitable environments, and preserve potential signs of life. Where soils are seasonally or perennially saturated by surface runoff or groundwater, wetlands and similar shallow aqueous environments form and can preserve high abundances of organics due to their strongly reducing conditions. Soils are preserved in the geologic record as paleosols, and the composition and morphology of paleosols preserve evidence of past climate, aqueous conditions, and life (Retallack, 2008). Examples of Mars analog paleosol sequences on Earth include the John Day Fossil Beds National Monument (e.g., Horgan et al., 2012) and the Painted Desert (McKeown et al., 2009; Noe Dobrea et al., 2009; Perrin et al., 2018). At these sites, horizons of diverse clay minerals, iron oxides and sulfates document changes in climate and redox conditions (Figure 1.15). On Mars, Noachian weathering profiles have been identified across the southern highlands (Carter et al., 2015), and possible paleosol sequences are present in Arabia Terra, in particular Mawrth Vallis (e.g., Bishop et al., 2008, 2013; Horgan et al., 2012).

More recent alteration on Mars has possibly led to less pervasive near-surface alteration. Potential near-surface activity includes mobility of Cl salts related to Recurring Slope Linea (RSL) (Ojha et al., 2015), long term surface weathering (Amundson et al., 2008), and melting of H₂O ice near the Phoenix landing site (Smith al., 2009) and in mid-latitude cliff sites (Dundas et al., 2018). Weak pedogenic alteration was also observed in Gusev crater (Arvidson et al., 2010). Surface environments can also be recorded in weathering rinds and rock coatings (e.g., Sak et al., 2004; Hausrath et al., 2008a, b; Navarre-Sitchler et al., 2009, 2011; Dorn, 2013; Bishop et al., 2011; Adcock et al., 2018). Rock coatings and rinds have been observed with rovers and landers at the martian surface (e.g., Hurowitz et al., 2006), and have been potentially identified from orbit (N. T. Bridges et al., 2001; Greeley et al., 1999; Haskin et al., 2005; Horgan & Bell, 2012; Salvatore et al., 2013; Clark et al., 2016; Farrand et al., 2016). These more modern surface environments could still be targets for biosignature or extant life investigations, as even in desert environments, terrestrial microbes inhabit chemically active zones just below the surface (Figure 1.16). Modern Mars-like soils on Earth include the Antarctic Dry Valleys, where despite the cold and dry surface conditions, near-surface changes in chemistry and mineralogy are attributed to an active zone in these sediments a few cm below the surface (e.g., Gibson et al., 1983; Burton et al., 2018). Thus, characterizing the nearsurface profiles of martian samples could provide information about chemical alteration occurring in

these sites despite a harsh surface environment. This could indicate near-surface water availability when the martian climate was cold and dry.

Ephemeral ponds are typically precipitation-sourced shallow lakes that can evolve into brines and can become acidic or alkaline. These ponds typically produce CI-salt, sulfate, or carbonate deposits, and could support either phototrophic surface communities or chemotrophic communities where chemical gradients are present. The possibility of acid waters on Mars was first proposed by Clark & Baird (1979) and confirmed in situ by the *Opportunity* rover in Meridiani (Squyres et al., 2004). Sulfate salts are common across the martian surface, and localized sulfates in locations like Mawrth Vallis have been interpreted as evidence of brines in ponds or wetlands (Horgan et al., 2015; Bishop et al., 2018). More neutral to alkaline evaporite deposits have also been identified on Mars, including localized CI-salt deposits that are distributed throughout the southern highlands (Osterloo et al., 2008). Terrestrial analogs for brines on Mars include the shallow, acid brine lakes in Western Australia that are rich in microbial life, have variable pH, and have unique mineral assemblages (clays, FeOx, sulfates, and CI salts) that could be representative of ancient habitable environments on Mars (Benison & Laclair, 2003; Benison & Bowen, 2006; Benison et al., 2007).

Cold springs are subaerial environments where ambient-temperature water emerges from the subsurface onto the surface. Typically, the flow path for the water is along faults or fractures, and changing chemical conditions as the water emerges onto the surface lead to the precipitation of mineral deposits. Spring-deposited tufas (calcium carbonates), clays, and iron (oxyhydr)oxide deposits can be preserved over geologic time, along with textural, mineralogical, and chemical biosignatures. Changing water chemistry can support chemotrophic communities, and flowing surface water can help to support phototrophs. In general, the significant energy availability produces abundant biomass in cold springs; therefore, biosignatures are highly concentrated in cold springs. Examples of these cold streams include ferrihydrite precipitating from runoff on tufas in Iceland (Bishop & Murad, 2002) and carbonates precipitating at Mammoth Spring at Yellowstone (Bishop et al., 2004). These systems would require environments supporting at least short-term liquid water on the surface of Mars. Deeper ground-water systems could provide a source for these springs and seeps on the surface.

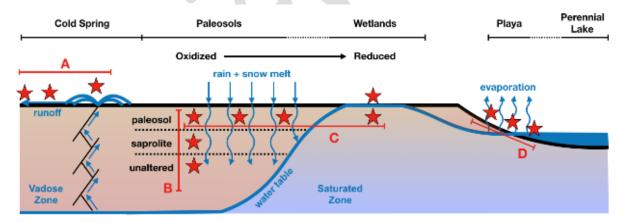


Figure 1.15: Possible relationships between spring deposits, soil horizons, and evaporite deposits. Stars indicate proposed sample locations. Sample suite (A) is of spring precipitate deposits at increasing distance from spring source along fluvial channels. Sample suite (B) are paleosol horizons at increasing depths from the paleosurface, from highly altered to unweathered parent material. Sample suite (C) are paleosols at variable redox states, including reduced wetland deposits. Sample suite (D) are playa evaporite deposits at increasing distance inward from highest lake level. Proposed samples not shown here include rock coatings and rinds.

1.4.2 Key Open Questions for Sub-Objective 1.4

What was the nature of the early climate and atmosphere of Mars? The nature of the early climate of Mars is highly debated, and models range from cold and dry to warm and wet. Subaerial

environments provide a record of direct atmosphere-surface interations in the depth, geochemistry, and mineralogy of soils (e.g., Sheldon & Tabor, 2009), and thus are a critical target for resolving the nature of the ancient Nochian climate (Carter et al., 2015; Horgan et al., 2017).

How habitable/inhabited was the <u>ancient surface</u> of Mars? Subaerial environments on Earth support a variety of microbial metabolic pathways both at the surface and in the near-surface environment, in part due to the complex chemistry created by surface-atmosphere interface, which creates redox gradients due to downward flow of precipitation in soils, groundwater fluctuations, evaporation and concentration of brines, subglacial fluid flow, and spring emergence. Thus, these environments can support chemotrophic and phototrophic microbial communities that may be present as microbial mats, endoliths, or other microbial communities of varying complexity and density. The terrestrial record shows that subaerial environments can preserve biosignatures from both surface (e.g., microbial mats) and subsurface life (e.g., concentrated organics).

How habitable is the <u>modern surface</u> of Mars, and what is the present-day surface/atmosphere water cycle? Despite the cold and dry surface conditions, the near-surface environment on Mars may have provided (or even still provide) in some locations access to liquid water, chemical alteration, and potentially habitable conditions. A full understanding of the presentday surface/atmosphere water cycle is still unknown to date. Modern soils integrate atmospheric processes over longer time spans than missions can sample (hundreds to millions of years). Practerization of modern soil and rock coating samples in the lab will enable a comprehensive understanding of near-surface present-day processes on Mars.

 Table 1.23: Key open questions for Sub-Objective 1.4: Understanding water/rock/atmosphere interactions at the martian surface

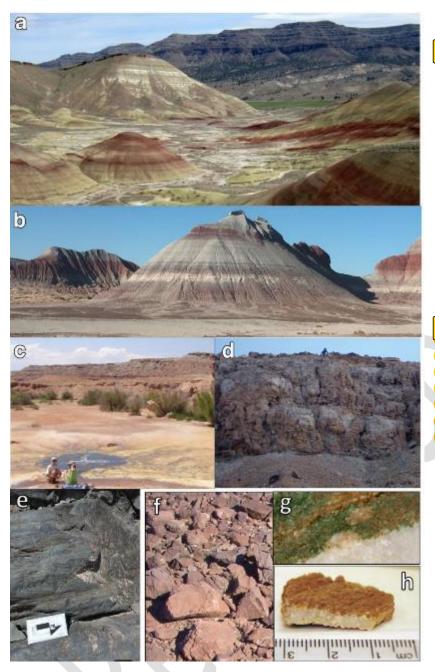
KEY OPEN QUESTIONS: SUB-OBJECTIVE 1.4	
What was the nature of the early climate and atmosphere of Mars?	

How habitable/inhabited was the <u>ancient surface</u> of Mars?

How habitable is the <u>modern surface</u> of Mars, and what is the present-day surface/atmosphere water cycle?

1.4.3 Why Returned Sample Studies are important for Sub-Objective 1.4

Laboratory analysis of samples from this diverse suite of surface environments will allow detailed characterization of the composition of minerals produced in these environments. Mainly because fluids in most of these environments are either sourced from or directly interact with the atmosphere, the isotopic compositions of authigenic minerals provide direct links to past atmospheric conditions. Furthermore, these environments record long-term surface processes through deep weathering to form soil profiles, so characterization of subaerial martian samples in the lab will include compositional analyses of sampled horizons in order to document changes in the geochemical environment over time. The investigation of samples from this kind of environments in the lab will also optimize the chances of finding biosignatures and will help to characterize the present day potential habitability of Mars.



The selected views of estrial subaerial environments: a) paleosol sequence, John Day Fossil Beds National Monument, Oregon. (b) paleosol sequence, Painted Desert outcrop, Petrified Forest National Park, Arizona. (c) Modern circumneutral cold spring supporting surface microbial communities near Green River, Utah, compared to (d) outcrop of Jurassic cold spring deposits in the Brushy Basin Member of the Morrison Formation, Colorado (modified from Potter-McIntyre et al., 6). (e) Glacially precipitated mea rock coatings (regelation) films) on North Sister volcano, Oregon, compared to (f-h) red iron (oxyhydr)oxide coatings on carbonate rocks from the Mojave desert (modified from Bishop et al., 2011).

1.4.4 Sample Investigation Strategies to achieve Sub-Objective 1.4

Four investigation strategies and 12 sets of measurements have been proposed to unveil the change with time of the martian surface water/atmosphere/rock interactions, characterize the past climate and geological changes and the potential of these environments to host and transport life and biosignatures as well as the redox states over time (Table 1.24). Below we detail the proposed Mars sample investigation strategies needed to interpret these aqueous environments and their potential biosignatures, listed in order of priority.

Table 1.24: Summary of sample-related investigation strategies to understand a martian water/rock/atmosphere interactions

Investigation Strategies (IS) for Objective 1 Sub-Objective 1.4		
1	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.
1.4	Subaerial	Understand water/rock/atmosphere interactions at the martian surface and how they have changed with time.
IS 1.4A	Investigate weathered materials such as soils, paleosols, weathering rinds or rock coatings to investigate the duration and nature of past climate and habitable surface environments.	
IS 1.4B	Iongevity of the waters, and their role in the formation of wetlands, ponds, and springs.Assess the aqueous and diagenetic history of the site, including the chemistry of past	
IS 1.4C		
IS 1.4D	Determine sediment provenance and transport history.	

<u>Investigation Strategy 1.4A</u>: Investigate weathered materials such as soils, paleosols, weathering rinds or rock coatings to investigate the duration and nature of past climate and habitable surface environments.

Temperature on Mars likely plays a role in the relative dominance of physical and chemical weathering and is reflected in the mineralogy of soils and paleosols. For example, smectite clays formed in surface environments on Mars required warmer temperatures than poorly crystalline aluminosilicates formed in neighboring surface environments (Fairen et al., 2011; Bishop and Rampe, 2016), thus indicating a change in climate (Bishop et al., 2018). Allophane and related poorly crystalline materials have been observed in cold terrestrial environments (e.g., Bishop et al., 2014; Scudder et al., 2017; Thorpe et al., 2017; Cuadros et al., 2018) rather than crystalline clays. Detailed analysis of the crystalline mineral and amorphous phase assemblages in weathering profiles could help to constrain the origin of these different minerals and their relationship to past environmental conditions (e.g., Gainey et al., 2017). Near-surface active zones in the Antarctic Dry Valleys are identified through changes from anhydrite to gypsum, from amorphous aluminosilicates to montmorillonite, and through elevated NaCl levels (Gibson et al., 1983; Englert et al., 2013; Bishop & Englert, 2016). Identifying similar mineral/chemical transitions with depth in martian samples could provide evidence of near-surface active zones on Mars.

In addition, on Earth, stable isotopes and geochemical profiles are used to constrain paleoprecipitation and paleotemperature in paleosols, and similar calculations may be possible using martian samples (e.g., Retallack et al., 1999; Sheldon & Tabor, 2009). The thickness of soils and weathering rinds can be used to interpret the duration of weathering (Sak et al., 2004; Hausrath et al., 2008; Navarre-Sitchler et al., 2009,2011; Adcock et al., 2018), and so ultimately these investigations will help to constrain the duration and degree of habitability of martian surface and the landing site and on Mars more generally. Sub-aerial environments could have been widespread on Mars, so if these environments were habitable, then the martian surface was probably largely habitable, habitats were well-connected, and Mars could have supported significantly more total biomass (e.g., Westall et al., 2015a). In addition, the composition and stable isotopes of minerals produced through alteration by meteoric water can be used to constrain atmospheric chemistry and atmospheric change through time (e.g., carbonates, Hu et al., 2015)—there is an important crosslink in the area with Objective 4 of this report. By comparing the composition of minerals from meteoric water sources vs. those from groundwater sources, we could also constrain the composition and history of different volatile sources and sinks on Mars. A critical component of this investigation is changes in mineralogy and chemistry with depth, which is a better indicator of past aqueous processes and climate than a single measurement or samples alone (e.g., Sheldon & Tabor, 2009). In addition, chemical profiles can preserve potential biosignatures in highly leached and oxidized paleosol profiles, including laterites. Although these types of soils have poor organic preservation potential, they can preserve chemical biosignatures, including "bleached" Fe-poor upper horizons attributed to organic acids from surface microbial communities (Gutzmer & Beukes, 1998; Neaman et al., 2005; Hausrath et al., 2011), phosphorus depletion in the upper portion of profiles that could indicate uptake by microorganisms (Horodyskyj et al., 2012), and potential impacts of biological Fe oxidation (Baumeister et al., 2015).

Table 1.25 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.4A and move towards understanding of water/rock/atmosphere interactions at the martian surface.

 Table 1.25: Samples and measurements implied by Investigation Strategy 1.4A

Samples identified to advance Investigation Strategy 1.4A:

- A suite of rocks or soils/paleosols representative of the range of depth and weathering, from most-altered to least-altered/unaltered parent material.
- Mineral deposits (e.g., iron oxides, salts, carbonates) precipitated in chemical gradients (e.g., springs) or due to evaporation (e.g., ephemeral ponds), especially those with evidence for long-term buildup.
- Rocks with precipitated coatings minds.
- masurements identified to advance investigation Strategy 1.4A:
- Measure variability in the mineralogy, chemistry (including identification and measurement of potential oxidants), mineral proportions and morphology of primary and secondary minerals and amorphous phases as a function of depth and/or degree of weathering, to constrain the duration of water interaction, water chemistry, water temperature, water residence time/drainage, and search for chemical trends that could be biosignatures.
- Analyze the chemistry and mineralogy of climate-sensitive minerals at nano-, micro-, and macro-scales.
- Measure the stable isotope compositions of secondary minerals to constrain the composition and history of atmospheric and crustal volatile sources.

Investigation Strategy 1.4B: Assess the history of surface water at the site, including the chemistry, source, and longevity of the waters, and their role in the formation of wetlands, ponds, and springs.

Subaerial environments include those environments where water ponds at the surface in the form of wetlands (stagnant, reducing bodies of water at the intersection with the local groundwater table), ponds (surface accumulation of water), lake shorelines, and cold springs. Whereas soils tend to form a chemical record by alteration of pre-existing parent materials, these subaerial environments can also cause significant sediment accumulation and mineral precipitation at the surface.

Surface mineral precipitates include direct precipitates, evaporites, and coatings, and can preserve fluid inclusions, trapped organics, and surface textures that, along with chemistry and mineralogy, can help to untangle the history of water at the site. Precipitates are also critical for preserving biosignatures. Cold springs in particular can produce a diverse suite of mineral deposits (e.g., carbonates, clays, sulfates/salts, amorphous minerals), which enable multiple biosignature preservation mechanisms. Ostwald ripening (where large crystals form at the expense of smaller crystals, resulting in massive, anhedral crystal habits in Jurassic tufas) has been shown to preserve microbial body fossils and trace fossils in carbonates on geologic timescales (Potter-McIntyre et al., 2016). Iron rich springs have also been shown to preserve lipid biomarkers (Parenteau et al., 2014). Evaporite deposits can preserve biosignatures in the form of filamentous structures and trapped organics in mineral crystals (e.g., Vreeland et al., 2000; Mormile et al., 2009). Redox changes in evaporates might represent a more direct link to changes in geochemical environment and potentially the presence of microbes (Benison & Bowen, 2006). In any precipitate, examination of organic inclusions could provide information about the geochemical conditions at time of emplacement and potentially provide clues to any microbes associated with them.

Table 1.26 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.4B and move towards understanding of water/rock/atmosphere interactions at the martian surface.

Table 1.26: Samples and measurements implied by Investigation Strategy 1.4B

Samples identified to advance Investigation Strategy 1.4B:

- Rocks formed under a variety of redox conditions, and especially those with evidence for sedimentation or mineral precipitation under reducing conditions.
- Mineral deposits (e.g., iron oxides, salts, carbonates) precipitated in chemical gradients (e.g., springs) or due to every ration (e.g., ephemeral ponds), especially those with evidence for long-term buildup.
- Rocks with precipitated coatings or weathering rinds.

Measurements identified to advance Investigation Strategy 1.4B:

- Evaluate the chemical and isotopic composition, speciation, and abundance of organics, lipids, etc. in sedimentary and mineral precipitate deposits, in particular those with reduced Fe/S minerals and mineral precipitates, in order to determine whether or not organics may be biotic in origin.
- Analyze the micro- and nano- scale morphology of mineral precipitates to search for textural biosignatures.

<u>Investigation Strategy 1.4C</u>: Assess the diagenetic history of the site, including the chemistry and redox state of past near-surface waters and groundwaters, how water sources may have interacted, and how they have changed through time.

Many locations on Mars show evidence for interaction with both surface waters and groundwaters during early alteration (early diagenesis). Downward leaching of surface waters into the near-surface produces paleosols. Where this process occurs well above the water table, an oxidized and well-leached paleosol is produced, but as the water table nears the surface, the paleosol can become seasonally or perennially saturated, to the point of becoming a wetland (Figure 1.15). Saturated soils and wetlands rapidly become reducing, and form less leached mineral phases. This process can create strong lateral, vertical, and temporal redox gradients that strongly affect biosignature preservation, enable chemolithic metabolisms in microbes, and alter the chemistry of the alteration fluids and their precipitated minerals. Both well leached (e.g., Carter et al. 2015) and reducing (e.g., Bishop et al., 2013; Farrand et al., 2014; Horgan et al., 2015) paleosol profiles have been tentatively identified on Mars, and these paleosols could preserve key chemical and mineralogical information about the surface and ground waters that formed them, and the interactions of these water sources.

This investigation is also critical for characterizing the organic preservation potential of soils and paleosols. Organics are most easily concentrated and preserved when they are deposited in a reducing surface or near-surface environment. Paleosols most commonly preserve organics when they are associated with seasonal or permanent waterlogging (e.g., wetlands), which in the more modern terrestrial environment can lead to the formation of lignites, tonsteins, and seatearths (Spears, 2012). However, paleosols associated with surface reducing conditions (e.g., ponds) have also been shown to preserve organic carbon for billions of years both at the surface and at depth at detectable levels (0.01 to 0.36 wt. %) from microbial communities (Gay & Grandstaff, 1980; Watanabe et al., 2000, 2004; Rye & Holland, 2000). Redox state appears to be the most critical indicator of this kind of preservation, as nearby contemporaneous oxidized and heavily leached profiles do not contain organics (Gay & Grandstaff, 1980). Studies of more recent paleosol sequences have shown concentrations of organics can also occur in association with sulfates (Noe Dobrea et al., 2016).

In addition, the advanced age of many martian geologic units also allows for significant ration post-burial (late diagenesis)—there is an important connection in this area to Subopective 1.3 of this report. This has been shown at the rover scale based on the presence of tures filled with precipitated minerals (e.g., Siebach & Grotzinger, 2014) and at the orbital scale based on the presence of resistant linear ridges, sometimes with alteration halos, interpreted as fractures through which diagenetic fluids flowed (e.g., Bramble et al., 2017). Comparison late of diagnetic features and those from surface deposition or early diagenesis would constrain the evolution of fluid compositions on Mars over time (e.g. Hausrath et al., 2018), and as late diagenesis can destroy previously preserved organics, would help to inform analyses of biosignature preservation potential.

In all these aqueous near-surface or surface environments, the solution chemistry of past aqueous environments is relevant to critical aspects of potential habitability and biosignature preservation. Samples that preserve evidence of that chemistry are therefore a high priority for sample selection. Important characteristics of habitability that can be preserved in aqueously altered samples include the nutrients and redox gradients present, and characteristics of liquid water such as temperature, pH, and salinity. Similarly, solution chemistry is critical to biosignature preservation, and solution chemistries high in Fe, phosphate, silica, and carbonate have all preserved different types of biosignatures on Earth. Reducing conditions are important for preserving organic compounds.

Table 1.27 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.4C and move towards understanding of water/rock/atmosphere interactions at the martian surface.

Table 1.27: Samples and measurements implied by Investigation Strategy 1.4C

mples identified to advance Investigation Strategy 1.4C:

- A suite of rocks or soils/paleosols representative of the range of depth and weathering, from most-altered to least-altered/unaltered parent material.
- Rocks formed under a variety of redox conditions, and especially those with evidence for sedimentation or mineral precipitation under reducing conditions.
- Mineral deposits (e.g., iron oxides, salts, carbonates) precipitated in chemical gradients (e.g., springs) or due to evaporation (e.g., ephemeral ponds), especially those with evidence for long-term buildup.
- Rocks with precipitated coatings or rinds.

Measurements identified to advance Investigation Strategy 1.4C:

- Measure variability in the mineralogy, chemistry (including identification and measurement of potential oxidants), mineral proportions and morphology of primary and secondary minerals and amorphous phases as a function of depth and/or degree of weathering, to constrain the duration of water interaction, water chemistry, water temperature, water residence time/drainage, and search for chemical trends that could be biosignatures.
- Analyze the chemistry and mineralogy of climate-sensitive minerals at nano-, micro-, and macro-scales.
- Measure the stable isotope compositions of secondary minerals to constrain the composition and history of atmospheric and crustal volatile sources .
- Measure radiometric ages of primary and secondary minerals with permissible mineralogy to determine ages of formation and diagenetic events.
- Determine the oxidation states of minerals to infer position of soils/paleosols relative to the paleo-water table, and exposure to reducing and oxidizing components (including photochemical).

Investigation Strategy 1.4D: Determine sediment provenance and transport history

Where they form in sedimentary units, paleosol samples serve a dual purpose as both records of chemical weathering and physical deposition of sediments)—there is an important connection in this area to Sub-objective 1.1 of this report. One of the biggest ongoing changes in our view of Mars is the recognition of the dominance of sedimentary processes over coherent bedrock (e.g., lava) on the surface. Recent investigations of the ancient southern highlands using morphology, thermal properties, and superposition relationships have shown that friable, layered rocks are much more common than previously thought (Edgett et al., 2016; Rogers et al., 2017), and when combined with known regional sedimentary layered deposits like Arabia Terra, Meridiani Planum, etc. (e.g., Malin & Edgett, 2001; Lewis et al., 2008; Noe Dobrea et al., 2010; Kerber et al., 2012), these observations suggest that Mars has had extremely active sedimentary cycle. However, the origins of the sediments themselves are not well understood. Detailed compositional and micromorphological analysis of returned sedimentary rock and modern sediment samples would help to constrain the origin and transport history of local sediments at the sampling location and more broadly on Mars.

Table 1.28 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.4D and move towards understanding of water/rock/atmosphere interactions at the martian surface.

 Table 1.28: Samples and measurements implied by Investigation Strategy 1.4D

Samples identified to advance Investigation Strategy 1.4D:

• A suite of rocks or soils/paleosols representative of the range of depth and weathering, from most-altered to least-altered/unaltered parent material.

Measurements identified to advance Investigation Strategy 1.4D:

- Analyze the microscale physical, chemical, and mineralogical properties of sediments to constrain transport history and determine the relative importances of physical and chemical weathering.
- Measure cosmogenic nuclides to determine exposure age and erosion rate.

UNDERSTAND A MARTIAN IGNEOUS SYSTEM	
Why is this objective critical?	<i>Key input into the mechanisms for formation of igneous rocks and the evolution of Mars on a planetary scale</i>
Which are the most important samples?	A suite of igneous rocks as diverse in composition and texture as possible. Both in situ (outcrop) and ex situ (float) sampling opportunities should be considered in order to maximize diversity.

1.5 Sub-Objective 1.5: Understand the essential attributes of a martian igneous system

1.5.1 Introduction and Current state of knowledge

Igneous rocks record the thermochemical evolution of a planet from its core to its atmosphere, and each rock type provides insights into the complexity of that history. In particular, basaltic rocks are a direct window into the planetary interior and provide constraints on the starting conditions for the isotopic composition of the atmosphere. Mars is fundamentally a basaltic planet: in situ compositional and mineralogical measurements on the Martian surface, combined with analyses of martian meteorites, indicate that most igneous rocks are lavas and volcaniclastic rocks of basaltic composition and ultramafic cumulates from basaltic magmas (McSween, 2015; Filiberto, 2017). However, alkaline and feldspathic igneous rocks have also been identified both in situ (e.g., Sautter et al. 2015), from orbit (e.g., Christensen et al. 2005; Rogers & Nekvasil, 2016), and in the meteorite collection (Nekvasil et al. 2007; Santos et al. 2015).

1.5.2 Key Open Questions for Sub-Objective 1.5

A key outcome of the comparison between the igneous rocks in the martian meteorite suite and those analyzed on the surface of Mars (e.g., by *Pathfinder*, MER and *Curiosity* rovers, or using orbital spectroscopy) is that the martian meteorites differ in elemental composition, age, isotopic composition, and inferred mantle source characteristics (Figure 1.17) and are thus not representative of the crust of Mars nor do they represent the isotopic compositions of the present day atmosphere (e.g., McSween et al. 2009; Filiberto et al., 2010a; Ehlmann et al., 2016; Villanueva et al., 2015; Stolper et al. 2013).

The dichotomy between the martian meteorites and the igneous rocks at the surface of Mars can be partially reconciled by our understanding of the impact-driven mechanism by which the meteorites are delivered from Mars to Earth (Head et al., 2002) and the bias that mechanism imparts towards more competent – i.e., younger, igneous – samples (Jones, 1989; Warren, 1994; Head et al., 2002; Walton et al., 2008). The shergottites, which are basaltic igneous rocks that crystallized as decameter-scale flows or shallow sills, are mostly late Amazonian in age (175 to 600 Ma); nevertheless, these rocks apparently tap mantle sources of varying geochemical characters that were established during the very early stages of differentiation of the martian mantle, by ~4500 Ma, probably through the crystallization of a magma ocean (e.g., Symes et al. 2008; Borg et al. 2016). The implication of this discovery is twofold: first, that the mantle of Mars has remained largely unmixed over most of its history, at least in the regions sampled by the shergottites (consistent with the lack of plate tectonic activity and the manifestation of convection via mantle plumes); second, that the mantle sources represented by the igneous rocks investigated at the surface of Mars (e.g., those investigated by Spirit and Curiosity rovers, which have estimated ages of ~3800 Ma) are distinct from those mantle sources represented by the martian meteorites. How the mantle inferred from the meteorites relates to the mantle inferred from the igneous rocks at the surface of Mars is a fundamental question in the geologic evolution of Mars (e.g., McCoy et al. 2011). Whether magma ocean crystallization is the default first-stage of terrestrial planet formation is an open and

fundamental question in planetary science and affects not only the lithosphere of a planet, but also the starting conditions for the atmosphere. Both of these questions can be addressed through return of igneous samples from Mars.

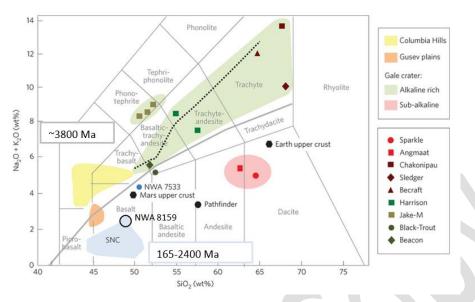


Figure 1.17: Comparison of the compositions of martian meteorites ("SNC") with igneous rocks investigated by rovers on the martian surface. NWA 7533 is a breccia more representative of the martian crust (paired with NWA 7034). NWA 8159 is a newly-recognized, augite-rich type that is 2400 Ma (Herd et al., 2017). Figure after Sautter et al. (2015).

 Table 1.29: Key open questions for Sub-Objective 1.5: Understanding martian igneous systems

KEY OPEN QUESTIONS: SUB-OBJECTIVE 1.5
Is the mantle of Mars as viewed from the shergottite meteorites applicable to all of Mars?
What is the diversity of igneous rock compositions? Have they changed over time?
What did the mantle of Mars look like > 3.5 Ga? Was metasomatism involved?

1.5.3 Why returned sample studies are important for Sub-Objective 1.5

Understanding the petrogenesis of igneous rocks sampled from well-documented locations within an igneous terrane would provide novel insights into the physical properties of martian magmas; the compositions of their mantle sources; the conditions of magma genesis; the timing, style, and duration of igneous activity; and the character and isotopic composition of volcanic emissions that would have been contributed to the martian atmosphere at the time of eruption.

As these diverse rock types can be related to different geodynamic settings, they provide important constraints on the geologic history of Mars. The geochemical composition of magmatic rocks is also required for experimental petrology studies that constrain the mantle composition, the conditions of melting, and subsequent magmatic evolution, as has been done previously for both martian meteorites and igneous rocks from Gusev and Gale (e.g., Filiberto et al., 2010b; Rapp et al., 2013).

Igneous rocks can probably provide a more definitive chronology than any other rock samples from Mars. With only one exception, the currently available martian meteorites are all igneous rocks (e.g., McSween, 2015; McCubbin et al., 2016a). However, they constitute a biased sampling of the igneous rocks on Mars, both in terms of geochemistry and age, their geologic contexts (sampling sites) are unknown, and they have been variably affected by shock metamorphism and terrestrial weathering (McLennan et al., 2012). Nevertheless, from them we can conclude that Amazonian magmatism has been reasonably well sampled. From these limitations, the prioritized list of most desirable igneous targets for sample return can be derived: Noachian and/or Hesperian probable age; relatively unaffected by shock or weathering; basaltic rocks likely representative of their parent magmas; igneous rocks that are more evolved (silicic and/or alkaline); and lavas that contain mantle xenoliths.

1.5.4 Sample Investigation Strategies to achieve Sub-Objective 1.5

The systematic exploration of an igneous terrane – for example, extrusive flows emanating from a vent – would involve the mapping and sampling of a range of igneous rock compositions. Sampling would likely need to occur over a wide area, given the sizes of igneous terranes on Mars (e.g., the Tharsis Montes, Hesperia Planum). One risk of this approach is that the suite of samples might not be meaningfully different from each other (e.g., similar ages, compositions, and textures), providing only a 'snapshot' of igneous activity at one point in Mars' history and in one location.

There are two approaches to the exploration of igneous rocks on Mars: maximize the compositional diversity by targeting loose boulders (e.g., as was done for igneous rocks at Gusev crater by the MER *Spirit* rover), and find igneous rocks still in place (i.e., in outcrop). While these two approaches may seem to be at odds with each other, the prioritization of the approach depends on the objective. Reconstructing the history of Mars as a planet, elucidating those processes that have affected the origin and modification of the crust, mantle and core (Objective 5) is best done with a diversity of igneous rock types for which knowledge of the source outcrop is not necessary. However, determining the evolutionary timeline of Mars, including calibrating the crater chronology timescale (Objective 3), would potentially involve locating an igneous rock which belongs to a previously-mapped unit with a known crater retention age. The latter approach is also necessary to provide radiometric age constraints on the deposition of interleaved sedimentary rocks included in the returned sample suite, and therefore context for the potentially life-hosting system being sampled (Objective 2).

As evidenced by previous rover missions (e.g., *Pathfinder*, *Spirit*, *Opportunity*, *Curiosity*), any landing site is likely to provide access to igneous samples as cobble- to boulder-sized rocks which have been removed from their original outcrops ("float" samples). While samples from *in situ* rocks are best (whether in the outcrop or proximal to it) for certain investigations (e.g., placing age constraints on the Mars timescale), these *ex situ* samples of opportunity would likely provide the compositional diversity required to constrain the time-resolved geodynamical evolution of Mars (e.g., Figure 1.18); any returned samples of igneous rock will be used to modify and expand existing models for the thermochemical evolution of Mars that were developed using data from martian meteorites and data returned from martian rover and orbital missions.

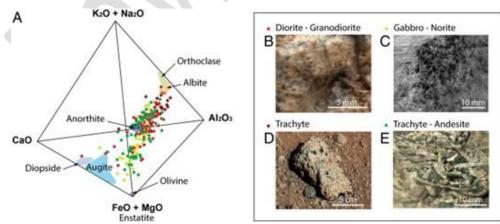


Figure 1.18: The 4 main types of igneous rocks found around Bradbury landing site (Gale Crater) (Sautter et al., 2016).

The following investigation strategy and 5 sets of measurements (Table 1.30) will enable the optimization of a suite of returned igneous samples from a given landing site, whether the samples are from rocks in place (in outcrop) or not (in float). Collecting samples of each rock type at a given

site is needed as a baseline to characterize the geology at that site. If igneous petrologic diversity exists at a site, or even within a specific sample (e.g., breccia clasts and xenoliths), examining the diversity from a geochemical and petrologic standpoint can provide important insights into the geologic processes that have operated at that site. Geochemical studies can be used to determine whether all the rocks are petrogenetically related and what processes relate them to each other, including magmatic differentiation and secondary alteration. Alternatively, if geochemical studies indicate that rocks are not related at a specifice site, it will indicate that the site hosts samples that are sourced from a wide catchment (e.g., through transport *via* impact or fluvial processes), and hence the igneous diversity can provide constraints on larger-scale global martian geochemical processes.

Investigation Strategies (IS) for Objective 1 Sub-Objective 1.5		
1	Geological environment(s)	Interpret the primary geologic processes that formed and modified the pre-Amazonian martian geologic record.
		the pre-Amazonian martian geologic record.
1.5	Igneous	Understand the essential attributes of a martian igneous system.
1.5	terrane	onderstand the essential attributes of a martial igneous system.
	Determine the co	ompositional and textural diversity of igneous rocks and the time-
IS 1.5A	resolved geologic	cal processes which relate them to each other and to martian
	meteorites.	•

 Table 1.30:
 Summary of sample-related investigation strategies to understand a martian igneous system.

<u>Investigation Strategy 1.5A</u>: Determine the compositional and textural diversity of igneous rocks and the time-resolved geological processes which relate them to each other and to martian meteorites.

Geochemical studies of igneous samples on Mars when coupled with studies of radiometric dating will help to identify any important correlations between bulk rock geochemistry and age. Broad changes in the geochemistry of magmatic liquids over time are expected as a planet evolves and cools. Moreover, if temporal changes in geochemistry are observed, they will provide important constraints on the thermochemical evolution of the martian mantle (e.g., potential mantle temperature, Fe/Si ratio, and volatile contents; Baratoux et al., 2011; Filiberto, 2017). In fact, temporal correlations between geochemical features in martian rocks have already been reported. For example, alkaline rocks are common in older terranes on Mars, and tholeiitic rocks occur in younger terranes (McSween, 2015; see also Figure 1.17). Currently, however, precisely measuring trace element abundances and isotope ratios can only be done in laboratories on Earth. Additionally, the oldest volcanic rocks at the surface of Mars appear to have equilibrated at much higher oxygen fugacity than more recent episodes of volcanism (Herd, 2003; Schmidt et al., 2013; Tuff et al., 2013). A suite of igneous rocks withages not represented among the martian meteorites will enable the determination of whether systematic variations in mantle source compositions and melting conditions have occurred over time (Filiberto et al., 2010b; Baratoux et al. 2011; Grott et al. 2013; McSween, 2015; Filiberto, 2017).

Table 1.31 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 1.5A and move towards understanding of martian igneous systems.



Figure 1.19: For igneous rocks, the lithologic, textural, and chemical diversity of the sample collection is far more important than collecting only rocks with known outcrop-scale context. There are multiple geological processes that could transport diverse rocks to places where the rover could sample them. Igneous sampling strategies need to encompass both *in situ* (in outcrop) and *ex situ* (transported) options. Image notes: Far left: Hawaii; Middle left: Low Ridge, Gusev (NASA/JPL-Caltech/Cornell/NMMNH); Middle right and Far right: Generic images from the web.

Table 1.31: Samples and measurements implied by Investigation Strategy 1.5A

Table 1.51. Samples and measurements implied by investigation strategy 1.5A
Samples identified to advance Investigation Strategy 1.5A:
 A suite of igneous rocks as diverse in composition and texture as possible, both in situ (outcrop) and ex situ (float).
Measurements identified to advance Investigation Strategy 1.5A:
 Measure variability in the mineralogy, texture, mineral proportions, and mineral chemistry (major, minor and trace element), and bulk compositions (major, minor and trace element, and radiogenic isotopes) of igneous rocks in order to classify them relative to other igneous rocks from Mars, and determine whether they represent primary mantle melts or melts affected by interaction with other mantle or crustal sources or components. Measure the compositions of any volatile-bearing minerals or melt inclusions, and the redox states of multivalent elements, in order to determine the conditions of magma genesis and crystallization (e.g., T, P, X, fO₂) for each silicate melt, and to elucidate any changes in conditions during crystallization (e.g., in oxygen fugacity and/or volatile content). Quantify the textures of igneous samples through crystal size distribution analysis and mineral mapping techniques, in order to determine their setting (e.g., intrusive or extrusive) and the conditions during magma ascent, emplacement, and solidification.
 Measure radiometric ages (e.g., U-Pb, Ar-Ar, Sm-Nd, Lu-Hf, Rb-Sr) of each igneous rock from as many systems as feasible in order to obtain crystallization ages.
 Measure stable isotopic compositions (e.g., O, S, Fe, Mg) of minerals and bulk rock samples in order to quantify primary igneous and secondary (e.g., alteration or other modification)

processes.

2 Objective 2: Assess and Interpret the Biological Potential of Mars

As discussed for Objective 1, Mars hosted a diverse array of environments that may vary widely in the type, abundance, and quality of biosignature evidence they retain. Efforts at life detection should be informed by assessments of (a) the nature and extent of habitability for a given environment, i.e., what conditions and processes supported or challenged life and over what timescales, (b) how might such environments have influenced the attributes of any biosignatures and also created nonbiological 'mimics' that would challenge their definitive identification, and (c) what conditions and processes enhanced preservation or degradation of biosignatures?

In describing Objective 2, we felt that the logic of the problem required that we break it down into sub-objectives (Table 2.1). However, unlike the sub-objectives of Objective 1, we expect that ALL of these would be achieved with returned samples. Objective 1 (previous chapter) addresses environmental habitability and some aspects of preservation—these are key inputs into the life question. Sub-Objective 2.1 acknowledges the central importance that carbon holds for life, both by shaping planetary environments and by creating the 'backbones' of biological molecules. Sub-Objective 2.1 addresses important carbon sources, planetary processes, environmental contexts and the abiotic mimics of biology, that is, the nonbiological "noise." Finding evidence of either past or extant life on Mars would be a watershed event. However, significant differences exist in the strategies, technologies, target environments, and forms of evidence that would be most appropriate in searching for ancient versus extant life. Sub-Objective 2.2 addresses the variety of substances, structures and patterns that constitute the known array of ancient biosignatures of past life. These features also might constitute evidence of extant life if they are found in geologically recent deposits. Sub-objective 2.3 is complementary to 2.2, in that it addresses additional biosignatures that could be sought as evidence of extant life. Thus, in certain respects, the analytic methodologies overlap between Sub-Objectives 2.2 and 2.3.

Objective 2	Life	Assess and interpret the biological potential of Mars		
Complete ALL of the following sub-objectives.				
Sub-Obj. 2.1	Carbon chemistry	Assess and characterize carbon, including possible organic and pre-biotic chemistry		
Sub-Obj. 2.2	Biosignatures- ancient	Assay for the presence of biosignatures of past life at sites that		
Sub-Obj. 2.3	Biosignatures- modern	Assess the possibility that any life forms detected are still alive, were recently alive		

 Table 2.1: Division of Objective 2 into Sub-Objectives

2.1 Sub-Objective 2.1: Assess and characterize carbon, including possible organic and pre-biotic chemistry

ASSESS AND CHARACTERIZE CARBON				
Why is this objective critical?	Understanding the martian carbon cycle in as much detail as possible is essential to understanding pre-biotic chemistry, habitability, the possibility of habitation, and the preservation of the evidence of all of the above.			
Which are the most important samples?	All of the samples collected as part of Objective 1 are of interest.			

2.1.1 Introduction and Current State of Knowledge

Evidence of habitability and habitation of Mars may be forthcoming by returning samples to Earth (McLennan et al., 2012). Clear objectives and associated choices of samples are essential to maximize the opportunities presented by returned samples. In the context of the solar system, the relative similarity of Earth and Mars generates an expectation of similar biochemistries for the two planets. We can confidently predict that any biochemical scaffolding on Mars would be based on carbon and any biochemical solvent would be based on water. To expect otherwise would require planetary conditions and chemistries (Taylor, 2011) that differ dramatically from those of either Earth or Mars. Reduced carbon is therefore a beacon for the potential discovery of evidence of life or prebiotic chemistry in a sample (Sephton and Botta, 2005). The Sample Analysis at Mars instrument suite onboard the Curiosity rover analysed Gale Crater mudstones and the detected inventory could contain the first potentially indigenous organic molecules on Mars. Chlorobenzene at 100s ppb levels and dichloroalkanes with up to four carbon atoms at 10s ppb levels were detected by heating up to < 400 °C (Freissinet et al., 2015). Diverse products including aliphatic hydrocarbons, thiophenes, and aromatic hydrocarbons were also detected at pmm levels in pyrolysis products of macromolecular components at 500 °C to 820 °C (Eigenbrode et al., 2018). In addition, oxidized forms of organic carbon (CO₂ and CO) with abundances ranging from ~200 to 2,400 ppm in Gale Crater lake sedimentary rocks have also been measured by *Curiosity* (Sutter et al., 2017). A similar range of organic C abundances in clay-rich seafloor sediments from the South Pacific Gyre is known to support microbial populations with cell densities of 10^3 to 10^5 cells g⁻¹ (D'Hondt et al., 2010, 2015). Yet the presence of reduced and oxidized carbon and organic compounds alone are not sufficient to indicate life. Reduced carbon has been found in meteorites from asteroids and from Mars (Table 2.3) and it is recognized that many non-biological processes produce concentrations of reduced carbon and even when present in organic structures the involvement of life is not conclusively indicated. Organic carbon-rich meteorites from asteroids (Grady et al., 2018) are good examples of the widespread nature of non-biological organic chemistry in the solar system (Sephton, 2013) and most organic materials in martian meteorites appear to indicate origins by non-biological processes, including; igneous, hydrothermal and impact based synthesis mechanisms (Steele et al., 2012; Steele et al., 2016). For example, trace levels (~ 4 to 130 ppb) of the straight-chain, amineterminal *n*- ω -amino acids glycine, β -alanine, γ -amino-*n*-butyric acid and δ -amino-*n*-valeric acid were identified in the martian meteorite RBT 04262 and were argued to be non-terrestrial in origin based on their unusual relative abundances and absence in proteints compared to known terrestrial occurrences (Callahan et al., 2013). For the amino acids detected in RBT 04262 there was no significant enantionmeric excess (a property believed to be fundamental to life) and all were likely to have been formed by non-biological Fischer-Tropsch-Type reactions at elevated temperatures either during igneous processing on Mars or during impact ejection of the rock from Mars. Martian meteorites provide an excellent reference for abiotic organic chemistry on Mars that can be compared to organic matter found in samples returned from Mars. Irrespective of the possible nonbiological origins of the organic materials in meteorites from asteroids and Mars the utility of organic carbon for known and potential inner solar system biochemistries ensures that it retains its status as a key indicator of life. Once detected, confirmation of an origin from life is then readily recognized by examining the detailed chemical nature and context of any organic carbon detected.

Table 2.2: Organic and inorganic carbon detected in samples of Mars, carbonaceous meteorites, Mars analogues on Earth and the Moon (simplified from Steininger et al. 2012 and references therein and updated using Agee, 2013; Steele et al. 2016).

Source	Sample	Organic carbon	Inorganic carbon (ppm)
Mars (in situ)			
Viking 1 &2	Soil	A few ppm	2–5 wt. % (?) MgCO₃
Phoenix	Soil	No definitive detection	3–5 wt. % CaCO₃
<i>Curiosity</i> Gale Crater	Aeolian sediments and sedimentary rocks (Cumberland mudstone)	Oxidized: 200-2,400 ppm Reduced: 300 ppb chlorobenzene; 70 ppb dichloroalkanes	< 0.7 wt. % carbonates
	14 specimens	Average: 18 (±26) ppm	
	Chassigny	Magmatic: 2.1 ppm	2.5 ppm C as carbonates
	Shergottites	Magmatic: Range: 2–110 ppm; Average: 4 ppm	?
Martian	Nakhla	Organic: ~ 150 ppm	188 ppm C as carbonates
meteorites	ALH84001	Magmatic: 13 ppm; Organic: 47 ppm	337 ppm C as carbonates
	RBT 04262	Reduced organics: ~4 to 130 ppb amino acids	
	NWA 7034	22 (±10) ppm	?
	СІ	3–5 wt. %	?
Other meteorites (not martian)	CM (mainly Murchison)	Macromol: ~ 1.5 wt.% C; Small organics: > 400 ppm	400–2000 ppm C as carbonates; 400 ppm diamond; 7 ppm SiC
	Micro-meteorites	10–12 wt. %	?
Moon			
	Soils and breccias	\sim 100 ppm (highly variable)	
Apollo sites	Rocks	Up to 50 ppm	
Earth			
Atacama	Soils	32 ppm	1414 ppm

2.1.2 Key Open Questions for Sub-Objective 2.1

How do Earth and Mars differ in their carbon reservoirs and fluxes? To understand Mars and its similarities and differences to Earth more completely is to understand its ability and likelihood of hosting life. Carbon on and in planets in the inner solar system is cycled through various reservoirs (Figure 2.1). On Earth those reservoirs are the atmosphere, hydrosphere, geosphere and, importantly, the biosphere. On Mars, carbon is or has been cycled through its atmosphere, hydrosphere and geosphere but the existence of a past or present biosphere is uncertain. There is no unambiguous evidence of past plate tectonic activity on Mars, stable surface water or biological activity, characteristics that may be connected owing to the interdependence of element recycling/resupply and Earth's biological activity. The fluxes and reservoir sizes reflect the functioning of the Earth's biogeochemical cycle and therefore contain stable carbon isotopic evidence (represented by δ^{13} C values) of biological activity. Discerning the effects of biology on a carbon cycle requires an understanding of what biology-free baseline values would be expected. For the martian carbon cycle, some insights have been gained from studies of martian meteorites (Grady & Wright 2006; Steele et al., 2016) and models (Hu et al., 2015) but much more work must be done to provide the background required to allow similarly detailed interpretations such as those made for the carbon cycle on Earth.

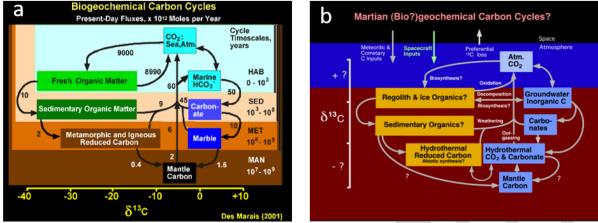


Figure 2.1: a) Earth's reasonably well-studied and understood carbon cycle (Des Marais 2001) and b) a hypothetical martian (bio?) geochemical carbon cycle, showing principal C reservoirs (boxes) in the mantle, crust, and atmosphere, and showing the processes (arrows) that might link these reservoirs (Des Marais, 2004). In a) the horizontal axis represents measured or calculated δ^{13} C values, while in b) the vertical axis at left represents the wide range of δ^{13} C values that might exist between mantle carbon and carbon in atmospheric and near-surface reservoirs whose δ^{13} C values have increased due to isotopic fractionation caused by atmospheric escape of C species.

How do Earth and Mars differences allow us to frame our investigations to detect martian life? As with comparisons of the carbon cycles of Earth and Mars, an appreciation of what biologyfree organic signals could be expected on Mars should be established. Any reduced carbon or complex organic molecules detected in samples from Mars should be extensivelt investigated for features that provide the ability to discriminate between non-life and life sources and, preferably, between an origin on Earth and Mars. For detecting life, the usefulness of organic carbon to biochemistry is in its ability to form complex and specific organic structures that perform certain functions including energy storage, structural roles and information carrying tasks. Recognizing the organic signatures of life is therefore an achievable goal if preservation has taken place (e.g., Killops & Killops, 2005). For discriminating provenance on Earth and Mars, one approach is to seek evidence of detailed chemical adaptions to the different environments. Although based on carbon and water the biochemical similarities between organisms on Earth and Mars would not be expected to be exact. Our terrestrial examples of environmental adaptations reveal substantial biochemical variations that reflect ecosystem diversity and the challenges and opportunities presented by the host environment (Sephton & Botta, 2005) and, we could expect similar recognizable biochemical adaptations for any life on Mars.

 Table 2.3: Key open questions for Sub-Objective 2.1: Assessment and characterization of martian carbon

KEY OPEN QUESTIONS: SUB-OBJECTIVE 2.1
How do Earth and Mars differ in their carbon reservoirs and fluxes?
How do Earth and Mars differences allow us to frame our investigations to detect martian life?
How and why do the controls on preservation of organic carbon vary between Earth and Mars?
How might the probably punctuated and geographically limited nature of organic carbon on
Mars affect our ability to determine DBS on returned samples?
What is the nature of potential organic bacteriomorphs on Mars compared to Earth, and what
are the strategies to be utilized to separate real from fake PBSs?

2.1.3 Why returned sample studies are important for Sub-Objective 2.1

To investigate the martian carbon cycles thoroughly and to interrogate any molecular indicators of non-biological or biological processes, returning samples to Earth is a powerful strategy. In situ analyses on planets and ex situ measurements following the return of samples to Earth seek to achieve the same objective and are complementary methods. In situ activities on Mars represent a practically unlimited amount of sample accessed by limited analytical facilities. MSR delivers a finite amount of sample to a wide range of laboratories with the most sophisticated and comprehensive analytical techniques available. Moreover, once on Earth curational practices ensure that returned samples are never exhausted, with diminishing sample mass potentially offset by continuous future analytical innovation and improvement. Returned samples are managed so that they are the gift that keeps giving: a good example of returned, curated and professionally distributed lunar material was provided by the Apollo missions (Allen et al., 2011). The number of publications in the literature from the Apollo effort is substantial and demonstrate the great and sustained benefit possible from sample return missions (Crawford, 2012). The Apollo experience indicates that the scientific rewards from returned samples substantially enhance those from in situ activities. For missions such as MSR the advantages are likely to be more enhanced when compared to the Apollo experience. The characterization of organic materials in samples of Mars that are expected to be present in trace amounts of sample return will benefit from access to analytical techniques that will never be space-compatible due to restrictions in weight, size and the need for complex sample preparation. For example, the use of organic solvents for extracting organic molecules from the crushed rock material is a key component for organic analysis on Earth. Because of environmental conditions on Mars, such as low surface pressure, these protocols are very hard to mimic on Mars. Even if one of these extraction protocols could be made Mars-compatible, the full range of protocols used on Earth involving many different solvents, which needed for extracting the full divesity of organic molecules, will never be available on Mars.

2.1.4 Sample Investigation Strategies to achieve Sub-Objective 2.1

Four investigation strategies and 10 sets of measurements are defined to elucidate the nature of carbon chemistry on Mars. These strategies must enable a comprehensive characterization of any inorganic and organic carbon present. The nature of the organic carbon must also be fully revealed by effective assessments of its detailed molecular architecture, its stable isotopic composition and its association with its host environment (Table 2.4).

Investigation Strategies (IS) for Objective 2 Sub-Objective 2.1					
2	Life	ife Assess and interpret the biological potential of Mars.			
2.1	Carbon	Assess and characterize carbon, including possible organic and pre-biotic			
2.1	chemistry	chemistry.			
IS 2.1A	Develop as complete an inventory as possible of the organic molecules present in the				
15 Z.1A	samples, as well as any oxidized carbon compounds.				
IS 2.1B	Determine isotopic fractionation between organic matter and carbon-bearing minera				
13 2.10	such as car	such as carbonates.			
IS 2.1C	Establish the indigeneity of any detected analytes.				
IS 2.1D Identify any aspe		y aspects of the environment potentially conducive to the existence and			
15 2.10	preservation of prebiotic chemistry and amenable to detection.				

 Table 2.4:
 Summary of sample-related investigation strategies to understand martian carbon chemistry

<u>Investigation Strategy 2.1A:</u> Develop as complete an inventory as possible of the organic molecules present in the samples, as well as any oxidized carbon compounds.

Investigation strategy 2.1A attempts to measure the presence, concentration, and characteristics of carbon in both oxidized and reduced forms on Mars. On our Earth, biogeochemical cycling transfers carbon between oxidised (e.g., carbon dioxide in our atmosphere and carbonate

rock in our geosphere) and reduced reservoirs (e.g., the biosphere, carbonaceous rocks in the geosphere). The varying oxidation states of the carbon reservoirs on Mars provide context for assessing the mechanisms of carbon cycling on the planet and whether biological activity is a driver for the flux of material between reservoirs. Reduced carbon reservoirs (e.g., Figure 2.2) may contain organic matter and that acts as a repository of information-rich molecular architectures that reveal synthetic mechanisms and therefore origins, including a potential variety or biological and non-biological processes (Summons et al., 2014).

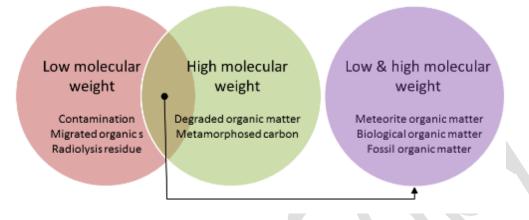


Figure 2.2: Molecular weight combinations commonly observed for organic matter assemblages and some possible interpretations (Sephton et al., 2014).

The examination of the co-association of organic matter relative to known mineral catalysts enables recognition of *in situ* and non-biological formation of organic matter. For example, the Fischer-Tropsch synthesis involves the conversion of carbon monoxide or carbon dioxide to hydrocarbons to produce a Schulz-Flory distribution, a steep decrease of relative abundance for hydrocarbons with increasing molecular weight (Salvi & Williams-Jones, 1997). Thermal metamorphism of carbonates alone can produce low molecular weight hydrocarbons alongside characteristic inorganic products such as calcium oxide and iron oxides (Giardini & Salotti, 1969), and when carbonates and graphite react methane can be produced (Holloway, 1984). Methane in the presence of serpentine (McCollom & Seewald, 2001) may imply the production of hydrogen, from the hydration of olivine, which then combines with carbon dioxide to produce methane (Abrajano et al., 1990). The relative abundances of organic compounds are also a source of useful information. In the terrestrial biosphere a predominance of either short or long chain fatty acids or their diagenetic product alkanes can reveal the influence of marine or land plants respectively (e.g., Killops & Killops, 2005). Analogous environmental signals may be detectable in collected samples that record a martian biosphere.

Table 2.5 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.1A and move towards understanding of martian carbon chemistry.

- Samples from environments listed in Objective 1 which contain organic matter in concentrations significantly above average. Especially samples obtained from below the surface
- Igneous rocks that have the potential for habitability or abiotic synthesis especially those inferred to have been recently exposed.
- Regolith.

Measurements identified to advance Investigation Strategy 2.1A:

- Measure the presence, concentration, and characteristics (e.g., redox state) of inorganic carbon including oxidized carbon (e.g., as carbonate) and reduced carbon (e.g., as graphitic or graphite-like carbon).
- Measure the presence, concentration and characteristics of simple and complex molecules and polymers containing C, H, N, O, P, Cl and S (organic carbon), and characterize organic matter features, including molecular structures (e.g chirality etc.), abundances and/or molecular weight distributions.
- Determine co-association of, and context for, organic matter relative to known minerals, especially mineral catalysts that produce organic material from C₁ gases.
- Measure cosmogenic nuclides to determine integrated surface exposure age and erosion rate.

<u>Investigation Strategy 2.1B:</u> Determine isotopic fractionation between organic matter and carbonbearing minerals such as carbonates.

Investigation strategy 2.1B seeks to identify where variations in zero-point energies for stable isotopes have led to fractionation of those isotopes in chemical reactions. Commonly the lighter stable isotope is more reactive than the heavier stable isotope and is used preferentially in chemical reactions. The overall stable isotope ratio of pooled reaction products is often different from those of the starting materials and the degree of difference, known as the fractionation, reflects the specific reaction taking place and, the relative sizes of the reservoirs. Enzyme-drived stable isotope fractionations associated with biochemistry can be used as diagnostic indicators of biological activity and help to distinguish biological organic products from their non-biological counterparts. The Fischer-Tropsch type reaction is one example of a prebiotic mechanisms that displays modest fractionations.

Table 2.6 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.1B and move towards understanding of martian carbon chemistry.

Table 2.6: Samples and measurements implied by Investigation Strategy 2.1B

Samples identified to advance Investigation Strategy 2.1B:		
• Samples listed from environments listed in Objective 1 that contain carbon (either oxidized or		
reduced) in concentrations significantly above average.		
Measurements identified to advance Investigation Strategy 2.1B:		
• Measure stable isotopic compositions (e.g., of C, H, N, O, P, S, Cl) in organic compounds in context with known isotopic pools.		

Investigation Strategy 2.1C: Establish the indigeneity of any detected analytes.

Investigation strategy 2.1C seeks to identify false positives and false negatives associated with contamination. The abundance of organic molecules and other carbon phases in martian samples can be expected to be low (Table 2.3) and can be easily overprinted by terrestrial organic compounds and carbon phases originating from sample collection on Mars, sample handling, and

contamination of samples by terrestrial organisms. Previous studies of martian meteorites have shown colonization of terrestrial organisms (Steele et al., 2000; Toporski & Steele, 2007). Even with the greatest care in sample management it is likely that some contamination will take place (Summons et al., 2014). Therefore, previous and current missions to Mars have established highest acceptable levels of allowed terrestrial organic contaminants (expressed as both total organic carbon (TOC) and individual compound classes) (Summons et al., 2014). Other important tools for tracking potential organic terrestrial contamination during sample collection and handling are witness plates and contamination knowledge for common terrestrial contaminants.

Similarities between carbon chemistry on Mars and Earth would make discriminating between the two sources difficult. Various ways have, however, been developed to in order determine if carbon phases found in martian samples are indigenous or later introductions. One important tool is to the D/H ratio of any organic carbon, which for martian material has been shown to be well above terrestrial values (Owen et al., 1988). Further diagnostic information may be forthcoming from organic matter-mineral associations that imply indigenous processes rather than the general addition of contamination. For example, a homogenous distribution of an organic compound, commonly found on Earth, such as polycyclic aromatic hydrocarbons, across a surface containing heterogeneous mix of minerals, would strongly suggest the addition of terrestrial contaminants (Stephan et al., 2003).

Table 2.7 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.1C and move towards understanding of martian carbon chemistry.

 Table 2.7: Samples and measurements implied by Investigation Strategy 2.1C

Samples identified to advance Investigation Strategy 2.1C:

- Samples from environments listed in Objective 1 which are found to contain carbon and reference materials of all material and substances that could have been contact with samples.
 Measurements identified to advance Investigation Strategy 2.1C:
- Evaluate the indigenous nature of any detected carbon and organic molecules. Rule out terrestrial sources of carbon and organic molecules.

<u>Investigation Strategy 2.1D:</u> Identify any aspects of the environment conducive to the existence and preservation of organic chemistry and amenable to detection.

Organic-carbon based records require suitable conditions for their preservation. The preservation of organic matter is a well-studied subject in Earth environments and it is recognized that oxidation is the major degrading mechanism that can remove signatures diagnostic of provenenance, making discrimitaion progressively more difficult and eventually impossible (e.g., Figure 2.3). On Earth, an association with fine-grained minerals protects organic matter by excluding oxidants (Tyson, 1995). Adsorption on mineral surfaces also makes organic matter less available for oxidation and the high surface areas of fine-grained minerals provide additional protection (Keil et al., 1994). Other minerals that can promote organic preservation include sulphates (Aubrey et al., 2006), iron oxides (Parenteau et al., 2014; Lewis et al., 2018), and silica (Westall et al., 2011). The matrices in which organic compounds, including biosignatures are preserved vary in their resilience; unstable matrices include ice or salts while silica or phosphate are highly resistant (Farmer & Des Marais, 1999).

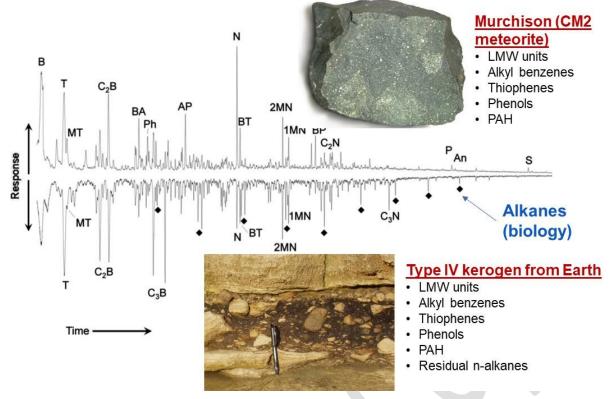


Figure 2.3: Detailed side-by-side comparison of total ion currents of pyrolysis products (600 °C, single step) of degraded but ultimately biological type IV kerogen, and Murchison, a type CM2 carbonaceous chondrite. The key responses from the non-biological organuc matter in the meteorite are also present in data from the degraded biological type IV kerogen. Yet, some discernable biogenic character remains in the type IV kerogen (e.g., presence of alkanes (\blacklozenge) and isomeric arrangements for substituted benzenes (C₂B and C₃B). Image after Mathewmann et al. 2013 Astrobiology, 13, 324-333.

If present, organic matter associated with both non-life and life processes could be expected at the surface of Mars where biological production, meteoritic infall or *in situ* synthesis can occur. Once present at the surface of Mars, organic matter would be subjected to processes that lead to its degradation. The martian surface is exposed to multiple radiation types. UV photolysis has been shown to be an effective destroyer of organic matter in the Atacama Desert on the timescales of martian days but mineral hosts such as calcite, calcium sulfate, kaolinite and clay minerals can provide protection from photolysis and promote preservation (Ertem et al., 2016). Ultraviolet radiation driven photochemistry has also been shown to produce oxidized minerals (Klein, 1978) including perchlorate (Carrier & Kounaves, 2015). Photolysis in the presence of minerals can accelerate the degradation of organic matter owing to catalytic processes. Minerals containing ferrous iron (dos Santos et al., 2016), magnesium oxide and forsterite (Fornaro et al., 2013) lead to reduced half-lives for biologically relevant organic compounds in UV irradiation experiments.

One way to acquire samples unaffected by oxidation and irradiation is to search for samples that have been recently delivered from the subsurface by natural processes such as impacts (Cockell & Barlow, 2002). Yet, this apparent advantage comes at a cost and organic preservation can be frustrated by the impact ejection process. High impact-related pressures appear to introduce sample bias where long chain hydrocarbon structures are degraded relative to aromatic structures (Montgomery et al., 2016). Degradation of organic signals can also occur during the analysis of samples. To date all *in situ* life detection missions to Mars have utilized thermal procedures to isolate organic matter from samples (Biemann et al., 1977; Mahaffy et al. 2012). Unfortunately, oxidizing minerals such as perchlorates (Mahaffy et al., 2012) and sulfates (Lewis et al., 2015) decompose during heating to release oxygen that promotes combustion of any organic matter present. The return of samples to Earth will provide opportunities to avoid oxidation-related

analytical issues. It should also be noted that prebiotic chemistry is unlikely to survive in a nascent or established biological world. Prebiotic organic compounds would be exploited by existing organisms, a consequence that was recognised by Charles Darwin who stated that such compounds would be instantly devoured (Darwin & Darwin, 1887).

Table 2.8 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.1D and move towards understanding of martian carbon chemistry.

Table 2.8: Samples and measurements implied by Investigation Strategy 2.1D

Samples iden	tified to advance	Investigation	Strategy 2 1D.
Sumples luell	lijieu lo uuvunce	Investigation	Strutegy 2.1D.

 Rocks of any type (including samples listed in Sub-objective 1-1) that have been recently exposed (and thus protected from radiolysis until recently), especially those whose formation age predates the cessation of the planetary magnetic dynamo.

Measurements identified to advance Investigation Strategy 2.1D:

- Identify potential components of pre-biotic chemistry (e.g., prebiotic organic carbon compounds, reactive phosphorous, etc.
- Identify the association of any organic carbon relative to known mineral catalysts and catalysis pathways.
- Assess organic inventory for similarity to known abiotic processes such as Strecker synthesis or Fischer Tropsch type reactions.
- Measure cosmogenic nuclides to determine surface exposure age and erosion rate.

2.2 Sub-Objective 2.2. Assay for the presence of biosignatures of past life at sites that hosted habitable environments and could have preserved any biosignatures

ASSAY FOR THE PRESENCE OF BIOSIGNATURES OF PAST LIFE	
Why is this objective critical?	The search for life is one of the driving objectives for
	Mars exploration in general, and sample studies are
	an essential component of astrobiology strategy.
Which are the most	All of the samples collected as part of Objective 1 are
important samples?	of interest.

2.2.1 Introduction and Current State of Knowledge

Seeking life beyond Earth is one of the great endeavors of humankind. It pushes us to probe frontiers of knowledge, space and time toward understanding our origin and whether we are alone in the Universe. Mars has long been identified as most Earth-like among the planets. Indeed, there is now strong evidence that Mars was likely to have been habitable early in its history (Objective 1), when water was present on its surface at the same time as life was taking hold on Earth. This knowledge from earlier discoveries has fueled interest in exploring for a fossil biosignature record in ancient martian terrains.

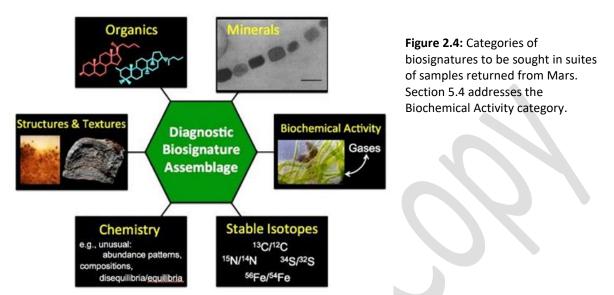
A biosignature (a "definitive biosignature") is an object, substance and/or pattern whose origin specifically requires a biological agent (Des Marais, 2008; M-2020 SDT, 2013). One key example is complex organic molecules and/or structures whose formation and abundances relative to other compounds are virtually unachievable in the absence of life. A potential biosignature is an object, substance and/or pattern that might have a biological origin and therefore compels investigators to gather more data before reaching a conclusion as to the presence or absence of life. The usefulness of a potential biosignature is therefore determined not only by the probability that life created it but also by the improbability that nonbiological processes produced it. Accordingly, because habitable planetary environments could create nonbiological features that mimic biosignatures, these environments must be characterized to the extent necessary to provide a context for scientific interpretations (Objective 1).

Our concepts of biosignatures and life are inextricably linked. To be useful for exploration, biosignatures must be defined in ways that not only tie them to fundamental attributes of life, but that also allow them to be measured and quantified. Universal attributes of life on Earth include its complex interacting physical and chemical structures, its utilization of free energy and the production of biomass (both organic structures and inorganic mineral phases) and wastes, and phenomena that can be sustained through self-replication and evolution. However, because of selective preservation we cannot expect all of the universal attributes of life to be expressed in ancient planetary materials. Useful biosignatures must be both preserved and amenable to detection (Hays et al., 2017). These can be broadly organized into three categories: physical, biomolecular, and metabolic (Westall et al., 2015a). Examples of physical features include individual cells and communities of cells (colonies, biofilms, mats) and their fossilized counterparts (mineralreplaced and/or organically preserved remains). Biological products within minerals and rocks often display increased morphological complexity by orders of magnitude relative to inorganic precipitates, allowing recognition of biosignatures through textural analysis of sample materials. Another physical example is biominerals, which are inorganic mineral structures that serve a functional use (e.g., magnetosomes in magnetotactic bacteria). Molecular biosignatures are those structural, functional, and information-carrying organic molecules that characterize life forms (e.g. on Earth these include lipids, proteins and nucleic acids). Metabolic biosignatures are characteristic imprints upon the environment of the processes by which life extracts energy and material resources to sustain itself – e.g., rapid catalysis of otherwise sluggish reactions, isotopic discrimination, mineral formation influenced by biological activity, and enrichment or depletion of specific elements. Significantly, examples can be found of abiotic features or processes that can resemble biological features in each of these categories. However, finding a suite of independent features can provide more robust evidence of biology. In addition, biologically mediated processes are distinctive due to their speed, selectivity, and a capability to invest energy into the catalysis of unfavorable processes or the handling of information. These processes can create features that can in turn be recognized as having biological origins.

Earth and Mars are quite similar in terms of planetary conditions and chemistries, in comparison to, for example, gas giants or icy moons. This similarity suggests that differences in life forms that originated independently on the two bodies would likely occur at a secondary, rather than first-order level, and therefore are not likely to differ at the fundamental levels of biochemical scaffolding (alternatives to carbon), or required solvent (alternatives to water). However, differences from terrestrial life become increasingly possible, and ultimately probable, with increasing levels of biochemical specificity (e.g., nucleic acids and peptides). Indeed, considering that on Earth, before LUCA (the Last Universal Common Ancestor) there was probably an RNA world, and maybe even a Pre-RNA world, several of the fundamental primitive biomolecules, especially nucleic acids, might have been different from the current ones. Such possible primitive biomarkers might also be taken into account when analyzing martian samples.

Highly diagnostic biosignatures recognized in studies of terrestrial systems, commonly represent extremely specific attributes of biochemistry (e.g., specific lipids or particular sequences of amino or nucleic acids in the case of molecular biosignatures), morphology, or processes. Although such specific markers of life would be unquestionably valuable if detected on Mars, the likelihood that the same markers (e.g., the same specific choices of biomolecules) would arise through an independent origin and elaboration of life seems low (nothwithstanding the potential for evolutionary convergence). Even though life detection strategies for Mars should ideally allow for the detection and characterization of Earth-like biosignatures, the highest priority should be given to approaches and methods that define and seek biosignatures in the broad, universal sense.

The types of currently recognized biosignatures are examples of objects, substances and/or patterns whose origins specifically require biological processes, and they can occur over a range of spatial scales (e.g., Farmer, 1999). The M-2020 SDT (2013) report identified the following categories of biosignatures: organic biomolecules, stable isotopic patterns, minerals, chemicals, and macroscale and microscale fabrics and structures (e.g., stromatolites, microfossils). Active biological processes are an additional category (see Section 5.4) - *Viking* mission's life detection experiments searched for these processes (Klein, 1978). Figure 2.4 indicates the six categories of biosignatures to be sought during the MSR campaign.



2.2.2 Key Open Questions for Sub-Objective 2.2

The search for biosignatures on Mars must address the array of important issues outlined above. Biosignatures must reflect fundamental attributes of life as we currently understand it. These include complex interacting biophysical and biochemical structures, the utilization of free energy, the production of biomass and wastes, and phenomena that can be sustained through selfreplication and evolution. To be useful for exploration, biosignatures must also be measurable and quantifiable, for example, as physical structures, substances, patterns, or combinations of these attributes. But habitable planetary environments can create nonbiological features that mimic biosignatures, and some environmental processes can alter or destroy them. Yet other processes can preserve biosignatures. Accordingly, we must characterize the environmental attributes, both past and present, of potential sites of exploration in order to evaluate their potential for preserving any biosignatures and to inform our scientific interpretations. The following table identifies the key questions that arise from these considerations.

Table 2.9: Key open questions for Sub-Objective 2.2: Assay for the presence of biosignatures of past life

KEY OPEN QUESTIONS: SUB-OBJECTIVE 2.2

What processes are key for preserving, altering or destroying any martian biosignatures?What are the attributes of physical structures that could be interpreted as biosignatures?What are the attributes of substances that could be interpreted as biosignatures?What physical, chemical and isotopic patterns could be interpreted as biosignatures?

2.2.3 Why returned sample studies are important for Sub-Objective 2.2

As has been learned from studies of the early fossil record on Earth, field analysis requires detailed laboratory follow-up to confirm potential biosignatures in early Archean rocks (4000–3200 million years ago, Ma), as various post-depositional processes often have obscured or may even

have destroyed signs of life (e.g., Brocks & Summons, 2004; Djokic et al., 2017). Indeed, evidence for Archean-age life is often equivocal and contentious (e.g., Brasier et al., 2002; Schopf et al., 2002; Brasier et al., 2005; Marshall et al., 2011; Schopf et al., 2012; Nutman et al., 2016; Dodd et al., 2017). Compelling arguments can only be made by use of multiple lines of evidence that include geologic and paleoenvironmental contexts, high magnification imagery in thin sections, and in situ geochemical analyses (e.g., Westall et al., 2011; Muscente et al., 2018). Returned samples from Mars would allow for such analyses to be performed that would otherwise not be possible using the rover instruments, although as noted, the M-2020 instrument suite will provide essential context for the cached samples. While Mars had a different geologic history compared to that of Earth, the same is likely to be true of any potential biosignatures discovered by future rovers or human-led missions to Mars. In other words, proof of martian life, if it ever existed, will only emerge from discoveries made in laboratories on Earth. The broadest, most rigorous investigations of potential biosignatures (PBS) can only be achieved in Earth-based laboratories (Figure 2.5). This seems required before the scientific community is inclined to accept any potential biosignatures as definitive biosignatures. State-of-the-art laboratory instrumentation typically requires sophisticated sample preparation techniques that, in turn, require initial lab-based observations that guide the selection and adaptation of these techniques.

State-of-the-art analyses are required to investigate fully the following potential attributes of samples: 1) preservation and degradation ("taphonomy") of microscale features; 2) Organic molecular structures – including their relative abundances, diastereoisomeric and structural isomer preferences, chirality, etc., all down to subnanomole abundances; 3) Stable isotopic abundance patterns within molecules and between molecules, compound classes and minerals – down to nanomole abundances; 4) Mineral diversity and trace element contents – down to submicrogram abundances; 5) Rock fabrics (and biological?) structures – from submicron to centimeter scales; 6) Inorganic chemistry – microscale compositional and spatial patterns.

Potential biosignatures in early Earth paleoenvironments require multiple lines of evidence to be accepted by the scientific community as definitive biosignatures. Accordingly, a single prepared sample often must be shared between multiple laboratories and analytical instruments in order to achieve the most definitive interpretations.

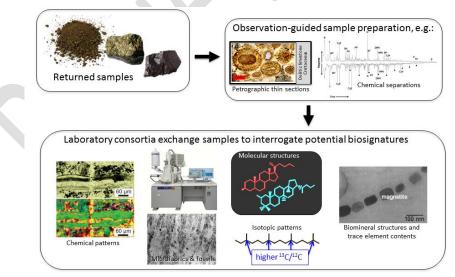


Figure 2.5: Potential biosignatures can be investigated thoroughly only by observation-guided sample preparation, followed by investigations by laboratory consortia that apply state-of-the-art techniques.

2.2.4 Sample Investigation Strategies to achieve Sub-Objective 2.2

To be useful for exploration, potential biosignatures must be both measureable and quantifiable. For each of the categories indicated in Figure 2.4, the potential for the observed

features to be biological varies significantly over a broad range of observations. For example, any observation of sedimentary reduced carbon could be biological in origin and thus would be regarded as a potential biosignature. Although the presence of such a deposit alone is not diagnostic of a biological origin, different types of observations could distinguish biotic from abiotic organic matter with varying degrees of confidence. For example, molecular compositions, chirality, molecular patterns, along with other potential biosignatures such as complex morphology, may provide an extremely high level of confidence, based on Earth-analog settings (Summons et al., 2011; Westall et al., 2011, 2015a). Ideally tests for biogenicity would be based on multiple lines of evidence at a given site explored by rovers equipped for sample caching and return. The potential for biosignature preservation needs to be evaluated for each paleoenvironment targeted for analysis because the processes that determine high quality preservation vs. modification or destruction of a particular signal vary with category, rock type, environment, and post-depositional history (see Section 4.5).

All the investigations in this section would make use of the sample suite(s) identified as part of carrying out Objective 1, particularly those samples having a high probability of having preserved organic molecules with relatively high fidelity. We have identified six investigation strategies and 18 sets of measurements to assay for the presence of biosignatures of past life at sites that hosted habitable environments and could have preserved any biosignatures (Table 2.10).

Table 2.10: Summary of sample-related investigation strate	egies to assay for possible biosignatures of a	ancient
martian life		

Investigation Strategies (IS) for Objective 2 Sub-Objective 2.2		
2	Life Assess and interpret the biological potential of Mars.	
2.2	Biosignatures-	Assay for the presence of biosignatures of past life at sites that hosted
2.2	ancient	habitable environments and could have preserved any biosignatures.
IS 2.2A	Characterize aspects of the environment that are conducive to the preservation or	
13 Z.ZA	degradation of biosignatures.	
IS 2.2B	Determine the presence and nature of any organic potential biosignatures.	
IS 2.2C	Characterize any patterns of stable isotopic abundances that might indicate biological	
processes.		
IS 2.2D	Identify any minerals that might indicate biological processes.	
IS 2.2E	Identify any morphological evidence of life.	
IS 2.2F	Identify any chemical evidence of life.	

<u>Investigation Strategy 2.2A</u>: Characterize aspects of the environment that are conducive to the preservation or degradation of biosignatures.

To the extent that sediments, cements, and other surface materials have escaped alteration after their formation, they can preserve information about earlier environmental conditions and, potential biosignatures (Summons et al., 2011). Certain minerals and rock types (e.g., silica, carbonates, phosphates, phyllosilicates, evaporite minerals, etc.) are particularly conducive to preservation (e.g., Farmer & Des Marais, 1999). Preservation can be compromised by weathering and erosion or by alteration *in situ* by oxidation, radiation, heating, and migrating fluids (Summons et al., 2011). For example, on Earth, nearly all portions of hydrothermal systems may be inhabited by microbial life, although preservation of an enduring geological record in "deep time" (hundreds of millions to billions of years old) depends on the intersection of favorable and sometimes fortuitous factors (e.g., Guido & Campbell, 2011; Sillitoe, 2015; Westall et al., 2015b).

This investigative component addresses preservation quality of potential biosignatures. Post-depositional diagenesis and geological activity have significant impacts on whether biosignatures are expected to be pristine, or whether they have been modified and could still be distinguishable. For example, microbial macro-textures commonly are preserved in siliceous and calcareous hot-spring deposits on Earth. However high quality, micro-scale preservation of biosignatures – producing convincing fossil biosignatures – depends on timing of mineralization (e.g., early silicification (Campbell et al., 2015a, b, and references therein; Djokic et al., 2017), type of overprinting (e.g., acidic fluids with drop in phreatic level, or regional late silicification), and whether late diagenetic processes have been local or regional in extent (e.g., Walter et al., 1996; Guido and Campbell, 2009, 2011, 2017). Mapping the diagenetic stage (e.g., Lynne and Campbell, 2003; Jones and Renaut, 2007), textural quality, and geochemical concentrations of relevant minerals and elements – at the microbial scale (e.g., Westall et al., 2015a, b) – may be achieved with key returned samples.

Because of Mars' thin atmosphere and absence of a global magnetic field, cosmic radiation affects the preservation of organic biosignatures that have been situated within a few meters of the surface for tens of millions of years or longer (Pavlov, 2014). Accordingly, samples should be sought that have been stored more deeply for most of their history, and their status should be validated by measuring cosmic ray exposure ages.

Table 2.11 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2A and move towards an assay of possible biosignatures of ancient martian life.

 Table 2.11: Samples and measurements implied by Investigation Strategy 2.2A

Samples identified to advance Investigation Strategy 2.2A:	
All samples collected as a part of Objective 1 are of interest.	
Measurements identified to advance Investigation Strategy 2.2A:	
• Determine the presence of phases (e.g., silica, carbonates, phosphates, phyllosilicates,	

- evaporite minerals, etc.) that are conducive to preservation.Identify evidence for post-depositional diagenetic alteration of sedimentary or hydrothermal
- deposits.
 Measure cosmogenic nuclides to determine surface exposure ages and erosion rates.

<u>Investigation Strategy 2.2B</u>: Determine the presence and nature of any organic potential biosignatures.

As the major component of living tissue, organic matter is likely to retain diagnostic evidence about the nature of carbon-based reactions on Mars. Concentrations of organic matter, especially in environments in which organic compounds are exposed to oxidative processes, imply a replenishment mechanism that might be biological (Lovelock, 1975). Biology uses enzyme-driven reactions to generate organic entities that are biochemically useful while non-biological reactions are rarely as specific in the generation of their products. One celebrated example of organic specificity is amino acid homochirality, where biology on Earth is dominated almost exclusively by one enantionmeric form (Bada & McDonald, 1996).

Diagnostic organic molecules (biomarkers) are probably the most definitive category of biosignatures. Anomalously high relative abundances of specific organic molecules in a rock might constitute evidence of a biological origin. For example, our biosphere is dominated by membrane fatty acids having sixteen and eighteen carbon atoms. Similar membrane lipids on Mars may reveal the influence of life. Detailed analyses of organic molecular structures can reveal information concerning the taxonomic affinities of ancient biota (with varying degrees of specificity), their physiologies, the environmental conditions that prevailed in the depositional environment and the thermal maturity of the host organic matter (Killops & Killops, 2005). Important organic molecules indicative of life (especially if associated with other biosignatures such as morphological structures) include proteins, nucleic acids (DNA and RNA) for extant life and amino acids, sugars, porphyrins, nucleobases and lipids for both extant and extinct life (Engel & Macko, 1993). For some molecules, for example amino acids and fatty acids, the presence of the molecules themselves does not represent conclusive evidence for life and it is necessary to look at distributions of the molecules (e.g., Killops & Killops, 2005; Georgious & Dreamer, 2014). Such distributions include chain-length

preference in lipids (increased intensity of even over uneven fatty acids and uneven over even alkanes) and homochirality of sugars and amino acids. For example, life on Earth uses left-handed (L) amino acids and right-handed (D) sugars. Some organic molecules have currently no known way of being abiotically produced. Important biomarker groups include membrane lipids such as hopanoids, sterols and archaeols, and their diagenetic products. Additional biosignatures include the molecular distribution of organic molecules combined with the isotopic signature of specific molecules. Ecosystems can be delineated by the presence of domain-specific organic compounds with recognizable evolutionary advances in biosynthetic processes. Our terrestrial biosphere recorded such advances with isoprenoid, hopanoid and steroid lipids reflecting Archaea, Bacteria and Eukarya and their progressively complex biosynthetic pathways, and may therefore be used for taxonomical assignments of these domains. (e.g., Killops & Killops, 2005; Des Marais & Jahnke, 2018). Effective measurements of the relative abundances of organic compounds will be facilitated by sample return, owing to the higher sensitivity and resolution of Earth-laboratory based systems.

Another organic biosignature identifiable in terrestrial and potential returned martian rocks is the association of organic carbon with the surfaces of volcanic sedimentary particles or volcanic rocks. Chemotrophic microorganisms colonise these kinds of surfaces: lithotrophs extract nutrients from them and obtain energy from redox reactions at their surfaces, sometimes leaving tell-tale corrosion tracks (Thorseth et al., 2003). Under favorable circumstances, such as abundance of nutrients, once moribund, they will be colonised in turn by organotrophs (Thorseth et al., 2001). They can be preserved *in situ* as a carbon coating on the surfaces of the particles, which can be encapsulated in a mineral cement and thus preserved. Thus, association of organic carbon with the kind of detrital particle or mineral surface that is metabolically useful for microbial metabolism could be considered as an interesting signature to be further explored further with *in situ* high resolution techniques. Examples exist from the early Earth in which volcanic particles were colonised and corroded by microbes and rapidly preserved by silicification (Westall et al., 2011b, 2015b; Foucher et al., 2010).

Table 2.12 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2B and move towards an assay of possible biosignatures of ancient martian life. Objective 2.1 presents additional details regarding diagnostic molecular attributes and gives examples of relevant measurement techniques.

Table 2.12: Samples and measurements implied by Investigation Strategy 2.2B

Samples identified to advance Investigation Strategy 2.2B:

• Samples from environments listed in Objective 1 that contain appropriate mineral assemblages, especially those which contain organic carbon in concentrations significantly above average.

Measurements identified to advance Investigation Strategy 2.2B:

- Measure the abundances of organic macromolecules and smaller molecules and characterize their attributes, including molecular structures, abundances and/or molecular weight distributions.
- Measure the relative abundances of species containing C, H, N, O, P and S.
- Evaluate the spatial relationships between organic matter and minerals and volcanic particles, especially such minerals that are compositionally and morphologically associated with biological activity or catalytic activity on Earth (e.g., Fe oxides and sulfides).
- Evaluate the relationship of potentially biogenic minerals and their associated organic material to the history of the host rock.
- Evaluate measurements of chemical and isotopic compositions of organic compounds to determine their conditions of formation and to seek evidence of chemical equilibria or disequilibria that are inconsistent with abiotic processes, and thus would be indicative of biological activity. Examples include widespread amino acid homochirality.

<u>Investigation Strategy 2.2C:</u> Characterize any patterns of stable isotopic abundances that might indicate biological processes.

Patterns of stable isotopic ratios within suites of substances can indicate conditions of formation and alteration (e.g., Shaheen et al., 2014, Williford et al., 2015) and provide evidence of chemical equilibria or disequilibria that is inconsistent with abiotic processes and thus might indicate biological activity (e.g., Hayes, 2001). The sulfur isotope and oxygen triple isotope compositions of sulfates and any sulfide minerals can be diagnostic, as can the carbon isotopes and the triple oxygen isotopes in carbonates (e.g., CaCO₃, MgCO₃, FeCO₃). The isotopic abundances of metals whose redox state can be affected by biological processes (e.g., Beard et al., 1999) are also informative.

The ${}^{13}C/{}^{12}C$ values of bulk organic matter are a summation of its individual molecular components (Hayes, 2001). Some of the most dramatic examples of isotopic discrimination are associated with the enzyme directed reactions. Differences in stable isotope ratios of elements can be used, therefore, as potential indicators of biological processes. The ¹³C/¹²C values of biological organic matter are determined by a series of processes (Figure 2.6) as follows: (i) the ¹³C/¹²C value of the carbon source, (ii) isotopic discrimination associated with the assimilation of carbon, (iii) isotopic discrimination associated with metabolism and biosynthesis, and (iv) partitioning of carbon isotopes at branch points in the metabolic reaction network (Hayes, 1993). The accumulated fractionations can lead to ${}^{13}C/{}^{12}C$ values of biomass and individual biochemicals that are distinctly lower than that of the carbon source by predictable and measurable amounts. Stable isotopic fractionation can also lead to relationships between individual organic compounds that reflect metabolic and biosynthetic processes that are detectable using compound specific isotope ratio methods. On Earth, $^{13}C/^{12}C$ patterns between organic phases and carbonates, and between individual organic and inorganic carbon compounds reflect contributions by phototrophs, chemotrophs and microbial diagenesis (Des Marais, 1994, Williford et al., 2015). These patterns are distinct from patterns in non-biological organic matter such as those found in carbonaceous meteorites in which the range of ${}^{13}C/{}^{12}C$ values is much greater (Sephton & Gilmour, 2001).

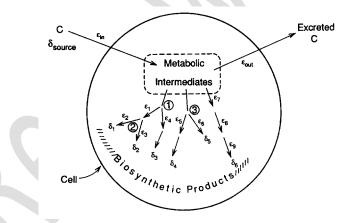


Figure 2.6: A schematic representation of the stable carbon isotopic fractionations associated with biological processes (Hayes 1993). Kinetic isotope effects are indicated by " ϵ ," stable isotope ratio values are represented by " δ " and branch points in carbon flow are indicated by numbers in circles.

Examples of methods for carbon-bearing minerals and other inorganic phases include isotope mass spectroscopy (MS) and laser spectroscopy; these should be able to target individual minerals and other phases. Examples of relevant methods for organic matter include MS, gas chromatography-MS, and laser spectroscopy. High resolution isotope ratio mass spectrometrey is one of the best tool for identification of isotopic fingerprints of biological molecules. Additionally, site specific isotopic patterns of C, O, and N that are characteristic of biomolecules are currently measurable only for samples that are returned to Earth-based laboratories. Table 2.13 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2C and move towards an assay of possible biosignatures of ancient martian life.

Table 2.13: Samples and measurements implied by Investigation Strategy 2.2C

Samples identified to advance Investigation Strategy 2.2C:		
All samples collected as a part of Objective 1 are of interest.		
Measurements identified to advance Investigation Strategy 2.2C:		
 Measure patterns of stable isotopic compositions of carbon-bearing minerals and other 		

- Measure patterns of stable isotopic compositions of carbon-bearing minerals and other inorganic phases.
- Measure isotopic compositions of bulk organic matter and also patterns of isotopic abundances between organic compounds and within individual compounds.

Investigation Strategy 2.2D: Identify any minerals that might indicate biological processes.

Minerals form as products of local chemical and physical conditions, and more than 5300 minerals have been formally recognized (see <u>http://rruff.info/ima</u> for a recent list). This vast array of crystalline compounds indicates diverse modes of formation - consequences of diverse physical, chemical, and/or biological environments. For example, because some carbon-bearing minerals probably occur exclusively as a result of biological activity, they represent promising biosignatures on Earth and possibly elsewhere. Suites of oxidized weathering minerals formed through oxidizing weathering following the Great Oxidation Event, therefore they are likely to be examples of more widespread potential biosignatures. Quoting from Hazen et al. (2008): "Biological processes began to affect Earth's surface mineralogy by ...~3.85–3.6 Ga, when large-scale surface mineral deposits ... were precipitated under the influences of changing atmospheric and ocean chemistry... Multicellular life and skeletal biomineralization irreversibly transformed Earth's surface mineralogy... Biochemical processes may thus be responsible, directly or indirectly, for most of Earth's ... known mineral species."

Minerals and volcanic particles should be sought that, on Earth, are compositionally and morphologically associated with biological activity or catalytic activity (e.g., carbonates, sulfur minerals, phosphates, phyllosilicates, transition metal oxides, etc.), relative to the rock's texture and any organic carbon. Mineral assemblages can document the constituents and environmental conditions that accompanied the formation of a geological deposit. These assemblages also reflect the processes that subsequently altered the rock and thereby provide insights into the history of local crustal environments. Relevant measurement methods include XRD, electron microscopy and IR spectroscopy. Table 2.14 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2D and move towards an assay of possible biosignatures of ancient martian life.

Table 2.14: Samples and measurements implied by Investigation Strategy 2.2D

Samples identified to advance Investigation Strategy 2.2D:

- All samples collected as a part of Objective 1 are of interest. Measurements identified to advance Investigation Strategy 2.2D:
- Detect individual minerals and map the spatial arrangements between minerals in formerly habitable environments.
- Determine the relationships between potentially biogenic minerals and the history of the host rock.

Investigation Strategy 2.2E: Identify any morphological evidence of life.

There exists a variety of morphological evidence for life that include, going from the macroscopic to the microscopic scale: (1) microbially-induced or influenced structures and textures, such as certain sinter textures, as well as clotted fabrics produced by chemotrophic colonies (thrombolytic textures), (2) biofilms, (3) microbial colonies, and (4) microbial cells. Different

analytical approaches are needed depending upon the spatial scale of the feature. Thus, the search for biosignatures would entail cataloging of spectral signatures in aqueous sedimentary rocks/minerals at a site, followed by selection of areas for targeted *in situ* observations that could produce spatially integrated maps of mineralogy and macro- and microtextures. Such mapping would help to evaluate whether facies (i.e., environmental) models of Earth's aqueous sedimentary systems provide appropriate analogs for analogous deposits on Mars.

A recent example at the macroscopic scale highlighting this approach is illustrated by study of the hydrothermal opaline silica deposit discovered by *Spirit* rover in Gusev crater (Squyres et al., 2008), which contains unusual, knobby, digitate structures inferred as a morphological PBS (Ruff et al., 2011). Comparison with siliceous hot-spring deposits (sinter) at El Tatio geothermal field in Chile reveal close similarities with respect to textures and mineral spectra (Ruff & Farmer, 2016), thereby strengthening the environmental framework and interpretation of the possible biotic nature of the structures. In particular, the knobby silica features at El Tatio constitute microstromatolites, entombing bacterial filaments within spring-derived hydrothermal silica (Figure 1.7). In analogous features forming in New Zealand hot springs, even the fine siliceous laminae that alternate with similar filamentous horizons to those at El Tatio have been shown to be biological in origin, produced by rapid silica cementation of microbially excreted EPS (exopolymeric substance) (Handley et al., 2005, 2008).

Volcanic sediments in hydrothermal environments on the early Earth provide other examples of morphological evidence of the type of anaerobic, chemotrophic life forms that we expect on Mars. For example, several cm-thick nutrient-rich layers of hydrothermally-fed volcanic sediments from the 3.33 Ga Josefsdal Chert, Barberton Greenstone Belt exhibit a clotted, thrombolitic, carbonaceous texture, visible at the macroscopic and microscopic scales. The features are caused by heavy microbial colonization of volcanic particles (Westall et al., 2015a, b). *In situ* elemental, carbon and mineral mapping documents the close association of organic carbon with the volcanic particle surfaces, showing at the same time irregularities in the surface coatings that could not be produced by abiotic processes. In this case, individual cellular fossils were not preserved. However, microbial colonization of volcanic particle surfaces from more oligotrophic environments (*i.e.* poorer nutrient resources) in the 3.45 Ga Kitty's Gap Chert, Pilbara Greenstone Belt, was much weaker and the individual microbial cells were well-preserved by rapid silicification from the silicasaturated Archean seawaters (Westall et al., 2011b). In the latter case, judicious gentle corrosion of the chert rock was necessary to expose the < 1 µm cells, many of which exhibit cell division and cell lysis.

While the macroscopic textures could be observed *in situ* on Mars, it is clear that the microscopic textures and the *in situ* organo-geochemical investigations discussed above can only be made in a terrestrial laboratory. Table 2.15 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2E and move towards an assay of possible biosignatures of ancient martian life.

 Table 2.15: Samples and measurements implied by Investigation Strategy 2.2E

Sa	imples identified to advance Investigation Strategy 2.2E:
•	All samples collected as a part of Objective 1 are of interest.
M	easurements identified to advance Investigation Strategy 2.2E:
•	Evaluate mounding and layers for indications of past biological activity. Microbial fabrics and mesoscale biolaminated sedimentary structures (e.g., stromatolites) can persist in rocks even after chemical biosignatures have been lost through oxidation, radiation or heating. Characterize microscale or macroscale rock or mineral fabrics and structures. For example, microbial biofilms can alter the chemistry and physical properties of sediments. Use thin sections and rock chips to search for microscale or macroscale rock, mineral or carbonaceous fabrics and structures that are consistent with formation or fossilization of biological entities (e.g., microbial biofilms and microbialites), but inconsistent with chemical or abiotic processes.
•	Evaluate the possibility of molds or other types of impressions (casts) or associated geochemical signals that may indicate past biological activity or organic matter which may now have vanished, including mineralogically replaced fabrics that may have once been microbially produced.
•	Characterize mineral surfaces and interiors to search for physical evidence of metabolic activity (e.g., pits and trails), especially where associated with redox gradients. Such features can indicate the former presence of endolithic microorganisms and communities (e.g., Friedmann, 1993; Reid et al., 2000; Foucher et al., 2010). Trace fossils (e.g., movement trails) could indicate microscale dissolution textures due to "mineral mining" by bacteria. Use microscopy to image mineral surfaces and interiors to search for physical evidence of

- metabolic activity (e.g., pits and trails), especially where associated with redox gradients.
 Undertake hyperspectral analysis of rock sample surfaces to investigate changes in organic
- carbon content, water content and mineralogy that may point to biological activity.
- Undertake high resolution, in situ investigation of textures and structures that may be related to fossilized microbial biofilms, colonies and cells.

Investigation Strategy 2.2F: Identify any chemical evidence of life.

The major elements in living organisms are carbon, hydrogen, oxygen, nitrogen, sulfur and phosphorus (Figure 2.7). Some elements, e.g., metals, are present in smaller amounts but have essential roles, while others have no significant roles. Post burial processes transform biological organic matter to geological residues with much less nitrogen, oxygen and, eventually, hydrogen (van Krevelen, 1950). The relative abundances of elements can therefore indicate the possible presence or former presence of biological organic matter and can be used to assess post-mortem processing steps that degrade any original biological signal. Biological activity can alter the chemical composition of its surroundings as it acquires energy *via* redox reactions or chemical building blocks by altering inorganic phases. Such patterns can indicate conditions of formation and alteration and also might provide evidence of chemical equilibria or disequilibria that is inconsistent with abiotic processes and thus might indicate biological activity.

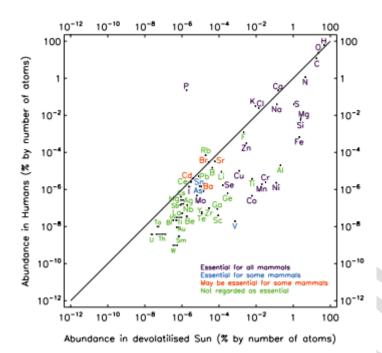


Figure 2.7: The abundances of elements in biological organisms (in this case humans) and the devolatilized Sun (Chopra & Lineweaver, 2008). Carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus are the major elements in living organisms.

Table 2.16 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.2F and move towards an assay of possible biosignatures of ancient martian life.

 Table 2.16: Samples and measurements implied by Investigation Strategy 2.2F

of interest.

Table 2.10. Samples and measurements implied by investigation strategy 2.21			
Samples identified to advance Investigation Strategy 2.2F:			
All samples collected as a part of Objective 1 are of interest.			
Measurements identified to	advance Investigation Strategy 2.2F:		
• Fe oxide or Fe sulfide p	• Fe oxide or Fe sulfide precipitates (e.g., framboids).		
• Fe or Mn redox fronts.			
 Fractures, vugs, vesicles sulfates, clays, oxides). 			
• Zones enriched in mine	rals formed by leaching or in situ transformations.		
Crystallographic structu	res and major- and minor-elemental abundances of individual phases.		
• Abundance patterns of			
compositions.			
• Example methods include XRD, raman spectroscopy, NMR, and TEM.			
2.3 Sub-Objective 2.3. Assess the possibility that any life forms detected are still alive, or were recently alive			
ASSAY FOR THE PRESENCE OF BIOSIGNATURES OF PRESENT LIFE			
	The search for life is one of the driving objectives for		
Why is this	Mars exploration in general, and sample studies are		
objective critical?	an essential component of astrobiology strategy.		
Which are the most	All of the samples collected as part of Objective 1 are		

important samples?

2.3.1 Introduction and Current State of Knowledge

Ancient Mars was more hospitable to life than it is today. Approximately 3.5 billion years ago, Mars' early atmosphere created warmer wetter conditions, enabling liquid water to flow on the surface (Hurowitz et al., 2017). Today, the martian environment is less conducive to life. It has a thin atmosphere and temperatures fluctuate wildly, averaging approximately -60°C and ranging from - 125°C to 20°C. Radiation bombards the surface. Because life on Mars is more likely to have existed in the hospitable past than under current conditions, the formal life-related objective of the Mars 2020 sample-collecting rover is to seek signs of extinct life.

Recent but debated discoveries suggest that liquid water may flow on Mars, either on the surface or directly beneath it (McEwen et al., 2011; Martin-Torres et al., 2015; Ohja et al., 2015; Dundas et al, 2017; Webster et al. 2018), opening the possibility that life may exist on modern Mars. If life arose on early Mars, it either adapted to the current extreme conditions or went extinct (Ulrich et al., 2012). To determine whether life is capable of survival and growth on modern Mars, investigations typically focus on extremophile isolates or microbial communities in analogous environments such as permafrost. Some extremophiles and spore-forming organisms from Earth can survive under simulated martian conditions or in space (Morozova et al., 2007; Onofri et al., 2015; Mickol & Kral, 2017). However, the subset of organisms capable of metabolic activity or replication is much smaller. Some heterotrophic organisms metabolize and/or divide under simulated martian conditions (de Vera et al., 2014; Nicholson et al., 2013; Schuerger et al., 2013), but they are not realistic model organisms because organic substrate is likely absent or extremely limited on the surface or subsurface. Chemolithoautotrophs (organisms that harness inorganic substrates for energy, electrons, and biomass) are more realistic model organisms.

There is evidence that some of Earth's chemolithoautotrophs—methanogens in particular can metabolize and divide in Mars simulation experiments (Chastain & Kral, 2010; Kral et al., 2013, 2016; Sinha et al., 2017). Metabolically active microbial communities exist in some Antarctic permafrost locations (the Earth analogue that best reflects conditions on Mars) (Bakermans et al., 2014; Faucher et al., 2017), but not in others (Goordial et al., 2016). The coldest, driest, and most oligotrophic Antarctic permafrost holds evidence of life (DNA), but not metabolic activity (Goordial et al., 2016). Together these data suggest that it may be possible for Earth microbes to grow in martian conditions, though we are nearing their cold, dry, and oligotrophic limits. However, for life exposed to these conditions for eons, it may be possible to evolve to survive, metabolize, and grow in such conditions. Together, these data show approximated Mars conditions represent Earth life's survival limits, but also suggest that life on Mars may be possible.

'Special Regions' are defined as places with sufficient water activity (0.5-1, where 0 is completely dry and 1 is pure water) and temperatures (\geq -25 °C) to have the potential to support the reproduction of terrestrial organisms (Rummel et al., 2014; MEPAG Special Regions Review, 2017). Exploration results from Mars to date show that most of Mars is not Special, and have been unable to identify with certainty any place that is Special. However, there are some places for which the data are insufficient to determine whether the environment is Special or not—for the purpose of Planetary Protection, these sites are treated as if they were Special until adequate data can be obtained. If Special Regions exist on Mars, we could speculate that extant martian life prefers them as a habitat, and therefore that they would be a good place to take samples to seek evidence of indigenous life. However, there are no known Special Regions anywhere on Mars, and no known potential Special Regions considerations will not apply to the M-2020-prepared sample collection.

2.3.2 Key Open Questions for Sub-Objective 2.3

The probability of discovering extant life at the martian surface (including by means of MSR) is generally considered to be low. However, its discovery would be so profound that it would shake the pillars of science. It would yield insight into the very fundamentals of life such as what are the

basic universal properties of living systems (Goldenfeld et al., 2017) and how life evolves. Should evidence for recent or extant life be discovered, we outline the following key open questions:

Table 2.17: Key open questions for Sub-Objective 2.3: Assay for the presence of biosignatures of present life

KEY OPEN QUESTIONS: SUB-OBJECTIVE 2.3	
What are life's universal requirements?	
Is the path to the emergence of life a universal phenomenon?	
How does martian life conduct the processes we presume are necessary for all life?	
Do life on Mars and Earth share a common ancestor?	

We necessarily base our assumptions about life's universal requirements on our understanding of life on Earth. We think that the most common life forms in the Universe and potential lifeforms on Mars must (i) be based on carbon, hydrogen, nitrogen, oxygen, phosphorus, sulfur and bio-essential metals (C, H, N, O being among the 6 most common elements in the Universe), (ii) require liquid water, (iii) use, transport, or store energy, (iv) have the ability to organize (e.g., create and maintain a cellular system), (v) regulate and repair its systems, and (vi) undergo adaptive evolution (NRC, 2007; Popa, 2015). The discovery of life on Mars would allow us to test those assumptions, possibly uncover novel ways in which these processes can be carried out, and identify the commonalities between life on Earth and Mars that may be universally required for the existence of life. It is difficult to overstate the magnitude of the impact such an important discovery would have, which is one of the significant reasons for returning the samples to Earth at substantial public expense.

2.3.3 Why returned sample studies are important for Sub-Objective 2.3

In order to investigate samples adequately for evidence of extant or recent life, detection analysis should be based on multiple independent investigative pathways and not limited to a specific feature (Figure 2.8). We cannot predict with any accuracy life's form and characteristics, whether it would be viable (Figure 2.9), or whether it shares a common ancestor with life on Earth. No single approach is sufficient for detecting and characterizing life given the potential variables. Thus, to account for these uncertainties, multiple approaches conducted in terrestrial laboratories are key to the successful detection of possible life in a sample. While the rover has limited capacity to house analytical equipment, returned samples can be analysed in a wide range of Earth's most sophisticated state-of-the-art laboratories. Beyond enabling access to many investigation strategies, returning the samples to Earth will circumvent another hurdle imposed by the limited capacity of a rover—sample handling. Many of the recommended investigation strategies require optimization based on sample physicochemistry and multi-step processing requiring close human attention. By way of example, we show the steps in extracting and sequencing DNA, which can change based on salt content, pH, and chemical composition, and requires multiple steps including cell lysis, DNA purification, preparation of DNA for sequencing, and the sequencing itself (Figure 2.9). Pre-decisional – For planning and discussion purposes only.

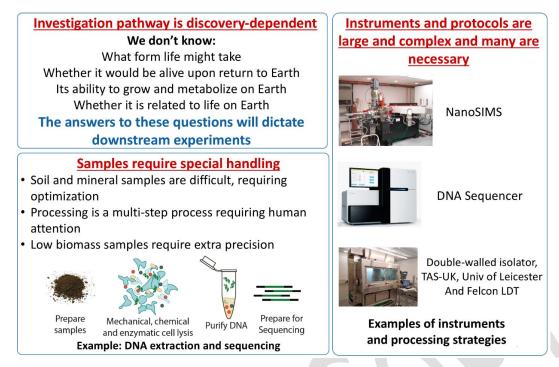


Figure 2.8: Factors necessitating returned samples to search for evidence of extant life. The search for extant life will only be possible through multiple techniques, most of which are not adaptable to the rover because of involved sample handling requirements and limitations on the size, weight, and complexity of analytical equipment.

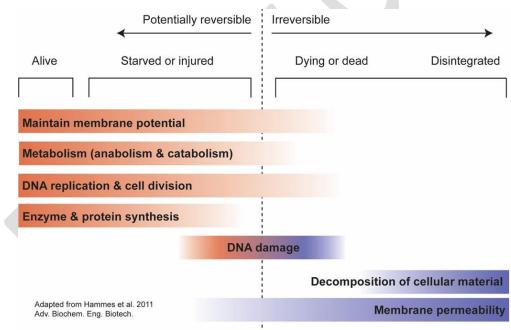


Figure 2.9: Stages of cell viability and the corresponding cellular processes. In returned samples, life may be found at varying stages of viability. Multiple analysis pathways should be followed so that evidence for life can be detected at any of the stages. Figure adapted from Hammes et al (2011).

2.3.4 Sample Investigation Strategies to achieve Sub-Objective 2.3

Life detection analyses should be based on a broad definition for life and an approach for detecting life not limited by the specific features of life, as we know on Earth. So far, no detailed methods and procedures for the detection of extant extraterrestrial life forms have been defined. A draft protocol for the identification of biohazards in martian samples was formulated in 2002 (Rummel et al., 2014) and a workshop report about life detection in martian samples was published

in 2014 (Kminek et al., 2014). All investigations rely on several assumptions about the properties we presume to be common to all life. A subset of the investigations will only be successful at detecting Mars life if it shares a common ancestor with Earth life due to travel on meteorites or space debris, whereas other suggested investigations are based on more general characteristics of living entities. Detecting and characterizing life in extreme environments on Earth is a common research goal, so some of the life detection analyses proposed for Mars return samples are modeled on terrestrial methods (Figure 2.10).

It is important to consider that the sample size of material used for destructive life detection should be appropriate to give significance to the results and assurance that life is or is not present. But it will also be necessary to preserve an amount of material for further scientific investigations, so biological assays that require small quantities are highly preferable if the results will be meaningful. Analytical methods for life detection can be divided into those that facilitate a wide survey of a representative portion of different sample types, and those that facilitate a more focussed, but highresolution, examination:

- Survey methods are less destructive of samples, and include microscopy, broadband fluorescence, surface scanning and chemistry, tomography, and isotopic measurements. These methods seek structural and basic chemical signatures, and local inhomogeneities.
- Higher resolution methods are generally more destructive, and include mass spectroscopic methods, combustion, DNA extraction, isotope analysis, and electron microprobe procedures for elemental mapping. These methods seek to characterize inhomogeneities and more complex structures, and are discussed below in further detail.

Summarizing, all the cited studies, as well as others of the same type not shown in this report, propose a list of techniques suitable for life detection, and contain extra input their applications, efficiencies, and limits. Nevertheless, a general, critical approach that compares and ranks the effectiveness of proposed techniques must still be developed.

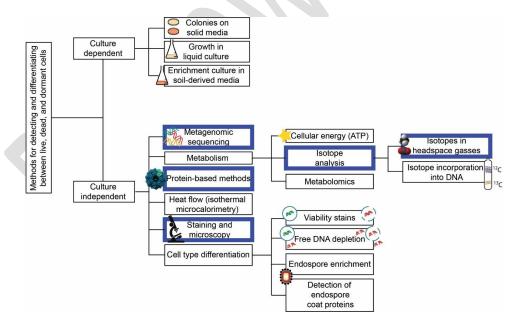


Figure 2.10: Common methods for detecting and differentiating between live, dead, and dormant cells in terrestrial samples. A subset of investigations recommended for initial investigations into Mars return samples are outlined in bold. Figure adapted from Emerson et al (2017).

We have identified four investigation strategies and 7 sets of measurements to assess the possibility that any life forms detected are still alive, or were recently alive (Table 2.18).

	Investigation Strategies (IS) for Objective 2 Sub-Objective 2.3		
2	Life Assess and interpret the biological potential of Mars.		
2.3	Biosignatures-	Assess the possibility that any life forms detected are still alive, or	
2.5	modern	were recently alive.	
	As part of developing a complete inventory of the organic molecules present, assess the		
IS 2.3A	presence and characteristics of molecules that are diagnostic of organisms that are		
	either alive, or were recently alive.		
IS 2.3B	Assess the possibility of metabolism and respiration.		
IS 2.3C	Assess the possibility that organisms within the sample are capable of reproduction in		
15 2.30	culture experiments.		
IS 2.3D	Exclude the pos	sibility of contamination with terrestrial life or terrestrial organics as a	
15 2.30	possible explanation for the data.		

 Table 2.18:
 Summary of sample-related investigation strategies to assay for possible extant martian life.

<u>Investigation Strategy 2.3A</u>: As part of developing a complete inventory of the organic molecules present, assess the presence and characteristics of molecules that are diagnostic of organisms that are either alive, or were recently alive.

Some mission objectives targeting extinct and extant life will overlap--many of the diagnostic biosignatures of ancient life apply to all life. However, there is a subset of these biomarkers that, if discovered, would provide strong evidence for extant (or recent) life. After death, cellular material decomposes into smaller fragments lacking distinctive features--their biological origins become unrecognizable (Westall et al., 2015a). In the search for extinct life, the best organic biomarkers are those that are stable in harsh environmental conditions, such as hopanes, isoprenoids, steranes, porphyrins, straight-chain hydrocarbons, long-chain fatty acids (Martins, 2011). In contrast, lower-stability molecular markers such as some proteins (e.g., ATP, NAD, phosphoenolpyruvate, cyclic AMP, coenzyme A), chiral amino acids, and nucleic acids are signatures of recent life (Aerts et al., 2014; Roling et al., 2015).

The short-term survivability of DNA means that its detection would be strong evidence of recent life. This investigative avenue is feasible only if life on Mars and Earth share a common origin and thus share DNA as genetic material. However, should this be the case, DNA sequencing throws open a window that would enable us characterize Mars life and its evolutionary history at a detailed level without the need for cultivation or further experimentation. In the fossil record on Earth, DNA persists on the order of tens of thousands of years (Noonan et al., 2005, 2006) and (in exceptional circumstances) hundreds of thousands of years (Orlando et al., 2013, Dabney et al., 2013)—a short period on the evolutionary timescale. Claims of DNA persisting for over a million years have been met with skepticism and are thought to stem from modern contamination (Vreeland et al., 2000; Graur and Pupko, 2001; Penney et al., 2013; Santiago-Rodriguez et al., 2014; Weyrich et al., 2014). The integrity of the DNA molecule (not just the presence or absence) also contains age-related information. Metabolically active cells repair DNA damage. In the absence of repair machinery that exists in a living cell, damage accumulates and DNA becomes fragmented (Dabney et al., 2013). Therefore, the extent of the damage (i.e. the size of the fragments) is an indicator of when life existed at a specific sampling location.

If DNA is discovered, in depth characterization would be conducted using an experimental system termed metagenomics, which is the process of isolating and sequencing all DNA directly from an environmental sample. Though metagenomics requires that life shares DNA as a common hereditary molecule, it does not rely on cultivation, nor does it rely on *a priori* DNA sequence information. Only minute amounts of input DNA are required for metagenomic analysis. Prior to sequencing, DNA is amplified through polymerase chain reaction. This makes the metagenomics approach attractive for Mars samples, which will likely be low biomass. On Earth, this has been done on low-yield samples from old and/or extreme environments such as Lake Vostok in Antarctica

(D'Elia et al., 2008; Knowlton, 2013), ancient permafrost (Mackelprang et al., 2017; Rivkina et al., 2016), and ancient hominid remains (Noonan et al., 2005; Noonan et al., 2006).

Unless Mars was recently seeded with Earth life, it should be phylogenetically different from modern life, either having diverged from the tree of life prior to the most recent common ancestor to life on Earth or showing a deep-branching evolutionary relationship (Figure 2.11). On Earth, environmental samples yield many sequences that do not match anything in sequence databases and repositories. These data are collectively referred to as 'microbial dark matter.' We expect the same phenomenon in martian DNA but to a much greater extent. However, there are common features and cellular machinery that all DNA-based life must share. These include ribosomes, DNA repair enzymes, and transcription/translation machinery. The genes encoding these proteins, enzymes, and RNAs are remarkably well conserved across all domains of life and will be the basis for evaluating the evolutionary history of life on Mars and determining how it is related to life on Earth. Analysis of other DNA sequences may yield insights into the metabolic and physiological functions and strategies. Though we expect that most sequences will be unidentifiable, those that show homology to known sequences will yield important insights.

Table 2.19 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.3A and move towards an assay of possible biosignatures of present martian life.

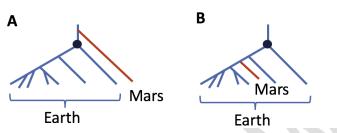


Figure 2.11: A) Expected evolutionary relationship between life on Mars and Earth in the scenerio where they share a common ancestor. B) Expected phylogenetic tree in the case where Mars return samples are contaminated with DNA from Earth organisms.

Table 2.19: Samples and measurements implied by Investigation Strategy 2.3A

Samples identified to advance Investigation Strategy 2.3A:

- All samples collected as a part of Objective 1 are of interest.
- Measurements identified to advance Investigation Strategy 2.3A:
- Measure the presence of biochemical species, especially pigments, proteins, DNA, RNA, lipids etc.

Investigation Strategy 2.3B: Assess the possibility of metabolism and respiration.

A primary objective of NASA's *Viking* Mission to Mars was to search for evidence of extant life. Two *Viking* landers carried out a series of biological experiments, including the labeled release experiment, which was designed to detect metabolic activity. In this experiment, simple ¹⁴C-labeled substrates, water, and martian soil were combined and monitored for the evolution of radioactive gases (Levin and Stratt, 2016) as evidence that microorganisms had metabolized the substrate. *Viking* instruments detected ¹⁴C labeled gas, however, it is widely accepted that those data were due to oxidizing agents in the regolith rather than microbial activity (Lasne et al., 2016).

Despite the controversy surrounding the labeled release experiment and the eventual conclusion that it did not find evidence of life, the rational underpinning of the experiment may be useful in guiding the search for life in the M-2020 returned samples—the idea to search for evidence of active metabolic processes. The orders of magnitude improvements in technology and the availability of sophisticated Earth laboratories will greatly improve sensitivity and allow us to test for metabolic processes beyond the ability to catabolize a handful of simple carbon substrates (a metabolism not likely to exist on the surface of Mars). It will also attenuate the probability of ambiguous and controversial results as seen during the *Viking* mission.

In this investigation, samples would be incubated with 'heavy'-isotope-labeled substrate using various combinations of deuterated water, ¹³C- or ¹⁵N-labeled substrates, and other stable isotope labeled substrates (Trembath-Reichert et al., 2017). The evolution of labeled gases in the headspace would be indicative of martian life and could yield information about the metabolic processes. An important consideration for this experiment is the potential contamination with Earth life. Unlike the metagenomic analysis described above, there is no clear way determine if a positive result originates from contaminates. We therefore recommend a series of well-designed controls, and that stringent measures be taken to prevent contamination. We also recommend an attempt at DNA extraction and sequencing of any samples showing evidence of metabolic activity as an assay for contamination (Figure 2.11).

Table 2.20 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.3B and move towards an assay of possible biosignatures of present martian life.

 Table 2.20: Samples and measurements implied by Investigation Strategy 2.3B

Samples identified to advance Investigation Strategy 2.3B:
All samples collected as a part of Objective 1 are of interest.

Measurements identified to advance Investigation Strategy 2.3B:

- Measure the abundance of isotopes, isotopologues and isotopomers.
- Extract and sequence DNA.
- Identify and measure evidence for cellular growth, metabolism, and respiration.

<u>Investigation Strategy 2.3C</u>: Assess the possibility that organisms within the sample are capable of reproduction in culture experiments.

Success in cultivating organisms from martian samples would be the ultimate proof of extant life. However, even on Earth we can only culture a few percent of all microbes from an environmental sample. The probability of finding the right cultivation conditions is negligible. These types of analyses would also need to be conducted in the sample receiving facility for planetary protection reasons. Culture attempts are, therefore, not recommended unless evidence of extant life is identified though other independent means.

Table 2.21 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.3C and move towards an assay of possible biosignatures of present martian life.

Table 2.21: Samples and measurements implied by Investigation Strategy 2.3C

1	Samples identified to advance Investigation Strategy 2.3C:
	• All samples collected as a part of Objective 1 are of interest.
	Measurements identified to advance Investigation Strategy 2.3C:

- Measure cell size, shape, and structure.
- Evaluate morphological indications of replication and specialized features like motility structures.

<u>Investigation Strategy 2.3D</u>: Exclude the possibility of contamination with terrestrial life or terrestrial organics as a possible explanation for the data.

A crucial component in assessing returned samples for evidence of extant life is to exclude the possibility of contamination with terrestrial life or terrestrial organics as a possible explanation for the data (Bass & Beaty, 2011). The issue of contamination is addressed in other sections, so we limit our discussion to topics relevant to the search for extant life. If indigenous modern life exists in martian samples, it will likely be present at low abundance similar to extreme environments on Earth. Thus, we will need to prepare for the return samples to be low-biomass, which are particularly sensitive to contamination. This means not only taking proper cleanliness precautions in the terrestrial laboratories to prevent contamination during sample preparation and analysis, but also employ a very strict organic contamination protocol on the development of the rover and all its parts (e.g., ten Kate et al., 2008). To remove or minimize contamination, tests and analyses should be performed periodically on cleanrooms and all subsystems that will be in contact or in proximity of collected samples. Tests have to assess the presence and abundance of:

- *Inorganic compounds:* ferromagnesian silicates, aluminosilicates, Fe and Cr oxides, phosphates, metals, sulphides, carbides, nitrides, and hydrated silicates (e.g., clays).
- Organic compounds: DNA, soluble carbonaceous and insoluble kerogenous-like compounds, graphite, aliphatic and aromatic hydrocarbons, heterocyclic compounds, amines and amides, alcohols, carbohydrates, biomolecules and, possibly, simple life forms.

To draw meaningful conclusions regarding the possibility of extant martian life, scientific investigations must have sufficient resources to rule out contamination. We assume that biological contamination will be detected in the spacecraft, receiving facilities, and returned samples. To appropriately interpret evidence for Mars life in returned samples, we must be able to distinguish between terrestrial contaminates and indigenous martian life. For this reason, a genetic inventory of both the spacecraft and sample processing/analysis facilities is critical (RSSB, 2018a). A genetic inventory represents an important part of the background information related to detection of genetic material in Mars spacecraft and returned samples. If DNA detected in returned samples is closely related to life on Earth, it would likely be the result of contamination rather than evidence of martian life (Figure 2.11).

Table 2.22 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 2.3D and move towards an assay of possible biosignatures of present martian life.

Table 2.22: Samples and measurements implied by Investigation Strategy 2.3D

Samples identified to advance Investigation Strategy 2.3D:

• All samples collected as a part of Objective 1 are of interest.

Measurements identified to advance Investigation Strategy 2.3D:

• Measure expected contamination levels and calculate their subsequent transfer on returned samples.

DETERMINE THE EVOLUTIONARY TIMELINE OF MARS	
	Quantitative comparison of the histories of Earth,
Why is this	Mars, and the Moon is a key input to understanding
objective critical?	the origin and evolution of the Inner Solar System,
	including the history of habitability.
	<i>Most/all of the samples collected as part of Objective</i>
Which are the most	1 are of interest, including clastic or chemical
important samples?	sedimentary rocks, igneous rocks, and impact
	breccias.

3 Objective 3: Quantitatively determine the evolutionary timeline of Mars

3.1 Introduction and current state of knowledge

Meteoritic evidence indicates that Mars accreted in the first 10 Ma after the formation of the first solids in the solar system (Kruijer et al., 2017) from material with an O-Ti-Cr-Ni isotopic

provenance more similar to ordinary chondrites than carbonaceous chondrites and distinct from the Earth-Moon system (Warren, 2011). It likely formed a deep, global magma ocean within ~30 Ma after solar system formation (Debaille et al., 2009; Borg et al., 2016; Kruijer et al., 2017), from which the martian core last equilibrated with its mantle at pressures of ~14 GPa (Righter & Chabot, 2011). After core formation, Mars likely accreted a late veneer that was less extensive than that inferred for the Earth's mantle, but from a similar provenance (Brandon et al., 2012). The formation of most of the mass of the martian crust is constrained to have occurred by 4.43-4.55 Ga (Humayun et al., 2013; McCubbin et al., 2016, Bouvier et al., 2018), and the mantle appears to have formed a series of isotopically distinct reservoirs from which subsequent magmas were derived with little subsequent mixing (Debaille et al., 2007). These inferences about Mars' earliest differentiation are based on the assumption that martian meteorites provide a representative sampling of the martian mantle and crust. However, since the known martian meteorites have Mars ejection ages that mostly fall within ~4 or so main clusters (Figure 3.1) and so likely derive from only a few ejection sites (McSween & McLennan, 2014), this assumption almost certainly is not valid.

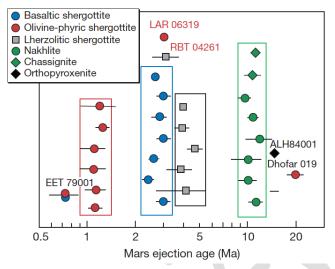


Figure 3.1: Mars ejection ages of the different petrologic types of known martian meteorites; the names of only those meteorites that do not fall within the ejection age clusters (boxes outlined in different colors) are given here (from McSween, 2008).

The earliest phase of martian magmatism (> 4.35 Ga) has been largely overprinted by impact melting in breccias, but four distinct episodes of igneous activity are known at ~4.1 Ga (Lapen et al., 2010; Cassata et al., 2010), ~2.4 Ga (Lapen et al., 2017; Herd et al., 2017), ~1.4 Ga (Cohen et al., 2017) and between 0.15-0.60 Ga (Nyquist et al., 2011; Moser et al., 2013). Remnant magnetization in martian meteorite ALH 84001 demonstrates a dynamo had initiated on Mars at or before 4.1 Ga (Weiss et al., 2008). Orbital evidence indicates that large parts of the highlands formed early in martian history with subsequent abundant volcanic resurfacing during the Hesperian (3.7 Ga to ~ 3.0 Ga). Volcanic activity was localized at the large volcanic provinces (Tharsis, Elysium and west of Hellas basin) (Werner, 2009), none of which is firmly linked to, and thus sampled by the meteorite collection. Calibrating the chronology of igneous activity for Mars will create a temporal frame for the interpretation of both interior (mantle) and exterior (atmosphere, cryosphere, hydrosphere) dynamics of Mars.

This objective seeks to provide radioisotope-based chronological constraints for major evolutionary events on Mars. This includes the timing of Mars' accretion and differentiation, the timing of magmatic, tectonic, magnetic, fluvial, and impact events and the timing of formation of major deposits of secondary minerals and geomorphologic features. Dating samples that can be definitively related to extended surface geologic units with crater size density distributions will allow meaningful comparisons to be drawn between Mars, the Moon, Earth, and other terrestrial planets and moons. Absolute ages of geological processes will enable a better understanding of the geological evolution of Mars and facilitate a comparison with equivalent processes on Earth. The record from Mars is important because it corresponds to Earth's early (Hadean-Early Proterozoic) history for which only little of the geologic record is preserved (Figure 3.2). The highest priority questions relating to the chronology of processes and events on Mars that remain to be answered, as well as the investigation strategies and samples to address these, are set out below in more detail.

Hadean	Eoa	Eoarchean		Paleoarchean		Mesoarchean	Neoarchean
re-Noachian	EN MN	l	N	EH	LH	Early-Amazonian	Hartmann
re-Noachian	EN MN	LN	EH	LH		Early-Amazonian	Neukum
	4.0			3.5		3.0	2.
	re-Noachian	re-Noachian EN MN re-Noachian EN MN	re-Noachian EN MN I re-Noachian EN MN LN 4.0	re-Noachian EN MN LN re-Noachian EN MN LN EH 4.0	re-Noachian EN MN LN EH re-Noachian EN MN LN EH LH 4.0 3.5	re-Noachian EN MN LN EH LH re-Noachian EN MN LN EH LH	re-Noachian EN MN LN EH LH Early-Amazonian re-Noachian EN MN LN EH LH Early-Amazonian 4.0 3.5 3.0

Figure 3.2: Comparison of the two separate martian crater chronologies that are widely used: (1) Hartmann (Hartmann, 2005) and (2) Neukum (Hartmann and Neukum, 2001; Ivanov, 2001), with the chronology of early Earth (which is calibrated by radioisotope ages) (modified from Ehlmann et al., 2016).

3.2 Key Open Questions for Objective 3

All planetary cratering chronology models are calibrated against the lunar cratering record established from Apollo and Luna samples, and have been applied to Mars (Hartmann & Neukum, 2001; Ivanov, 2001; Hartmann, 2005; Werner et al., 2014). However, the earliest lunar bombardment history is still poorly understood for the time period between 4.2 and 3.9 Ga (e.g., Morbidelli et al., 2018). Application of chronology models based on the lunar cratering record to Mars potentially introduces uncertainties of hundreds of millions of years (Figure 3.2), in part because they include additional uncertainties relating to whether the crater forming projectile flux was monotonically declining or if (late) giant planet migration caused one or more peaks in the flux.

The first ever *in situ* age determination on an extraterrestrial body, a 4.21±0.35 Ga age for Noachian-Early Hesperian materials in a mudstone at Gale crater (Farley et al., 2014), unfortunately has uncertainties that are too large to make a confident calibration of the cratering chronology possible. This fact strongly argues for Mars sample return to address precise and accurate sample age determination in calibration of the cratering record. In particular, sample return can potentially eliminate the uncertainties associated with adoption of the lunar cratering record to Mars.

Chronologic studies of well-characterized and carefully selected martian surface materials are needed to address the important question of whether or not the lunar cratering record can be used for calibration of surface ages on all terrestrial planets. However, such investigations would also provide fundamental insights into the terrestrial planet formation processes of accretion and differentiation, and subsequent evolution of the interior and surface of Mars through geologic time. The following are some fundamental open questions relating to the Mars which would be addressed through careful analyses of appropriate returned samples in Earth-based laboratories:

Table 3.1: Key open questions for Objective 3: Constraining the evolutionary timeline of Mars

KEY OPEN QUESTIONS: OBJECTIVE 3
How does the impact flux on Mars compare to that on the Moon, and was there a period of late
heavy bombardment on Mars?
Was there an early dynamo and how long did it last?
What were the accretionary building blocks of Mars, and how long did the processes of crust
formation and metal-silicate segregation (core formation) take?
What was the duration of igneous activity on the surface of Mars?
What are the timescales of aqueous, hydrothermal and sedimentary processes (including rates
of burial, uplift and erosion of surfaces) on Mars?

3.3 Why returned sample studies are important for Objective 3

Our current understanding of the timescales of martian geological processes is hampered by the fact that no unambiguous links between well-dated meteorites and martian surfaces (e.g., by

association with known craters) have been made and in situ ages at Gale Crater have large uncertainties. Therefore, MSR is essential to achieve high precision, high accuracy dates for samples from known sites that would provide crucial information for understanding the chronology of processes on the surface and in the interior of Mars. In particular, the specific open questions noted above can only be addressed with the level of precision and accuracy that can be achieved through state-of-the-art radiogenic isotope analyses on well-characterized samples in Earth-based laboratories. Importantly, some chronometers are disturbed by alteration and metamorphism associated with impact on the martian surface, so that the reliability of individual age determinations can only be confirmed by analyses in Earth-based laboratories where concordant ages from multiple isotopic systems can be obtained. Furthermore, in any given sample, ages determined for different components within a rock type can provide the timing of distinct events. For example, an impact breccia may contain clasts that represent igneous or sedimentary lithologies or impact melts. Remote in situ analyses of such a rock type on Mars would yield an "age" that could be meaningless given that the different lithologies and clasts may represent separate events occurring at very different times in martian history. Also, it is important to note that ages determined on martian meteorites using whole rock isochron techniques do not constrain the formation age of the samples, but instead reflect mixing processes that often have little chronologic significance.

To date a specific event that is recorded within particular components of a rock, it is important to characterize that sample and its components typically using microbeam techniques (such as scanning and transmission electron microscopy and electron probe microanalysis). Following this characterization, it is typically necessary to separate individual phases prior to further processing involving chemical separation of elements under ultraclean laboratory conditions for high precision isotope analyses. For the foreseeable future, such complex sample characterization and processing can only be performed by humans in Earth-based laboratories equipped with state-of-art facilities and instrumentation (Figure 3.3). Given this, it will be important to return martian samples to Earth for the chronological investigations necessary to address the open questions noted above. Finally, measurement precision and techniques are continuously being improved, and these technological and analytical advances often open up completely new and unforeseen avenues of research and methods of investigation. Thus, the full potential in terms of information to be gained from sample analyses can only be realized on returned martian samples.



Figure 3.3: For state-of-the-art high precision radioisotope analyses, sample handling and chemical processing in a clean laboratory such as the one shown here are typically required. Image credit: Center for Meteorite Studies at Arizona State University.

3.4 Sample Investigation Strategies to achieve Objective 3

To a certain extent, geochronology overlaps with all of the other scientific objectives in this report. We want to know not only HOW and WHY various geologic processes operated on Mars, but also WHEN. Thus, there is an important link between geochronology and our Objective 5 (which relates to planetary-scale processes), an additional link to Objective 2 (when were environmental conditions in the habitable window), an additional link to the specific geologic processes described in Objective 1 (for example, when did hydrothermal activity take place?), and further connections to Objective relating to when the volatile reservoirs formed and were modified. However, quantitative

isotope geochronology is so important to Mars science in general that we felt it had to be called out separately. Within the general subject area of geochronology, the subject matter experts within iMOST were able to decompose it into seven discrete investigation strategies (Table 3.2), which are listed in approximate priority order. These strategies have different implications for samples desired, and for the measurements that would be done on those samples.

We have identified seven investigation strategies and 13 sets of measurements to allow quantitative determination of the evolutionary timeline of Mars (Table 3.2).

Table 3.2: Summary of sample-related investigation strategies to constrain and quantify the evolutionary
timeline of Mars.

		Investigation Strategies (IS) for Objective 3			
3	Geochronology	Quantitatively determine the evolutionary timeline of Mars			
IS 3A	Calibrate the crate	ering chronology method by determining the radioisotope age for the			
13 5A	formation of one or more geologic surfaces which has a well-defined cratering density.				
IS 3B	Assess the existence of a late heavy bombardment on Mars, for comparison to the				
13 30	impact bombardment history of the Moon.				
	Quantify the ther	mal/magnetic history of Mars in order to test the present model of			
	Martian mantle convection, in particular the possible early existence of plate tectonics vs				
IS 3C	stagnant lid convection, and the dynamo history (including the timing of magnetic field				
	cessation), and th	eir relationships to other major changes in martian geologic history,			
	particularly atmospheric escape.				
	-	e of specific events associated with the Martian hydrosphere, such as			
IS 3D	sedimentation, hy	drothermal activity, activity associated with deep groundwater,			
	subaerial weather	ing, and associated possible transitions in habitability.			
	Improve our unde	erstanding of the timing, nucleosynthetic isotope anomalies, noble gas			
IS 3E	compositions and	distributions, and stable isotopic variations involved in the accretion			
	and early differen	tiation of Mars.			
IS 3F	Determine the his	tory of surface exposure, including the timing and rates of crustal			
13 31	uplift/erosion and	l burial on Mars.			
IS 3G	Constrain long-du	ration near-surface temperatures using radiogenic and cosmogenic			
13 30	noble gas thermo	chronology.			

<u>Investigation Strategy 3A:</u> Calibrate the cratering chronology method by determining the radioisotope age for the formation of one or more geologic surfaces that has a well-defined cratering density.

Cratering chronology has proven to be extremely useful for interpreting the relative ages of planetary surfaces, and it can be done from orbit. Absolute calibration of the cratering rate has only been possible for the Moon because the age of Apollo and Luna samples, dated by radiometric techniques, can be matched with the cratering age of known terrains on the Moon to deduce a chronology for the entire body. The lunar cratering chronology can be applied to other bodies based on impact rate determination, but it has not been possible so far to get a direct calibration of the chronology using radioisotope ages. However, in order to compare what was happening in different parts of the solar system at the same time, especially for comparison to Earth, which does not have a defined cratering density, quantitative radiometric calibration is necessary. Important progress has been made on this for the Moon, using the returned Apollo samples, however, even there it is to some extent still a work in progress Martian crater chronology models are calibrated against the lunar cratering record (Ivanov, 2001; Hartmann & Neukum, 2001; Hartmann, 2005; Werner et al., 2014). However, the timing of the earliest (4.2-3.9 Ga) lunar bombardment history is still debated (e.g., Morbidelli et al., 2018), so that application to Mars potentially introduces uncertainties of hundreds of millions of years (Ehlmann et al., 2016). These issues are fully addressable with Mars sample return. For the best age resolution, calibration of the cratering rate for >3.5 Ga and <1 Ga

represent the highest priorities. For Mars, the earliest direct calibration attempts relied on observations of a 40-year period of surface imaging by martian orbiting space probes to obtain the rate of new crater formation. Application of the observed cratering rate to the recent past is hampered by the fact that there are rate variations with a period of a few millions of years due to the slightly elliptical orbit of Mars. The only *in situ* dated samples at Gale crater have other unsolvable challenges, as the error range of the dates is very large and the source material (sediments, see discussion below) contains inherited material, the age of which is not well constrained. Thus, dating one or more igneous rocks returned from an extensive lava flow in the >3.5 Ga and <1 Ga age ranges from surfaces for which well determined cratering statistics have been established provides the ideal analogue and/or extension to lunar crater chronology.

Another approach is to date individual craters using samples returned from the craters. The ⁴⁰Ar-³⁹Ar dating of impact melt extracted from breccias associated with large basin-forming impacts could constrain the earliest (> 4 Ga) martian crater chronology (Mercer et al., 2015). However, for the earliest >4 Ga impactites there is the possibility of later disturbance by hydrothermal activity, as seen in the meteoritic regolith breccia NWA 7034 (McCubbin et al., 2016). Single-grain U-Pb ages of zircon and monazite have retained the formation time of large, ancient terrestrial impact craters despite a younger hydrothermal history (Moser, 1997). High temperature impact melts in large, deeply eroded martian craters (e.g., basin fill unit exposed in Jezero crater) could potentially be used to constrain the timing of their formation.

 Table 3.3: Samples and measurements implied by Investigation Strategy 3A

Samples identified to advance Investigation Strategy 3A:

- Igneous samples from an extensive lava flow in the >3.5 Ga and <1 Ga age ranges from surfaces for which well determined cratering statistics have been established
- Samples, including impact melts, taken from individual craters

• Breccias associated with large basin-forming impacts

Measurements identified to advance Investigation Strategy 3A:

- ⁴⁰Ar-³⁹Ar measurements
- U-Pb measurements, especially of zircons or monazites

<u>Investigation Strategy 3B:</u> Assess the existence of a late heavy bombardment on Mars, for comparison to the impact bombardment history of the Moon.

A late heavy bombardment (cataclysm) on the terrestrial planets is expected to be manifest by an overabundance of impact craters at a single period in time, whereas a decaying impactor flux would be a natural result of a slowly depleting source region. The cataclysm hypothesis envisions an intense spike in the bombardment rate at ~3.8-4.1 Ga, perhaps triggered by the orbital migration of the outer planets during their growth period (Levison et al., 2001). The accretionary tailing hypothesis maintains that impact rates gradually declined. The debate has not been resolved with returned lunar samples because the Apollo and Luna sampling sites were all located on the near side of the Moon, in a small area dominated by several large impact basins: Imbrium, Nectaris and Serenitatis, so that biased age sampling of these basins might have skewed the age distributions. Therefore, new information from Mars could establish whether there was a monotonic decay of the bombardment flux or whether orbital rearrangements of the giant planets caused flux variations during this period.

Post-accretion meteoritic bombardment of the martian highlands is evident from the heavily cratered southern highlands. There are virtually no intact geological formations dating to this period (Hadean) on Earth, so our knowledge of the bombardment chronology comes from dating lunar breccias and impact melt glasses (Tera et al., 1974; Cohen et al., 2000; Nemchin et al., 2012). Two competing hypotheses for the bombardment rate involve distinct scenarios for the pre-3.8 Ga impact history of planets with important ramifications for early life (Abramov & Mojzsis, 2009). From

a biosphere point of view, bombardment of basin forming projectiles can be seen as a series of "planet-sterilizing" (Sleep et al., 1989) events, with implications for when Mars started the 'habitability clock' and the initial reference conditions for reconstructions of paleobiology, atmosphere, hydrosphere and interior evolution.

The ages available from *in situ* missions, 4.21±0.35 Ga (Farley et al., 2014), and from meteorites, 4.43-4.35 Ga zircons in NWA 7034/7533 (Humayun et al., 2013; McCubbin et al., 2016), and 4.09±0.03 Ga for ALH 84001 (Lapen et al., 2010), provided mixed support for the Late Heavy Bombardment on Mars. Returned samples from Mars should help evaluate the validity of a solar system-wide late heavy bombardment. On the one hand, if samples obtained from multiple localities yield a range of impact resetting ages, a monotonic decrease in impactor flux rate would be inferred. On the other hand, late heavy bombardment would be supported if numerous resetting ages of ~3.8-4.1 Ga were obtained.

While it has been demonstrated that the timing of martian igneous and shock events can be preserved in mineral grains down to the scale of microns (e.g., Moser et al., 2013; Humayun et al., 2013), shock metamorphic effects and isotopic re-setting within rocks and impactites are often spatially heterogeneous. A sample site/unit with very well characterized primary textures will, regardless of dating method, be necessary to accurately infer the age of a large length-scale cratering event or cratered surface from the geochronology of microscopic minerals. Such a sample would also serve multiple other iMOST objectives and investigation strategies (e.g., 3.4, igneous history).

 Table 3.4: Samples and measurements implied by Investigation Strategy 3B

 Samples identified to advance Investigation Strategy 3B:

 • A sample suite with well characterized primary textures

 Measurements identified to advance Investigation Strategy 3B:

 • Isotopic age dating (⁴⁰Ar-³⁹Ar and U-Pb)

<u>Investigation Strategy 3C</u>: Quantify the thermal/magnetic history of Mars in order to test the present model of martian mantle convection, in particular the possible early existence of plate tectonics vs stagnant lid convection, and the dynamo history (including the timing of magnetic field cessation), and their relationships to other major changes in martian geologic history, particularly atmospheric escape.

Martian surface lithologies are iron-rich and strongly magnetized, likely dating back to the Noachian epoch when the surface may have been habitable. Paleomagnetic measurements of returned samples could transform our understanding of the martian dynamo and its connection to climatic and planetary thermal evolution and provide powerful constraints on the potential preservation state of biosignatures in the samples. Although Mars presently does not have a core dynamo magnetic field, the discoveries of intense magnetic anomalies in the ancient southern cratered terrain by the Mars Global Surveyor mission (Acuna et al., 2008) and remnant magnetization in martian meteorite ALH84001 (Weiss et al., 2004, 2008) provide strong evidence of a martian dynamo during the Noachian epoch. The timing of origin and subsequent decline of the field are poorly constrained but have critical implications for planetary thermal and tectonic history (Stevenson, 2001) as well as the evolution of the martian atmosphere and climate (Jakosky, 2001). Coupled magnetic and geochronologic measurements on a suite of samples spanning the lifetime of the martian dynamo could establish when the dynamo was active and ceased. Furthermore, time sequences of paleodirectional measurements of oriented samples could constrain the rates of polar wander. To address these issues, samples of *in situ* igneous rocks for which magnetic paleointensities had been obtained and that are amenable of radioisotopic dating are be required. Ideally, these samples would be oriented so that polar wander rates can be constrained. However, unoriented samples could still be used to constrain the lifetime and intensity of the dynamo.

 Table 3.5: Samples and measurements implied by Investigation Strategy 3C

Samples identified to advance Investigation Strategy 3C:

- Samples of rocks with well-constrained ages, ideally with known orientation
- Time sequences of oriented *in situ* igneous rocks
- Measurements identified to advance Investigation Strategy 3C:
- Coupled magnetic and geochronologic measurements
- Magnetic paleointensities and orientations

<u>Investigation Strategy 3D:</u> Determine the age of specific events associated with the martian hydrosphere, such as sedimentation, hydrothermal activity, activity associated with deep groundwater, subaerial weathering, and associated/possible transitions in habitability.

Geologic processes involving water produce a variety of sedimentary rocks that can be dated using a variety of analytical techniques. Age determinations on these materials place constraints on the timing of sedimentation, hydrothermal activity, and subaerial weathering in hydrous environments. Age distributions for rounded, abraded (detrital) grains from sediment place a maximum age of sediment deposition. Low temperature overgrowths on sedimentary grains rims can be used to date low-temperature secondary alteration from the action of fluids in upper crustal deposits. This determines the timing of water/rock interaction processes (hydrothermal alteration, acid-sulfate alteration, diagenesis, weathering, aqueous precipitation). Secondary carbonate minerals in cements and fractures can also be dated by the U-Pb method with reasonable precision by LA-ICP-MS (e.g., Hansman et al., 2018). Hydrothermal sulfides and Fe-Mn oxyhydroxides could be dated by Re-Os ages or by Pb model ages. Diagenetic or hydrothermal clays and K-bearing sulfates could be dated by K-Ar (⁴⁰Ar-³⁹Ar) or Rb-Sr methods.

In addition, there now exist robust, stable isotope signatures (e.g., oxygen isotopes) that indicate the presence of liquid water in the martian rock cycle. These signatures are preserved for billions of years in silicate minerals, particularly the refractory geochronology minerals such as zircon and baddeleyite, both of which can be measured with high precision using ion microprobe techniques (e.g., Nemchin et al., 2014; Davies et al., 2018). Application of ion beam techniques that both measure the oxygen isotopic composition of these refractory minerals, as well as determine their ages using the U-Pb system, can identify times at which water was present in the crustal system. Li isotopes in zircon are likewise valuable indicators of cumulative aqueous weathering in the rock cycle (Ushikubo et al., 2008). All these approaches can be applied to the same sample in order to understand the history of surface and underground water on Mars.

 Table 3.6: Samples and measurements implied by Investigation Strategy 3D

Samples identified to advance Investigation Strategy 3D:

• Unaltered sedimentary rocks

• Sedimentary and Igneous rocks displaying signs of secondary hydrologic activity Measurements identified to advance Investigation Strategy 3D:

- Oxygen isotopic composition
- Appropriate dating analyses for each sample (e.g., REE in phosphates, Li isotopes, U-Pb, Re-Os, K-Ar, ⁴⁰Ar-³⁹Ar or Rb-Sr methods)

<u>Investigation Strategy 3E:</u> Improve our understanding of the timing, nucleosynthetic isotope anomalies, noble gas compositions and distributions, and stable isotopic variations involved in the accretion and early differentiation of Mars.

It has been demonstrated that not all solar system materials are derived from the same proportions of nucleosynthetic sources (e.g., Burkhardt et al., 2016). This challenges the premise that the isotopic compositions of primitive meteorites are a perfect proxy for the composition of bulk planets. For an early-formed body like Mars, and given the likelihood of the absence of efficient mixing and homogenization of the martian mantle, nucleosynthetic isotope variations ("anomalies") may exist within its crustal and mantle reservoirs. Such nucleosynthetic anomalies would serve as genetic tracers for the compositions of the building blocks that accreted to form this planet. In this context, it is important to note that the known martian meteorites do not record nucleosynthetic isotope variations at the level of precision currently achievable by state-of-the-art analytical techniques. However, as discussed earlier, the martian meteorites are unlikely to a representative sample of the martian crust (Figure 3.1) and the lack of such variations in the martian meteorite record may simply reflect sampling of a limited number of ejection sites. Thus, returned martian samples will be key to assess as to whether nucleosynthetic isotope heterogeneity exists within Mars. In order to better understand the building blocks of Mars, and the variation of nucleosynthetic sources contributing to terrestrial planet formation, stable isotope measurements of returned martian samples are required. These data could be obtained from the same samples being used for geochronology of igneous rocks as collateral benefits. In addition, similar data could be sought from martian clastic sediments (which are not represented among the known martian meteorites).

Although Mars is thought to have differentiated early (e.g., Shih et al., 1982; Harper et al., 1994; Kleine et al., 2002; Borg et al., 2016; Kruijer et al., 2017), the exact age of differentiation is still debated. This debate stems largely from the fact that different isotopic systems yield different ages. Specifically, ages of differentiation based on the isotopic systematics of the basaltic shergottites range from 4.50 Ga (Sm-Nd system) to 4.54 Ga (Hf-W system). To complicate the issue, the nakhlite meteorites do not demonstrate the same isotopic systematics as the shergottites, and appear to have experienced a more complicated geologic history. This makes the significance of the differentiation age based on shergottites difficult to extrapolate to a global geologic system. For example, the isotopic equilibrium observed in the shergottites might indicate that their whole rock isochron age records the time of solidification of a global magma ocean. Alternatively, the lack of equilibrium between the shergottites and nakhlites could be interpreted to indicate that the differentiation age determined from the shergottites only reflects localized equilibrium of a relatively small portion of the mantle.

To address these issues samples from a wide range of geographic locations are needed. If the whole rocks all mantle-derived samples fall on a single coherent isochron, then equilibrium of these isotopic systems probably existed on a global scale. On the other hand, if various mantle lithologies are not in isotopic equilibrium, then either the existing ages do not record differentiation, or secondary processes occurring in the mantle obscured the chronology. By examining a suite of mantle-derived samples, the age at which Mars differentiated into a core, mantle, and crust can be determined.

Due to its short half-life, the Hf-W system in particular could be used to date formation of the earliest martian crust (Kruijer et al., 2017). Although the ¹⁸²W and ¹⁴²Nd systematics of martian meteorites suggest that Mars' differentiation commenced within the first 30 Ma of solar system history, this conclusion is based on the likely invalid assumption that martian meteorites provide representative sampling of Mars' geochemical reservoirs. As such, the ¹⁸²W-¹⁴²Nd systematics of any returned martian sample would provide a key test for current models of Mars' earliest differentiation and the subsequent evolution of the martian mantle.

Table 3.7: Samples and measurements implied by Investigation Strategy 3E

ples identified to advance Investigation Strategy 3E:			
gneous or clastic sedimentary rocks from a wide range of geographic locations			
surements identified to advance Investigation Strategy 3E:			
¹⁸² W- ¹⁴² Nd measurements			
Hf-W measurements			

<u>Investigation Strategy 3F</u>: Determine the history of surface exposure, including the timing and rates of crustal uplift/erosion and burial on Mars.

Oxidation of organics by exposure of sedimentary rocks at the martian surface to cosmic radiation for >300 Ma has been raised as a serious concern (Pavlov et al., 2012). Thus, an important aspect of sampling for possible organics in martian sedimentary rocks is the selection of the most recently exposed rocks near cliff faces, around impact craters or where erosion rates have been high. Studies of isotopic anomalies and of geochronology of rocks, including for Sm-Nd dating (e.g., Borg et al., 2016) and Hf-W dating (Leya and Masarik, 2013), may require corrections for cosmogenic neutron capture on the nuclides of interest. To understand regolith residence times and sediment production rates by aeolian erosion and erosion rates of the martian surface for quantitative geomorphology requires a knowledge of the exposure history of rock units. Erosion rates and exposure histories could be obtained by cosmogenic nuclide (³He, ²¹Ne, ¹⁰Be, ²⁶Al, ³⁶Cl) dating of surface rocks. Measurement of the isotopic compositions of nuclides with high neutron capture cross sections (e.g., B, Cd, Sm, Gd) in soil, regolith, and other rocks, would help elucidate the exposure histories of materials in the upper few meters of the martian surface and constrain the neutron fluences experienced by the rock units (e.g., Russ et al., 1972; Hidaka et al., 2009). Such measurements also provide constraints on the organic preservation potential of sedimentary rock units for astrobiological objectives. To limit the effects of oxidation and ionizing radiation, the sampling of impact-excavated rock for martian organic geochemical studies has been proposed (Montgomery et al., 2016). On cooling at the surface, material excavated from depth would lock in the ⁴He formed by alpha decay allowing U-Th-He dating of U-Th-rich accessory minerals (apatite, zircon, etc.). This could constrain the residence times of ejecta. U-Th-He dating might also be useful for geomorphic evolution of martian surfaces associated with impacts or very rapid erosion rates.

Rock samples needed for this work would include all returned Mars samples, including clastic or chemical sedimentary rocks recovered for biomarker analysis, igneous rocks, impact breccias, etc. Cores that retained stratigraphy would prove useful for evaluating erosion rates from cosmogenic nuclide abundances measured as a function of depth.

Table 3.8: Samples and measurements implied by Investigation Strategy 3F

Samples identified to advance Investigation Strategy 3F:

- All returned Mars samples, including clastic or chemical sedimentary rocks, igneous rocks, impact breccias.
- Cores that retained stratigraphy would prove useful for evaluating erosion rates from cosmogenic nuclide abundances measured as a function of depth.

Measurements identified to advance Investigation Strategy 3F:

- Sm-Nd dating
- Hf-W dating
- Cosmogenic nuclide (³He, ²¹Ne, ¹⁰Be, ²⁶Al, ³⁶Cl) dating of surface rocks
- Isotopic compositions of nuclides with high neutron capture cross sections (e.g., B, Cd, Sm, Gd) in soil, regolith, and other rocks
- U-Th-He dating of U-Th-rich accessory minerals

<u>Investigation Strategy 3G</u>: Constrain long-duration near surface temperatures using radiogenic and cosmogenic noble gas thermochronology.

Obtaining quantitative constraints on near-surface thermal conditions on Mars over different durations is important for a variety of questions on Mars, including feasibility and potential duration of liquid water stability, potential magmatic/geothermal activity, impact history, paleomagnetic records, and landscape evolution. Applications of both radiogenic and cosmogenic noble gas thermochronology can provide quantitative constraints on permissible thermal conditions over the last 10⁶ to 10⁹ years at planetary surfaces (Shuster and Weiss, 2005; Tremblay et al., 2014; Shuster

and Cassata, 2015). Whereas the open-system behavior of radiogenic ⁴⁰Ar observed in Martian meteorites has been used to place long-duration thermal constraints on the Martian surface (Shuster and Weiss, 2005; Cassata et al., 2010), significant uncertainties result from elevated temperatures associated with ejection from Mars, and transit and atmospheric entry to Earth. In addition, meteorites are not amenable for the use of cosmogenic noble gas thermochronometry due to their exposure during transit to Earth. The returned samples will provide an opportunity to use both radiogenic *and* cosmogenic noble gas thermochronology (as has been done on returned lunar samples; Shuster and Cassata, 2015; Tikoo et al., 2017) to place thermal constraints over timescale that spans from rock crystallization to today, and during most recent time when the collected samples were exposed to cosmic ray interactions in the uppermost few meters of the Martian surface. Depending on their specific lithology and mineralogy, the returned samples will be amenable to ⁴⁰Ar/³⁹Ar and ⁴He/³He thermochronology, as well as the use of open-system behavior of cosmogenic ³⁸Ar, ^{21,22}Ne and ³He. A major advantage of these approaches is that laboratory observations of returned samples provide sample-specific temperature sensitivity, *via* quantification of noble gas diffusion kinetics (e.g., Shuster and Cassata, 2015).

 Table 3.9: Samples and measurements implied by Investigation Strategy 3G

- Samples identified to advance Investigation Strategy 3G:
- All collected samples are of interest

Measurements identified to advance Investigation Strategy 3G:

- ⁴⁰Ar/³⁹Ar and ⁴He/³He thermochronology, as well as cosmogenic ³⁸Ar, ^{21,22}Ne and ³He.
- 4 Objective 4: Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system

MARTIAN VOLATILES: INVENTORY, HISTORY AND INTERACTIONS		
Why is this objective critical?	Understanding martian volatiles is essential both to astrobiology strategy and to the evolution of Mars as a planetary object.	
Which are the most important samples?	Atmospheric gas sample(s); rocks with minerals recording volatiles including hydrous silicates, carbonates, sulfates, nitrates and chlorides; samples with fluid inclusions.	

4.1 Introduction and Current State of Knowledge

Volatiles have clearly played a key role in the evolution of Mars atmosphere, hydrosphere and geosphere, with effects ranging from the geomorphological evidence for outflow channels and valley networks early in Mars' history to formation of alteration products in rocks (e.g., Treiman, 2005; Bibring et al., 2006; Ehlmann et al., 2011a; Vaniman et al., 2014; Melwani Daswani et al., 2016) to the current seasonal changes in the polar caps. The atmosphere of Mars was measured for the first time by the *Viking* lander (Chamberlain et al., 1976; Hess et al., 1977). State-of-the-art instrumentation on the *Phoenix* (Niles et al., 2010) and *Curiosity* (Mahaffy et al., 2013; Webster et al., 2013; Wong et al., 2013; Atreya et al., 2013; Mahaffy et al., 2015; Webster et al., 2015; Franz et al., 2015; Conrad et al., 2016) missions have furthered our understanding of the origin of some volatiles, and orbiters such as Mars *Odyssey* have measured global distributions of some, with regional spatial resolution (Boynton et al., 2002; Keller et al., 2006).

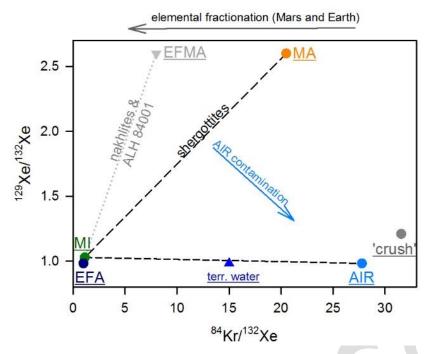


Figure 4.1: End-members as commonly used in martian meteorite heavy noble gas research. Endmembers are underlined, mixing and fractionation trends are indicated by arrows and lines. 'Crush' is an as yet unexplained component, first measured by Wiens et al. (1988).

In addition, martian meteorites have added important evidence on the noble gas content of Mars - ranging from the similarity of the trapped gases, especially the heavy noble gases, in the shergottitic glasses with unfractionated martian atmosphere as measured by *Viking* (and now also *Curiosity*), to fractionated martian atmosphere in the nakhlites, to martian interior components with and without additions of radiogenic decay products to Xe (Ott, 1988; Ott & Begemann 1985; Ott et al., 2018; Mathew & Marti 2001, 2002; Swindle, 2002). Figure 4.1 shows the most important endmembers – MI, martian interior (Ott, 1988); MA, martian atmosphere as measured by *Viking*; and the fractionated signature, which can be extrapolated to EFMA – an elementally fractionated martian atmospheric component. Also plotted are terrestrial air (AIR) and the two elementally fractionated terrestrial air signatures: noble gases dissolved in water (terr. water) and incorporated in terrestrial alteration minerals (EFA; Schwenzer & Ott, 2006). There are several theories for the genesis of the elementally fractionated martian atmospheric component, which have different implications for martian climate and for rock-atmosphere interactions.

4.2 Key Open Questions for Objective 4

Despite the wealth of information obtained through in situ measurements of martian volatiles over the last two decades, there remain some unresolved conflicts between these different measurements - the most significant being the relative abundances of minor species nitrogen and argon in the atmosphere and a large difference (~ 10 ‰) between the carbon isotopic composition of atmospheric carbon dioxide measured by Curiosity and Phoenix. Similarly, the carbon isotopic composition of nakhlites is difficult to interpret with our current understanding of the CO₂ cycle. The noble gases in the meteorites show at least two – potentially three – different signatures: unfractionated heavy noble gas signatures in the shergottites, fractionated heavy noble gas signatures in the nakhlites and the ancient meteorite ALH84001, but the latter two could also be two different signatures (Ott, 1988; Murty & Mohapatra, 1997; Swindle, 2002; Schwenzer et al., 2018). It is thus clear that the absolute and relative abundances of various volatiles have changed through time via differentiation and magma ocean solidification, volcanic degassing, atmospheric loss, and interactions with the crust (Filiberto & Schwenzer, 2018; Haberle et al., 2017; Shaheen et al., 2014; Agee et al., 2013; McSween et al., 2010). Understanding some of the key details, however, is hindered by constraints imposed by the different sources: in situ missions place the samples into a detailed geologic context, but are limited in their capability to heat samples (currently ~900 °C),

which makes it impossible to quantitatively degas any sample. In contrast, martian meteorites can be degassed fully in terrestrial laboratories, but they originate from unknown locations on Mars (although potential source craters have been suggested for a few) with no geologic context and an unknown history before their delivery as meteorites, and have experienced irradiation by galactic and cosmic radiation in space, which adds another layer of complexity in the interpretation of the environment and ejection of various minerals. Terrestrial weathering generates further complications. For example, the two most unique meteorites, ancient (~4 Ga) martian orthopyroxenite ALH 84001 and martian impact breccia, NWA 7034 and its pairs, are finds, rather than falls, as are most of the other known martian meteorites (see Mars Meteorite Compendium for details). This makes a returned sample our only option to measure the full suite of volatiles within a martian rock and connect it to its geologic context, especially for the more tightly bound magmatic and interior gases.

Martian basaltic magmas are presumably the ultimate mechanism of transfer of volatiles from the mantle to the surface and atmosphere (e.g., Hirschmann & Withers, 2008; Johnson et al., 2008; Righter et al., 2009; Carr & Head, 2010; King & McLennan, 2010; Grott et al., 2011; Stanley et al., 2011; see Filiberto et al., 2016a for a review). Volatile degassing from martian magmas has been linked to both acidic weathering on the surface as well as regional and global climate change (e.g., Tosca et al., 2004; Poulet et al., 2005; Bibring et al., 2006; Carr & Head, 2010; Ehlmann & Mustard, 2012). Therefore, in order to understand the concentrations of volatiles in the crust, it is fundamental to first constrain the volatile budget of martian magmas and the interior. Estimates for the volatile content of martian volcanic rocks largely comes from analyses of martian meteorites, which are all relatively young and from a depleted source region. These studies have led to a significant debate about the past and present volatile content of the martian interior (e.g., McSween et al., 2001; Medard & Grove, 2006; Nekvasil et al., 2007; Filiberto & Treiman, 2009; McCubbin et al., 2010, 2012; Gross et al., 2013; Taylor, 2013; Jones, 2015; Filiberto et al., 2016b; McCubbin et al., 2016). Estimates of the volatile content of ancient martian magmas and the interior are seriously lacking because of a paucity of ancient volcanic samples in our collection.

The samples in our collection have sparked a debate about the evolution of the martian atmosphere, which is currently still unresolved, 30 years after it was first discovered (Ott, 1988): Kr/Xe ratios are fractionated against the modern martian atmospheric ratios (as measured by Viking) in two groups of martian meteorites: the nakhlites and ALH 84001. Both meteorite groups are older than the shergottites, which carry a modern atmospheric signature and which all have crystallization ages less than about 600 Ma. The nakhlites are ~1.3 Ga and ALH 84001 is 4 Ga old, but this is not the only difference from the shergottites: shergottites carry no, or very little, alteration material, while nakhlites and ALH 84001 have undergone some hydrous alteration (e.g., Treiman, 2005; Hicks et al., 2014; Melwani Daswani et al., 2016; Shaheen et al., 2015a). Moreover, they were ejected at different times from Mars than the shergottites, which could be important if the atmospheric composition changes on the timescale of millions of years (the time between ejection events) or shorter (Swindle et al., 2009). Thus, there are several ways to explain their elementally fractionated heavy noble gases fingerprint: a) an internal (possibly crustal) gas reservoir, with its host rocks melted or assimilated into the meteorites' parent magmas (Gilmour et al., 1999); b) elementally fractionated martian atmosphere in the rocks' aqueous alteration minerals (Swindle et al., 2000); c) fractional adsorption of atmospheric noble gases onto mineral surfaces (Gilmour et al., 2000); and d) incorporation of an unfractionated martian atmosphere, which was changed with time either seasonally or over millions of years (Swindle et al., 2009; see also Schwenzer et al., 2016) for a more complete literature list). Without establishing the daily, seasonal and long-term variability of the martian atmosphere, and the incorporation pathways into the rocks we already have, it is impossible to decipher the compositional clues from the data in hand. Sample return is the only way to obtain a sample with geologic context and Mars' contemporary atmosphere.

Table 4.1: Key open questions for Objective 4: Understanding the origin and evolution of martian volatiles

KEY OPEN QUESTIONS: OBJECTIVE 4
Where did the volatiles on Mars originate?
How do the martian crust and atmosphere interact and exchange material over time?
How has the martian interior contributed to the volatile composition of the surface and
atmosphere?
How has Mars' atmospheric composition evolved over geologic time?
How does Mars atmosphere vary over seasonal, and other, time scales?

4.3 Why returned sample studies are important for Objective 4

In addition to studying the current martian atmosphere and ancient trapped gasses in martian sedimentary, igneous and impact samples, there is considerable knowledge to be gained by examining the unaltered compositions of sedimentary rocks, dust, and secondary minerals that are especially sensitive to climatic influences such as obliquity-driven changes. For example, detailed isotopic and chemical analyses of sediments from a variety of different ages on Mars will provide tremendous insight into the composition of the atmosphere and how it has changed through time including details such as its oxidation state as well as the relative amounts of volcanic emissions and atmospheric loss. Results from the Curiosity rover indicate that it is possible to obtain highresolution chemostratigraphic climate records from rhythmically bedded sedimentary rocks using in situ measurements (Grotzinger et al., 2015) - a capability that M-2020 is also expected to have (e.g., with SuperCam and PIXL). Analysis of selected returned samples from such in situ records would be extremely important in confirming and fully understanding such records. As another example, understanding the relationship between sedimentary rock, regolith and secondary mineral compositions and the contemporaneous atmosphere would also greatly expand our understanding of kinetic and equilbrium isotope fractionation patterns, crucial for the interpretation of the paleoclimatic conditions on Mars by revealing how the sedimentary record responds to such changes. Finally, there is growing capability of applying a variety of radiometric techniques to dating of the time of sedimentation and obtaining such dates from climate-sensitive sedimentary sequences would greatly help to tie down the timescales of past climate changes.

With the advent of more precise and highly reproducible state of the art techniques, it has become possible to measure the history of changes in volatiles, thus providing constraints on the causes of the massive environmental changes on Mars over the course of its geological history. In turn, these can be compared with similar understandings of Earth, and ultimately Venus, to develop genetic models for the causes and effects of environmental evolution on the terrestrial planets. Additionally, these measurements will help to constrain the early Earth climate models as well when we have a better understanding of how the atmosphere, hydrosphere and geosphere interact in harsh environmental conditions, such as exposure to high energy cosmic and galactic radiation (MeV- GeV), higher UV flux and more intense solar wind.

4.4 Sample Investigation Strategies to achieve Objective 4

The most sophisticated studies of volatiles that definitively allow separating reservoirs from rocks with complex histories (e.g., overprinting aqueous alteration) will be accomplished by analyzing returned solid samples with a variety of analytical techniques only possible in terrestrial laboratories and capable of analyzing detailed chemical and isotopic variations on a nano-scale and differential heating to correlate trapped volatile with the mineral compositions. *In situ* analyses on Mars (Figure 4.2) demonstrate the promise of such techniques. Volatiles can be trapped in solids – as vesicles in volcanic rocks, implanted in shock melts, in igneous volatile-bearing minerals (such as apatite and amphibole), trapped during alteration mineral formation during hydrothermal events, and incorporated into some sedimentary minerals during diagenesis or by evaporation. In addition, many volatiles are incorporated in rocks during interactions with fluids of various sorts.

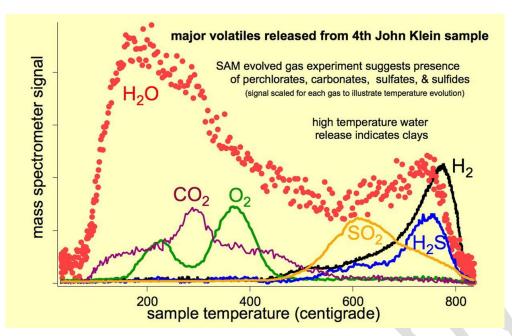


Figure 4.2: The Sample Analysis at Mars (SAM) system on *Curiosity* has measured a variety of volatiles released from solid samples. The volatiles released from this mudstone were incorporated at some unknown time in the past. With returned samples, it would be possible to provide a more detailed accounting of what volatiles are associated with specific lithologies and potentially to obtain chronologic information about the time of incorporation. Figure from NASA-JPL-CalTech, based on data in Ming et al., 2014.

With the limitations of *in situ* atmospheric measurements to date, one or, preferably more, dedicated samples of the current atmosphere will also be required. The headspace gas in the sample tubes will be collected and analyzed as a supplement to understanding the nature of the solid samples and for evaluating any potential reactions that might have occurred inside the sample tube after collection. The likelihood of post-collection degassing, or other sample-gas interactions make the headspace gas less than ideal for evaluating small seasonal variations because it will be nearly impossible to eliminate the possibility of sample-gas interactions as a source of any variations observed. However, a dedicated set of atmospheric samples can provide a detailed baseline for seasonal variations that can be used to interpret results from headspace gas analyses.

We have defined four investigation strategies and 19 sets of measurements to constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system (Table 4.2).

Table 4.2: Summary of sample-related investigation strategies to constrain and quantify the inventory, actions,and effects of martian volatiles.

Investigation Strategies (IS) for Objective 4				
4	Volatiles	Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system.		
IS 4A	Determine	the original source(s) of the planet's volatiles, and the initial isotopic		
13 44	compositions of the constituent gases in the atmosphere.			
IS 4B	Understand crustal-atmospheric interactions and feedbacks, especially for C, O, S, N, Cl			
13 40	and H, in order to interpret present and past geochemical cycling on Mars.			
IS 4C	Quantify the history of the composition of the atmosphere, and the history of			
15 4C	contributions from the interior (e.g., H, C, Cl, N, O, noble gases and radiogenic products).			
	Assess temporal (seasonal) variations in the composition of the present-day atmospher			
IS 4D	to determi	ne seasonal changes to both major and minor species as a means for		
	evaluating	crust-atmosphere cycling.		

<u>Investigation Strategy 4A</u>: Determine the original source(s) of the planet's volatiles, and the initial isotopic compositions of the constituent gases in the atmosphere.

The original source(s) is key information for understanding the formation of Mars, and by extension, all the terrestrial planets. Determining the original bulk and isotopic composition is complicated by the processes that occurred on the planet during its history. However, studies of the volatile content of minerals (i.e., apatite, amphibole, and nominally anhydrous minerals) in unaltered Noachian-aged samples can provide clues to the bulk volatile content of Mars. Further, there are some isotopes (such as the triple-isotope system of O in rocks) that are expected to change little, and be highly diagnostic of their origin. Although the triple isotope system of O has been altered by mass-independent fractionation processes in the atmosphere, that of the interior of Mars should have experienced only mass-dependent fractionation processes, and can be diagnostic of the source materials from Mars (Clayton, 1993). Notably, the unusual basaltic breccia NWA 7034 has a Δ^{17} O value of 0.5‰, compared to the value of ~0.3‰ for all other martian meteorites, suggestive of a surficial component (Agee et al., 2013). The higher Δ^{17} O value is likely due to ozone production with a mass-independent fractionation. Interestingly, this sample - despite being ancient and an impact breccia - shows shergottitic, modern atmosphere noble gas signatures (Cartwright et al., 2013), which questions the hypothesis derived from the other old martian sample (ALH 84001; Murty & Mohapatra, 1997) that fractionated atmospheric signatures indicate an earlier atmosphere. The carbon and oxygen triple isotopic compositions of carbonate minerals in ALH84001 indicate two generations of carbonates (~3.8 Ga formed by the interation of magma with the atmosphere and carbonates formed at the time of ejection). Despite significant age differences, oxygen isotope anomaly remained constant ($\Delta^{17}O_{(CO3)} = 0.7\%$) and suggests much less variations in the hydrological cycle of Mars (Shaheen et al., 2015b; Farguhar et al., 1998). The elemental abundances of the heavier noble gases (Ar, Kr, and Xe) may also contain diagnostic information about the origin of the volatile-rich material on Mars (Pepin & Porcelli, 2002). The noble gas elemental ratios may be altered by atmospheric escape (Jakosky et al., 1994; Pepin, 1997), or even seasonal or climatic variations (Swindle et al., 2009), but even in that case, measurement of the atmospheric ratios will provide insight into important properties of the martian atmosphere.

 Table 4.3: Samples and measurements implied by Investigation Strategy 4A

Samples identified to advance Investigation Strategy 4A:

- Atmospheric gas sample, preferably at least two at two different points in the Mars year.
- Unaltered Noachian-aged Igneous rock sample

Measurements identified to advance Investigation Strategy 4A:

- Measure the noble gas elemental abundance in the present martian atmosphere.
- Measure the oxygen triple isotopic composition, C isotopes and clumped isotopes in igneous rocks.
- Measure the sulfur quadruple isotopes of oxidized and/or reduced minerals in igneous rocks.
- Measure the indigenous noble gas signature of a geologically well-defined igneous sample.
- Measure the volatile content in unaltered apatite from a Noachian igneous sample.

<u>Investigation Strategy 4B</u>: Understand crustal-atmospheric interactions and feedbacks, especially for C, O, S, N, Cl, and H, in order to interpret present and past geochemical cycling on Mars.

Although present conditions are much different than those earlier in Mars' history, quantifying the current interactions as well as the past interactions by analysis of volatile-bearing mineral phases will provide important constraints on the past history of volatiles as well as on current processes.

Modern day interactions involve atmospheric chemistry without liquid water or where such water only exists in few molecule films. The surface of Mars is covered with ~0.5-1 % perchlorates as measured by *Viking*, *Phoenix*, and *Curiosity* (Leshin et al., 2013). Perchlorate is a strong oxidizing

agent and may have implications for the preservation/destruction of organic matter on the surface of Mars (a potential source of energy for perchlorate reducing bacteria), and for the past and present hydrological cycle of Mars such as brine formation due to high deliguescence of chloride salts (Court et al., 2014; Kounaves et al., 2016). Analyzing the chlorine isotopes in different chlorinebearing species will provide information on the kinetic and equilibrium processes occurring. The equilibrium δ^{37} Cl fractionation between perchlorate and chloride is approximately 73 ‰ at room temperature (Schauble et al., 2003). Terrestrial perchlorates have δ^{37} Cl values that are far less than the equilibrium fractionation (0 ± 10 ‰, Barnes & Sharp, 2017), indicating strong isotopic disequilibrium during formation. The Cl isotope compositions of surficial Cl measured by the Mars Rover are scattered but generally less than -40 ‰ (Farley et al., 2016). This is in contrast to the measured δ^{37} Cl values of martian meteorites, which range from -4 % for mantle-derived samples to +8 ‰ for surface contaminated samples (see Barnes and Sharp, 2017 for a review). The meteorite data are explained as two-component mixing between a mantle reservoir (δ^{37} Cl = ~-5 ‰) and a heavy crustal component due to loss of light ³⁵Cl to space. The discrepancy between the *in situ* data from the rover and meteorite samples remains unresolved, although it may be explained by lack of a robust calibration for the rover data. Additional samples would allow for the discrepancy to be resolved.

Regolith and dust samples are key components in the heterogeneous chemistry of the atmosphere. Analysis of SO₄, and CO₃ and respective O-isotope anomalies in these samples will be key to our understanding of how the atmospheric chemical reactions are preserved in different minerals. The SO₂ gas released during volcanic eruption is oxidized by various oxidizing agents in the atmosphere which include ozone, hydrogen peroxide, water vapor and hydroxyl radicals (Figure 4.3). Similarly, the Δ^{17} O values of secondary mineral and rock samples will be an indirect measure of the oxidizing capacity of the martian atmosphere. Sample analysis of rocks of different ages could be used to constrain the evolution of the martian atmosphere. In addition, measuring the heavy noble gases will allow us to understand the incorporation of those gases into the regolith, thus providing important data points for the regolith as a (fractionating?) sink of non-reactive atmospheric species.

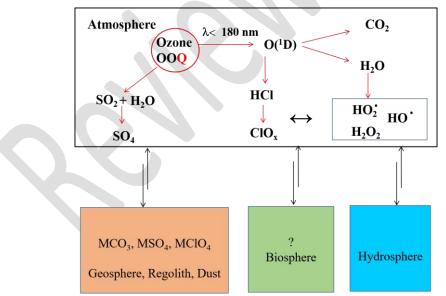


Figure 4.3: Interaction of ozone with sulfur dioxide (SO₂) in the atmosphere to produce stable SO₄ molecule (Shaheen et al., 2013, 2014; Farquhar et al., 2001). Photolysis of ozone at wavelengths shorter than 184 nm produce excited oxygen atoms O(¹D), which can react with carbon dioxide to produce isotopic anomalous carbon dioxide, which is preserved as carbonate. Interaction of O(¹D) and water vapor can yield peroxy radicals and form of hydrogen peroxides in the atmosphere. The oxygen triple isotopes of water adsorbed on mineral surfaces will reflect the odd oxygen cycle on Mars. Both O(¹D) and hydroxyl radicals can react with chlorine to produce perchlorates, thus preserving a signature of radical chemistry and photolysis of HCl in the atmosphere of Mars.

In contrast, water played a major role in mediating water-rock reactions in Mars' past, leaving behind an extensive and diverse record in outcrops at the Mars surface (e.g., Bibring et al. 2006; Murchie et al., 2009). Hydrous minerals have been observed in meteorites and in ancient stratigraphies exposed by rover missions. The key questions concern the nature of the environments, i.e., the temperature, pH, Eh, and geochemistry of waters from which these minerals formed, the timing of their formation, and the communication of waters with the atmosphere. For example, phyllosilicates are found globally in Noachian terrains across Mars. But it is debated whether they were formed by surface weathering, hydrothermalism/groundwater alteration, deuteric precipitation from lavas, or early in a primordial atmosphere (Ehlmann et al., 2011a; Carter et al., 2015; Meunier et al., 2012; Cannon et al., 2017). The answer has important consequences for the sources and sinks of martian water, including whether these were primarily lost to space or to the crust, as well as for habitability. Petrology at sub-mm scale, D/H and oxygen isotope data, and – when possible – age-dating hydrous mineral phases are necessary. Recent MSL data have confirmed at larger-scale findings from meteorites that aqueous alteration may have persisted longer in Mars history than previously believed with ages < 2 Ga derived from jarosite (Martin et al., 2017). What climate processes control this long-term rock-water interaction is not understood.

A second example is the nature of the carbon cycle. Carbonates are found in select terrains seen in orbital data (Ehlmann et al., 2008; Michalski et al., 2013; Edwards and Ehlmann, 2015; Wray et al., 2016), were observed *in situ* in rocks by the *Spirit* rover (Morris et al., 2010), but in Gale crater were found in only in trace amounts in dust (Leshin et al., 2013) rather than in lake sediments, raising questions as to whether this is because of low pCO₂ (Bristow et al., 2016; Tosca et al., in review). Carbonates are also found in martian meteorites, though their formation environment has been debated (Changela & Bridges, 2010; Halevy & Head, 2014). How the carbonates formed has important implications for past atmospheric pressure (Hu et al., 2015) and the precentage of atmosphere lost to space vs. sequestered in rock. The way to differentiate various scenarios of atmospheric loss is to examine the isotopic C and O record preserved in carbonates. Such an isotopic record can only be understood, however, with petrology that informs the formation environment.

To that end, rock samples with mineral phases that trap volatiles from time periods on ancient Mars are of high priority for understanding martian geochemical cycles, changing martian climate and geology, and long-term crust-atmosphere interaction.

 Table 4.4: Samples and measurements implied by Investigation Strategy 4B

Samples identified to advance Investigation Strategy 4B:

- Dust and soil sediments.
- Atmospheric gas sample.
- Rocks with minerals recording volatiles including hydrous silicates, carbonates, sulfates, nitrates, and chlorides, particularly if the age of incorporation can potentially be determined.
 Measurements identified to advance Investigation Strategy 4B:
- Measure the carbon and oxygen triple isotopic composition of CO₂ gas from atmosphere samples, and evolved from solid samples.
- Measure D/H, the oxygen triple isotope composition and O-isotope anomaly (Δ¹⁷O) of water vapor in the atmosphere and phyllosilicate species and other hydrated mineral phases in ancient rocks.
- Measure the Δ ¹⁷O values of hydrated and anhydrous silicates
- Measure the Δ ¹⁷O values of sulfate minerals in dust and rocks.
- Measure the C and O-triple isotopes of carbonates and water in rocks, dust and regolith samples.
- Measure the chlorine and oxygen triple isotopic composition of perchlorate and chlorides on Mars
- Analyze compound-specific isotopes of H, C, O, N, Cl, and S in molecular species in the atmosphere and in regolith, sediment, and rock samples.
- Measure sulfur quadruple isotopes and S-isotope anomalies (Δ^{33} S, Δ^{36} S) of sulfate in dust, regolith, rock, and soil samples.

<u>Investigation Strategy 4C:</u> Quantify the history of the composition of the atmosphere, and the history of contributions from the interior (e.g., H, C, Cl, N, O, noble gases and radiogenic products).

Changes in the martian atmosphere with time are clearly coupled to changes in the martian environment. A key part of those changes are the contributions and losses to the atmosphere. Outgassing (most likely volcanic (Figure 4.4), but perhaps related to impact) is the primary source for contributions to the atmosphere and degassing from martian magmas has been linked to both acidic weathering on the surface as well as regional and global climate change (e.g., Tosca et al., 2004; Poulet et al., 2005; Bibring et al., 2006; Carr & Head, 2010; Ehlmann & Mustard, 2012). Analyses of the volatile content and S, Cl, C, and O isotopic ratios of minerals (i.e., apatite, amphibole, carbonate, and nominally anhydrous minerals) in unaltered Noachian-aged samples can provide clues to the primary contributions of volcanic degassing to the atmosphere. Further, it should also be possible to put constraints on the amount of outgassing by determining the history of the composition, elemental, molecular, and isotopic, of the martian atmosphere. The history of the composition of the atmosphere can also constrain loss processes, particularly when coupled with the measurements by the MAVEN mission of present-day loss. Returned samples are needed to determine the history of the martian atmospheric composition by measuring samples that contain Noachian-aged unaltered igneous hydrous minerals, that contain samples of paleo-atmosphere, that have exchanged with the atmosphere at known times in the past, and/or have minerals that formed from interactions with waters in contact with the atmosphere.

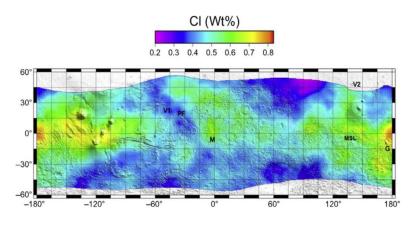


Figure 4.4: Cl abundances are highest near volcanic vents, suggesting ongoing outgassing of Cl from the interior. Volatiles in key Noachian-aged minerals could provide key constraints on the amount and timing of such outgassing. (figure from 2001 Mars Odyssey Gamma-Ray Spectrometer (U. Arizona/NASA); original data from Keller et al., 2006 and Boynton et al., 2007, modified by Filiberto et al., 2018.

 Table 4.5: Samples and measurements implied by Investigation Strategy 4C

Samples identified to advance Investigation Strategy 4C:

- Rocks and regolith of known age containing hydrated minerals (carbonates, sulfates, sulfides, chlorides, perchlorates).
- Dry, clay-free dune material to study adsorption and dry implantation processes of atmospheric species in contrast to trapped fluid inclusions in next sample type.
- Any rock of known age containing minerals with trapped fluid inclusions.
- Highly shocked rock containing impact melt pockets or veins, where the timing of the shock event is known.
- Rock samples with the mineral phases above which preserve volatiles and may have formed from surface or near-surface waters specifically ancient apatite-bearing samples and silicates with differing degrees of crustal assimilation.

Measurements identified to advance Investigation Strategy 4C:

- Analyze rocks/minerals/regolith that may have exchanged with the past atmosphere, at specific times in its history, e.g. carbonates (δ¹³C, δ¹⁷O, δ¹⁸O, Δ¹⁷O), sulfates (δ³³S, δ³⁴S, δ³⁶S) and perchlorates (δ³⁷Cl, δ¹⁷O, δ¹⁸O, Δ¹⁷O) and adsorbed or chemically bound water, especially in hydrous minerals (δD, δ¹⁷O, δ¹⁸O, Δ¹⁷O).
- Analyze trapped gases within mineral inclusions and vesicles for the full range of atmospheric species, stable isotopes (especially H-, N- and O-isotopes) and noble gas isotopic and elemental compositions.
- Analyze volatile species (e.g., H₂O, SO₃, H₂S, CO₂, Cl) preserved either as stoichiometric components of minerals (e.g., carbonates, sulfates, sulfides, chlorides, apatites, perchlorates) or adsorbed onto mineral/grain surfaces or trapped within fluid inclusions for their stable isotopic compositions (e.g., ^{2/1}H, ^{18/17/16}O, ^{13/12}C, ^{15/14}N, ^{36/34/33/32}S, ^{37/35}Cl), including clumped isotopes where possible.
- Analyze atmospheric gas implanted into impact melt.

<u>Investigation Strategy 4D</u>: Assess temporal (seasonal) variations in the composition of the presentday atmosphere to determine seasonal changes to both major and minor species as a means for evaluating crust-atmosphere cycling.

Carbon dioxide, Ar, N2, O2, H2O, H2O2, and D/H have been measured in situ to vary seasonally during the martian year (Trainer et al., 2016; Encrenaz et al., 2015; Franz et al., 2015; Villanueva et al., 2015), and it has been proposed that other trace species might vary seasonally or following a partially modified pattern (e.g., Swindle et al., 2009). As seen in Figure 4.5, measurements of methane have also been variable (Webster et al., 2015, 2018), with at least part of the variation correlated with time of the year (Webster et al., 2018). Seasonal variations may be driven by heterogeneity within polar cap reservoirs whose exchange of material drives seasonal atmospheric pressure variations. It is important to understand whether the observed variations are

seasonal or the result of some other cause by addressing the possibility of seasonal variability. In addition, there are other features of Mars, from dust storms to Recurring Slope Lineae (which may be associated with the absorption and release of H2O) that have a seasonal variability (McEwen et al., 2011; Bhardwaj et al., 2017), and it is important to know how the movement of volatiles influences, or is influenced by, these other effects. Finally, the amount and variability of oxidizing components at the surface (perchlorates, oxychlorines, atomic oxygen, superoxide and other ions, ozone, hydrogen peroxide H₂O₂, and free radicals such as hydroxyl, perhydroxyl, etc.) and their heterogeneous catalytic destruction in the regolith is still unknown (see Kounaves et al., 2014; Carrier & Kounaves, 2015, Lasne et al., 2015; Atreya et al., 2017), but some of these may be difficult to measure in a returned sample because of reactions during storage and transit. The gas in the headspace of samples collected in different seasons may provide some information on the temporal variability of various species in the atmosphere, but the volume of headspace is not likely to be large enough to make detailed measurements of trace species, and for reactive species, interaction between the gas and solid sample may make interpretation of the original composition difficult.

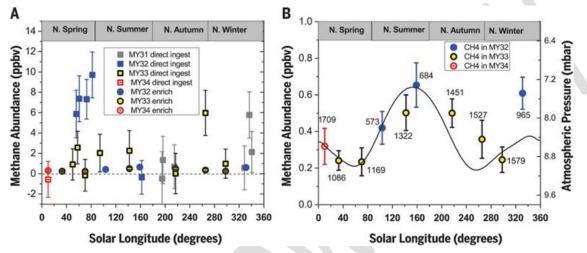


Figure 4.5: Temporal variations in methane abundance of the martian atmosphere at Gale Crater, as measured by the SAM Tunable Laser Spectrometer (TLS). Large excursions to several parts per billion by volume (ppbv) are seen in the full data set (A), as well as seasonal variations in the background levels measured with higher precision. (Webster et al., 2018)

Table 4.6: Samples and measurements implied by Investigation Strategy 4D

Samples identified to advance Investigation Strategy 4D:

- Atmospheric gas samples obtained at least two, preferably four, different seasons *Measurements identified to advance Investigation Strategy 4D:*
- Determine the seasonal variability of the elemental composition of the atmosphere, including, but not limited to, carbon dioxide, noble gases (particularly Kr and Xe), H₂O, perchlorates, H₂O₂ and other oxidizing species and methane.
- Analyze compound-specific isotopes of H, C, O, N, Cl, and S in molecular species.
- 5 Objective 5: Reconstruct the processes that have affected the origin and modification of the interior, including the crust, mantle, core and the evolution of the martian dynamo

ORIGIN AND MODIFICATION OF THE MARTIAN CRUST, MANTLE, AND CORE			
Why is this objective critical?	Understanding the formation and modification of the martian core, mantle and crust is a key input to our planetary models.		

Which are the most	a suite of diverse igneous rocks, oriented igneous or			
important samples?	sedimentary rocks, ancient rocks, and impactites			

5.1 Introduction and Current State of Knowledge

Mars is a fully differentiated planet with a core, rocky mantle and crust. Gravity measurements from orbiting spacecraft and ranging to surface landers indicate a fluid metallic core size of radius 1300-1840 km (Folkner et al., 1997; Yoder et al., 2003; Khan et al. 2018). However, Mars lacks an active dynamo today and one of the fundamental questions about the evolution of Mars is the timing and consequences of the cessation of the dynamo.

In situ compositional and mineralogical measurements on the martian surface, combined with analyses of martian meteorites, indicate that most igneous rocks are lavas and volcaniclastic rocks of basaltic composition and cumulates of ultramafic composition (McSween, 2015). Alkaline rocks are common in Early Hesperian terranes and tholeiitic rocks dominate younger Amazonian martian meteorites (McSween, 2015). The volcanic rocks provide indirect information on the composition of the mantle and core. Radiogenic isotopes in martian meteorites indicate that distinct mantle source regions have remained isolated since earliest martian history (e.g., Debaille et al., 2007). Very uncommon feldspathic rocks represent the ultimate fractionation products, while granitoid rocks have not been identified.

The impact-driven delivery mechanism for the martian meteorites (Head et al., 2002) biases in favor of more competent samples – young, coherent igneous rocks (e.g., Jones, 1989; Warren, 1994; Walton et al., 2008) – and against rocks that are more representative of the martian crust (e.g., McSween et al., 2009). Comparisons of rock types found among the meteorites to those documented by landed missions demonstrates this bias unequivocally (McSween, 2015); furthermore, of the over 100 martian samples represented by the martian meteorites, only one (NWA 7034 and its pairs) is a regolith breccia (e.g., Agee et al., 2013; Humayun et al., 2013).

Like other terrestrial planets, Mars has had a protracted history of impacts, including massive collisions that produced huge impact basins. Martian meteorites provide some insights into shock metamorphism and limited impact melting, although the effects of planetary-scale impacts are not recorded in these samples. Shergottites contain a variety of high-pressure polymorphs, as well as pockets of impact-melted glass. The role of impacts in producing subsurface geothermal systems has been advocated based on spectroscopic identification of altered minerals (e.g., Ehlmann et al., 2011a) and studies of terrestrial craters.

5.2 Key Open Questions for Objective 5

While the meteorites provide important insights into the nature of the silicate portion of Mars, including the origin of mantle components with differing geochemical characteristics (e.g., McCoy et al., 2011), they do not provide information on the composition of the original crust of Mars, nor the nature of the mantle sources from which ancient rocks at the martian surface have been derived (e.g., igneous rocks at Gusev and Gale craters). Indeed, whether the martian mantle as viewed from the meteorites is applicable to all of Mars is also unknown (McCoy et al., 2011). The mostly young ages, prevalence of shock effects, and lack of information constraining the original orientations of meteorites has prevented determining the lifetime of the martian dynamo and from measuring the direction of the ancient martian magnetic field.

Table 5.1: Key open questions for Objective 5: Understanding the origin and evolution of the martian interior

KEY	OPEN	QUESTIONS:	OBJECTIVE 5

What was the long-term petrologic and geochemical evolution of Mars?

What was the intensity of the ancient martian dynamo, did it undergo reversals, what phases record the paleomagnetism, and when did it cease to produce a magnetic field?

What is the history of core segregation/solidification and mantle convection, and did Mars ever experience plate tectonics?

Understand the nature, timing, and pervasiveness of shock metamorphism and melting on Mars.

5.3 Why returned sample studies are important for Objective 5

The objective of reconstructing the history of Mars as a planet, including the fundamental processes of planetary differentiation into a primitive crust, mantle, and core, and the subsequent evolution of those components in composition and character, requires specific types of samples. In order to address the evolution of the mantle of Mars, samples that record igneous compositional diversity (in major, minor and trace elements and isotopes) reflecting differences in mantle source characteristics and/or igneous fractionation processes are needed. Oriented samples with magnetic minerals are extremely valuable as records of the evolution of the martian dynamo. In order to investigate the nature of the processes that formed and affected the primitive crust of Mars and that formed during the expected lifetime of the dynamo, samples as ancient and as unaltered as possible are required (Early Noachian and pre-Noachian). Impactites of varying type are needed to provide insights into the nature of cratering on Mars.

5.4 Sample Investigation Strategies to achieve Objective 5

Strategies for collecting samples relevant to this objective are varied. In order to obtain a diverse suite of igneous rocks for Investigation 5A, a strategy similar to that outlined for Investigation 1.5A will be required; that is, sampling of igneous rocks encountered in "float" (cobbles or boulders along the rover traverse). A suite of samples appropriate for paleomagnetic studies (Investigation 5B) – specifically, oriented samples of fine-grained basaltic rock or clastic or chemical sedimentary rock – will require sampling from outcrops where the relative and absolute orientations of the samples are known. Key science objectives for paleomagnetic studies are given in Figure 5.1. Samples needed to investigate the composition and nature of the early martian crust (Investigation 5C) will require a strategy complementary to, and in parallel with, investigations of water/rock interaction during the Pre-Noachian (Objectives 1.2, 1.3, 1.4). Lastly, the collection of samples that record the processes associated with impact cratering will require the detailed mapping of impactites at the landing site, and the careful selection of samples within their outcrop context; of the four sample types required for this Objective, this is perhaps the most challenging due to the complex nature of impactites.

We have defined four investigation strategies and 17 sets of measurements to reconstruct the processes that have affected the origin and modification of the interior, including the crust, mantle, core and the evolution of the martian dynamo (Table 5.2).

Figure 5.1: Key science objectives related

to paleomagnetic investigations. Those marked with an asterisk (*) require oriented samples After Weiss et al.,

(2018).



Characterize the intensity and timing of the Martian dynamo.



Characterize the dynamo reversal frequency and conduct magnetostratigraphy.



Test the hypotheses that Mars experienced plate tectonics and true polar wander.



Determine the major mineral carriers of Martian crustal magnetization

Table 5.2: Summary of sample-related investigation strategies to understand planetary-scale martian geologic and geophysical processes, including those that have affected the origin and modification of the crust, mantle and core.

Investigation Strategies (IS) for Objective 5						
5	Geology	Reconstruct the processes that have affected the origin and modification of the interior, including the crust, mantle, core and the evolution of the martian dynamo.				
IS 5A		the long-term petrological evolution of Mars, from core segregation to crustal ation, and the origin of chemically distinct mantle reservoirs.				
IS 5B	Determine the thermal and magnetic history of the interior of Mars, including core					
IS 5C	Determine the composition, petrology, and origin of the early martian crust					
IS 5D	shock-rela	e the chemistry, mineralogy, and geochronology (both relative and absolute) of ated rocks and mineral assemblages, impact-induced melts, impact-related rmal alteration, and impact-deposited sediments.				

<u>Investigation Strategy 5A:</u> Constrain the long-term petrological evolution of Mars, from core segregation to crustal differentiation, and the origin of chemically distinct mantle reservoirs.

Radiogenic isotopes record a time-integrated history of the planet's geodynamic evolution from its beginning to its present-state, including core formation, crustal differentiation, and subsequent modifications by impacts. By sampling igneous rocks, especially those of basaltic composition, geodynamical models can be developed to represent the entire global history of Mars. Such modelling is based upon results from the study of a diverse suite of igneous rocks (Section 4.5) that can bring deep insights on magma production and differentiation, and secondary alteration. Notably, the study of the abundance of highly-siderophile elements (HSE) in a diverse suite of igneous rocks, coupled to short-lived chronometers (e.g., Hf-W), nucleosynthetic anomalies (e.g., Ru, Mo), and stable isotopic composition of siderophile elements (e.g., Pt, Ru) can provide insights on the timing and nature of metal-silicate segregation on Mars as a whole, and also on the meteoritic input that has gardened the martian surface over the last 4.5 billion years. Additionally, by applying these approaches to all igneous rocks sampled, we can further constrain the bulk crust and mantle composition of Mars, as well as isotopically distinct reservoirs, and compare results to those obtained from the martian meteorites. These studies will allow for the identification of any new geochemical reservoirs and determine whether they reside in the crust or mantle, and provide novel insights into martian geodynamic evolution. The study of the elemental concentration and isotopic composition of moderately volatile elements (e.g., K, Zn, Rb) can be used to estimate the volatile inventory of Mars and the origin of the volatile delivery to Mars compared to the Earth and other planets, which are major unresolved questions.

While much has been inferred about the mantle of Mars from studies of martian meteorites (e.g., Borg & Draper, 2003; Herd, 2003; McCoy et al., 2011; McCubbin et al., 2016b), no direct sample of the martian mantle or lower crust exists among the meteorites. A sample of a mantle xenolith would provide potentially significantly improved constraints on the mineralogy of the martian interior and allow tests of mineralogy inferred from meteorite studies (e.g., Bertka & Fei, 1997) as well as information complementary to that obtained by geophysical methods (e.g., Khan & Connolly, 2008) including expected results from the NASA InSight Mission

(https://mars.nasa.gov/insight/). A sample suite that included mantle xenolith(s) with basaltic melt counterpart(s) would enable the full characterization of martian mantle sources and their derived melts (e.g., Figure 5.2). A xenolith from the lower crust would also be very useful, for placing constraints on the composition of the primitive crust of Mars and for assessing models involving assimilation of/contamination with ancient crust (e.g., Herd et al., 2002).



Figure 5.2: An example of a peridotitic mantle xenolith from Earth (Creative Commons). Imagine if such a sample could be found on Mars!

 Table 5.3: Samples and measurements implied by Investigation Strategy 5A

Samples identified to advance Investigation Strategy 5A:

• A suite of igneous rocks and breccias representative of the diversity of available igneous rock types. Basalts and highly fractionated rocks are especially informative. An ultramafic igneous rock within a basaltic igneous host rock would represent a potential mantle or lower crustal xenolith.

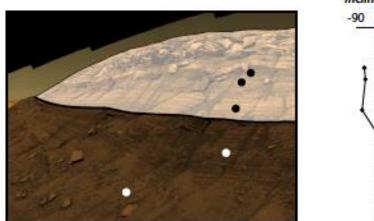
Measurements identified to advance Investigation Strategy 5A:

- Measure variability in the mineralogy, texture, mineral proportions, and mineral chemistry (major, minor and trace element), and bulk compositions (major, minor and trace element, and radiogenic isotopes) of all igneous rocks and igneous clasts within brecciated samples, or as xenoliths in basaltic samples in order to classify them relative to other igneous rocks from Mars, and determine whether they represent primary mantle melts or melts affected by interaction with other mantle or crustal sources or components.
- Measure radiometric ages (e.g., U-Pb, K-Ar, Sm-Nd, Lu-Hf, Rb-Sr) of each igneous rock from as many systems as feasible in order to obtain crystallization ages and ages of source regions. (Note that although the Hf-W system would be of interest, this may or may not be possible using samples collected by M-2020, because of potential contamination from the drill bit).
- Measure stable isotopic compositions (e.g., K, Zn, Rb, O, H) of minerals and bulk rock samples in order to quantify primary igneous and secondary (e.g., alteration or other modification) processes.
- Measure the HSE abundances of all breccia clasts and each igneous rock type sampled in order to gain insights into the original composition of Mars and core-mantle segregation and mantle differentiation processes

<u>Investigation Strategy 5B</u>: Determine the thermal and magnetic history of the interior of Mars, including core crystallization, mantle convection, plate tectonics, true polar wander, and the nature of dynamo generation (intensity, secular variation, and reversal history).

Although Mars does not have an active dynamo today, spacecraft measurements of the martian crust (Acuna et al., 2008) and paleomagnetic measurements of martian meteorite ALH 84001 indicate that a core dynamo was active on Mars by at least the Early Noachian epoch (Weiss et al., 2004, 2008; Cassata et al., 2010). One of the key hypothesized mechanisms for and the subsequent transition to the current cold dry conditions is that the loss of this early dynamo led to stripping of the atmosphere by the solar wind. Paleomagnetic measurements of ancient returned samples could test this hypothesis by establishing the relative timing of the decline of the dynamo to climate change as recorded by surface rocks, especially if the orientations of the returned samples were known (Figure 5.3). Furthermore, because the original orientations of martian meteorites are unknown, all Mars paleomagnetic studies to date have only been able to measure the paleointensity of the martian field. Therefore, paleomagnetic studies from returned martian bedrock samples would provide unprecedented geologic context and the first paleodirectional information on martian fields. Such data could be used to test the hypotheses that early Mars underwent plate tectonics and/or true polar wander. Furthermore, these data could be used to characterize the dynamo reversal frequency with magnetostratigraphy, which could be used for relative chronometry and to constrain the mechanism of the martian dynamo and core flows. In addition, the times that the dynamo initiated and ceased may constrain the thermal evolution of the martian core and mantle. Finally, paleomagnetic studies of folds and conglomerates, including the Early pre-Noachian megabreccia blocks, would constrain the peak temperature and timing of aqueous alteration on samples returned from these materials, which would be important indicators of the preservation state of their biosignatures (Weiss et al., 2018; Mittelholz et al. submitted).

We note that this Investigation Strategy has deep links with Investigation Strategy 3C but nevertheless is fundamentally distinct. Investigation Strategy 3C focuses on determining the *timing* of the dynamo history and polar wander by coupling paleomagnetic measurements on well-dated rocks. By comparison, Investigation Strategy 5B focuses on determining the mechanism and geometry of the dynamo, establishing the existence of plate tectonics and true polar wander, constraining the nature of martian ferromagnetic minerals, and constraint the thermal and aqueous alteration history of the samples. None of the latter topics require well-dated samples and several of them do not relate to planetary history at all (magnetic mineralogy, and alteration history of the samples). As a result the two Investigation Strategies have differing optimal sample suites: Strategy 3C requires well-dated rocks, ideally oriented, while Strategy 3B requires samples with a more diverse set of properties but with less focus on their absolute age. Pre-decisional – For planning and discussion purposes only.



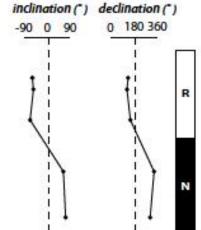


Figure 5.3: Schematic diagram showing the utility of oriented samples obtained *in situ* for paleomagnetic investigations.

Table 5.4: Samples and measurements implied by Investigation Strategy 5B

Samples identified to advance Investigation Strategy 5B:

 Igneous rock sample (ideally fine-grained basaltic rock), or sedimentary (clastic or chemical) samples for which the orientation during the time they became magnetized is known (Figure 5.3)

Measurements identified to advance Investigation Strategy 5B:

- Measure the absolute direction and intensity of magnetization in oriented martian bedrock materials as a function of time.
- Determine the major mineral carriers of martian crustal magnetization by measuring their rock magnetic properties.
- Measure the ages of rocks that contain geomagnetic anomalies to constrain the age of the dynamo and martian magnetic history.

<u>Investigation Strategy 5C:</u> Determine the composition, petrology, and origin of the early martian crust

The processes involved in the formation of the earliest martian crust are largely unknown, but likely involved aqueous alteration under neutral to acidic conditions during the Noachian to early Hesperian (Sub-Objectives 1.2, 1.3, 1.4). Initial formation may have involved magma ocean crystallization, analogous to what happened on the Moon, followed by overturn or large-scale stratification (e.g., Ehlmann et al. 2016 and references therein). The main purpose of this investigation is to "see through" aqueous alteration of the early martian crust, in order to determine its composition and the processes (e.g., magma ocean crystallization) involved in its formation. Samples of igneous rock as relatively unaltered clasts within a suite of probable Noachian-aged altered rocks, or relict mineral clasts within sedimentary deposits such as alluvial fans, would be required to address this investigation.

 Table 5.5: Samples and measurements implied by Investigation Strategy 5C

Samples identified to advance Investigation Strategy 5C:

• A suite of ancient rocks that are the most likely candidates for the original crust of Mars, including those subjected to the least amount of apparent aqueous alteration.

Measurements identified to advance Investigation Strategy 5C:

- Measure variability in the mineralogy, texture, mineral proportions, and mineral chemistry (major, minor and trace element) of rocks that have been modified by water/rock interactions.
- Identify cross-cutting relations, and measure radiometric ages of primary (igneous) and secondary (alteration) minerals with permissible mineralogy.
- Measure stable isotopic compositions (C, H, O, N, S) of minerals from veins and cavities.
- Determine the composition of fluid inclusions and reconstruct trapping temperatures from phase relationships within those inclusions.
- Determine the conditions of (metamorphic) equilibration of rocks, including temperature and pressure.

<u>Investigation Strategy 5D</u>: Determine the chemistry, mineralogy, and geochronology (both relative and absolute) of shock-related rocks and mineral assemblages, impact-induced melts, impact-related hydrothermal alteration, and impact-deposited sediments.

The impact cratering record of Mars includes a wide range of crater sizes, ages, crater densities, and conditions of impact and preservation (e.g., Ehlmann et al., 2016 and references therein). In addition to the timing of specific impact events (in particular of large, basin-forming events such as lsidis), much remains unknown regarding the relationship between impact cratering and induced hydrothermal activity, and the duration of hydrothermal systems as a function of crater size (Osinski et al., 2013). Improvements to our understanding of cratering as a process for modifying the martian surface are needed. Although impact processes are recorded in martian meteorites, none of them are impact breccias (sensu stricto); however, an impact breccia from a major basinforming impact event would provide insights into the nature of the target rocks (Figure 5.4), whether clays were formed during widespread alteration conditions at the martian surface, or *via* impact-induced alteration (e.g., Tornabene et al., 2013), and potentially the compositions of subsurface ice, paleofluids and/or atmospheric gases from the time of impact (e.g., Usui et al., 2015). Sedimentary deposition in the form of fallback breccia or ejecta flow may be important in the impact process on Mars; a sample of rock that records this process would be useful, as long as it can be distinguished from rocks deposited by water or wind (e.g., Objective 1.1).



Figure 5.4: Melt-bearing breccia (aka suevite) from the Mistastin Lake impact structure, Canada; courtesy G. Osinski. anles and massurements implied by Investigation Strategy FD

ements implied by Investigation Strategy 5D			
Samples identified to advance Investigation Strategy 5D:			
 Hydrothermally altered impact breccia or in-place rocks modified by impact-induced hydrothermal activity; any impactite or heavily shocked rock of any type (Figure 5.4). 			
advance Investigation Strategy 5D:			
 Measure variability in the mineralogy, texture, mineral proportions, and mineral chemistry (major, minor and trace elements) of rocks that have been formed or modified by impact-induced hydrothermal activity. Determine cross-cutting relations, and measure the radiometric ages of the primary and 			
 secondary minerals with permissible mineralogy. Measure the isotopic composition (e.g., Cr) of rocks that have been formed by impact in order to determine the origin of the meteoritic material impacting Mars. 			
g relations, and measure the radiometric ages (e.g., by Ar-Ar, Rb-Sr, d secondary minerals with permissible mineralogy.			
 Constrain the shock pressures and temperatures experienced by the minerals and melts during impact. 			
6 Objective 6: Understand and quantify the potential martian environmental hazards to future human exploration and the terrestrial biosphere			
VIRONMENTAL HAZARDS TO HUMAN EXPLORATION			
The gaps in our knowledge related to martian environmental hazards, risk to the terrestrial biosphere, and the safety of engineered systems need to be closed.			
Airfall dust, and surface regolith containing dust-sized particles.			

6.1 Introduction and Current State of Knowledge

Mars has long been a captivating target for future human exploration, but there are still unknowns in terms of potential hazards posed by the martian environment. There are three principal classes of hazards to be considered: 1) those that could cause harm (biological or chemical) to human explorers visiting (or living on) the martian surface, 2) hazards to the systems that human explorers would rely on to survive on Mars, and 3) potential biological hazards that could be transported back to Earth. Mars sample return would present an ideal opportunity to improve our understanding of these hazards (Bass et al., 2012). Furthermore, sending humans to Mars is incompatible with present Planetary Protection Policy requirements for robotic missions. These policies will be revised under a future (dramatically different) planetary protection paradigm that does not yet exist. To inform this policy development, new data with a very high degree of confidence is required, necessitating evaluation of the hazardous nature of an array of martian samples including some representative of the globally circulating dust.



Figure 6.1: Apollo 17 astronaut Eugene Cernan covered in lunar dust (Photo Credit: NASA). Pervasiveness of lunar dust on exterior of suits and interior of lunar module demonstrates exposure hazards for astronauts and the back-contamination of Earth.

As demonstrated by our experience with Apollo, once the crews opened the seals to their landed systems to carry out EVA explorations, it was impossible to avoid getting dust on the outsides of the spacesuits as well as into the living quarters (Figure 6.1; Gaier, 2005). The lunar dust caused more than just acute health hazards (Armstrong & Collins, 1969; Cain, 2010; Sheenan, 1975), it also caused numerous problems with the space suit including jamming joints and degrading seals as well as abbraiding away multiple layers of the Kevlar-like material on the boots (Cooper, 2008). This effect may be amplified on Mars given: 1) the longer duration of the currently-envisaged martian exploration missions where the duration of the surface exposure is weeks-years, compared with the lunar landed missions on the order of hours-days (e.g., NASA, 2009) and 2) the presence of local and global dust storms, as well as the effects of spacecraft ascent/descent engine plumes, which lift and transport dust (Figure 6.2). Futhermore, on the martain surface, there is an extra concern that there is also a biological hazard to human explorers and engineering systems (in addition to the geochemical hazards) given the possibility of biofilm formation on sensitive surfaces which could lead to biocorrosion (Levine et al., 2018; Winterhalter et al., 2018).

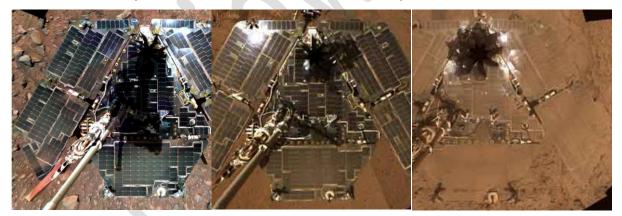


Figure 6.2: Mastcam views of the change in the Spirit rover dust coverage. (Photo Credit: NASA). Pervasiveness of martian dust on the Spirit Rover demonstrates exposure hazards for astronauts and potential back-contamination of Earth.

Given the previous text, which describes the high likelihood that crews will be exposed to uncontained martian material, the action of returning the astronauts to Earth at the end of the mission reveals the possibility of exposure of the terrestrial biosphere to martian material. Although consensus is that this would pose a low but as-yet undefined risk as both a human health concern and as a concern for the terrestrial biosphere (NRC, 2002), it is vital to fully understand all possible outcomes.

A preliminary description of the measurements required to determine the presence of extant life and assess if dust were the mechanism for its transport is described in the NASA Draft Test Protocol for detecting possible biohazards in martian samples returned to Earth (Rummel et al., 2002). This test protocol is now over 15 years old, and was developed in the context of an outdated Mars sample return concept that is not representative of the current sampling concept and anticipated returned sample suite. It would need to be updated in the future months and years in response to instrumentation advances, refinement in knowledge of the sample material to be returned, and an increased understanding of Mars and of life itself.

Specifically, given our improved knowledge of Mars and recognition of at least 12 different habitable environment types (Ehlmann & Edwards, 2014), attention needs to be paid to the method and statistics of assessing the biohazard risk of a returned sample set that might have material from multiple environments (SSB, 2009). This needs to take place in conjunction with preliminary scientific examination, as they are complementary and intrinsically related (Haltigin & Smith, 2014; Kminek et al., 2014). In addition, the revision ought to take into consideration terrestrial technological advances in the intervening period, particularly in the context of robotic handling (e.g., surgical equipment and microelectronics industries) and life detection instrumentation and technologies (e.g., -omics type approaches) (Johnson et al., 2017; Reuter et al., 2015; Dauphin et al., 2009).

6.2 Key Open Questions for Objective 6

The gaps in our knowledge that would be informed by returned samples fit into three primary groups: human health hazards, terrestrial biosphere risk, and engineered systems safety (Figure 6.3)

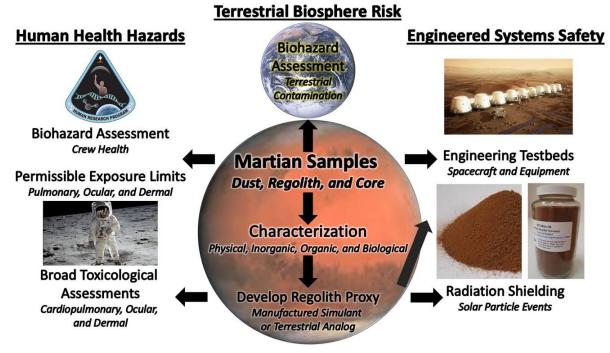


Figure 6.3: Schematic of Objective 6 - Constrain the nature of the potential hazards to future human exploration. The five primary knowledge gaps are highlighted.

Table 6.1: Key open questions for Objective 6: Understanding potential hazards to human exploration

KEY OPEN QUESTIONS: OBJECTIVE 6

Does the martian environment contain biological hazards that might have adverse effects on Earth and terrestrial beings (Planetary Protection)?

Does the martian environment contain biological hazards that might have adverse effects on a future mission?

Does the martian environment contain geochemical hazards that might have adverse effects on a future crewed mission?

What are the physicochemical differences (bulk, fine, and trace) between the global dust and near-surface/surface regolith material?

Is the martian surface safe for human operations (e.g., hardware maneuverability, structural integrity, launch- and landing-pad safety)?

Can martian regolith be effectively utilized as a radiation shield for humans on the surface?

6.3 Why returned sample studies are important for Objective 6

For this objective, samples are needed for toxicological and engineering assessments and also to generate simulants for larger-scale hazard evaluations. Under the international consensus COSPAR policy for planetary protection, material returned from Mars is to be treated as hazardous (meaning be kept under strict containment) until proven otherwise (Kminek et al., 2017). The concern is that the uncontrolled release of an unknown martian organism (should one be present) would present a threat to the home planet, both as a potential human pathogen, and as a replicating entity with the potential to, in some way, disrupt the terrestrial ecosystem more broadly.

In the context of biohazard assessment, interrogation of the returned Mars samples has the potential to inform the level of threat from martian material, informing and reducing risk for subsequent missions, including crewed ones. The same measurements to test the scientific hypothesis that there is martian life in the sample can also be employed to test the competing hypothesis of planetary protection concern: that there is no detectable life in the sample (Allwood et al., 2013; Kminek et al., 2014). Additionally, under the COSPAR policy, biohazard assessment is a pre-requisite for release of uncontained martian sample, and so would be required in order to perform some of the other analyses proposed in this document.

Some of these knowledge gaps have been studied in international workshops, including the 2016 COSPAR workshop on "Refining Planetary Protection Requirements for Human Missions". The report from this workshop (Kminek et al., 2018) identified potential ways for addressing the knowledge gaps. An excerpted subset shown in Table 6.2 below, features the knowledge gaps identified by three splinter groups that can be addressed fully or in part by interrogation of samples returned from Mars:

Table 6.2: Excerpted table showing the MSR-relevant subset of knowledge gapsfrom "Report of the COSPAR workshop on Refining Planetary Protection Requirements for Human Missions" Prioritized H/M/L with highest priorities highlighted (Kminek et al., 2018)

	Priority/0	Priority/Criticality	
GROUP 1: Microbial & Human Health Monitoring	Prioritization	Mission Criticality	
1A. Microbial monitoring of environments	Н	н	
1D. Operational guidelines for planetary protection and crew health	L	L	
GROUP 2: Technology & Operations for Biological Contamination Control			
2A. Bioburden/Transport /Ops during short v. long stays at Mars	М	М	
2C. Protocols (Decontam/Verific/Monitor) to remediate releases	м	н	
2D. Design of quarantine facilities/methods -for different mission phases	L	L	
2E. How do Mars envmtl conditions vary over time wrt growth of Earth microbes	L	н	
2F. Research needed to make ISRU & PP goals compatible	М	м	
2G. Level of "acceptable contamination" left behind/Constraints for venting	L	L	
21. Approach to achieve 'Break the Chain" requirements	L	L	
2K. Evolution of PP Reqts/goals from robotic to human missions & zones	Н	М	
GROUP 3: Natural Transport of Contamination on Mars	Prioritization/Mission Criticality Combined		
3A. Measurements/Models for Mars atmospheric transport of contaminants	н		
3B. Measurements/Models for subsurface transport of contaminants	М		
3C. Effect of Biocidal Factors on survival/growth/adaptation of microbes on Mars	Н		
3D. Determination of acceptable contamination rates & thresholds	Н		
3E. Protection mechanisms for organisms on Mars	N	1	
3F. Degradation of landed materials by the martian environment	N	1	

For returned samples, a step called "<u>breaking the chain of contact</u>" is necessary to manage the risk of release of uncontained martian material. This involves ensuring the containment (to a high level of assurance) of all returning Mars material, while at the same time preventing the return to the Earth of any items that have been exposed the martian environment and might have uncontained martian material on them. Although this is believed to be technically achievable for robotic missions, <u>it is not for a crewed mission</u>; guaranteeing prevention of human contact with the martian dust in all credible circumstances is judged to be impossible with currently available or foreseeable exploration technologies (NRC, 2002; NASA 2009). *Thus, it is necessary to determine in advance whether or not that dust is biologically hazardous.*

There will only be a limited quantity of martian material returned to Earth, yet there are an array of applications that require exposure to martian dust to ensure both crew health and engineering success. Characterization of the returned sample will enable synthesis of a high-fidelity simulant. Not only will this simulant be utilized to complete a broad toxicological assessment (necessary to fill gaps in knowledge resulting from limited quantities of primary samples) but these simulants can be utilized in an array of engineering testbeds (e.g., landing/take-off platforms, rover mechanics) as well as understanding ways in which martian regolith can be utilized as a protective agent (i.e., radiation shield). Knowledge of each of these elements is necessary before crewed missions are sent to Mars - and Mars sample return is necessary in order to acquire this knowledge.

6.4 Sample Investigation Strategies to achieve Objective 6

Analyses under this MSR investigation activity (alongside other relevant *in situ* martian, lunar or terrestrial studies) would aid in reducing risk levels to acceptable, but as yet undefined, standards as they pertain to: 1) the human flight crew of a future Mars mission, 2) humans on Earth, and 3) the

terrestrial biosphere. We have defined four investigation strategies and 20 sets of measurements to understand potential hazards to human exploration (Table 6.3).

Investigation Strategies (IS) for Objective 6					
6	Hazards	azards Understand and quantify the potential martian environmental hazards to future human exploration and the terrestrial biosphere.			
Biological IS 6A		Biohazard Assessment. Determine if martian environments contain biological hazards that might have adverse effects on a future mission (e.g., crew health or spacecraft systems) or on humans or other terrestrial species if uncontained martian material were released on Earth.			
GeologicalIS 6BGeochemical Hazards (human health). Assess risks to crew heat performance and set appropriate permissible exposure limits characterizing the regolith/dust samples and generating simul will determine potential acute toxicity resulting from exposure martian dust.					
Engineering	IS 6C	Geochemical Hazards. Assess broader risks to crew health and performance by characterizing the regolith/dust samples and generating simulants which will allow for an array of acute to chronic toxicity testing to be performed.			
	IS 6D	Characterize the martian regolith for its efficacy as a radiation shield for humans on the surface from a solar particle event. This would include determination of the types and quantity of radiation that can be shielded and the degree to which other biologically relevant particles are formed after passing through the substrate.			

Table 6.3: Summary of sample-related investigation strategies to understand potential hazards to human exploration.

The first two investigation strategies relate to understanding any **hazard to human health** from martian dust, as outlined in the MEPAG report of 2015: *successful Mars exploration, including future human missions to the Mars surface, requires a functional crew free from debilitating health risks imposed by the martian environment, and with the capability to return to Earth safely.*

<u>Investigation Strategy 6A</u>. Biohazard Assessment. Determine if martian environments contain biological hazards that might have adverse effects on a future mission (e.g., crew health or spacecraft systems) or on humans or other terrestrial species if uncontained martian material were released on Earth (amplified from starter material produced by The Mars 2020 Returned Sample Science Board).

The risks in question relate to the: 1) inevitable exposure of surface crew to martian dust containing potential biohazards and 2) potential exposure of humans and other terrestrial species to uncontained martian biohazards, contained within regolith and dust, that would certainly be on the outside of the vehicle and habitats, within the cabin, or even within the astronauts' bodies when the crew leaves Mars. The first step is to assess if the returned samples contain a biohazard. It is important that this is performed first since it is possible that: 1) if the samples contain microorganisms they may not be virulent which could unnecessarily limit further investigation of the returned samples or 2) virulent microorganisms might not be identifiable and overlooked. Given the importance of this investigation, it is vital to assess an array of samples that originate near or are representative of the area in which the human martian surface operations will take place. Surface dust is the main concern for the human explorers, however, information on the subsurface is also important since the crew will disrupt the surface and be exposed to the subsurface during daily operations (e.g., structure building, sample collection) and some of this uncontrolled material will make the journey back to Earth.

Exposures, analyses, and characterizations should first establish what threat a martian organism (or community of organisms) pose to the mission (e.g., pathogenicity to the crew, the ability to compete for or spoil critical resources, and the threat of degrading hardware/systems performance) and to the terrestrial ecosystem (e.g., humans, animals, plants, and resources needed for survival), resulting from the inevitable exposure of the crew on the martian surface and release of uncontained Mars material that will result from the return of the crew to Earth. These tests also establish whether sending crew to the martian surface would inevitably result in exposure to a martian organism, while simultaneously confirming or refuting established wisdom on the limits of life. In the case of virulence, antibiotic resistance will also be assessed.

The second step is to determine if extant life is present in the martian material and identify it. Understanding this is important in order to determine if the biohazards are martian or from virulent terrestrial contamination and also if air-borne dust is a mechanism for its transport. This test establishes whether sending crew to the Mars surface would inevitably result in exposure to a martian organism, while simultaneously confirming or refuting established wisdom on the limits of life. Previous studies (Rummel et al., 2002) have indicated that approximately 10% of the total MSR sample may be required for adequate biohazard assessment. However, other studies have proposed that this could potentially be reduced if biohazard assessment and science studies are performed concurrently on the same sample (Allwood, 2013). Because of the limited nature of the returned sample, strategies will be employed to allow for thorough assessment while minimizing sample usage. Furthermore, it is recognized that other authorities may recommend a different sampling approach in a future update of the biohazard assessment protocol:

The degree of mixing observed for martian dust means that a sample of fine (airfall) dust will be a representation of the geological, chemical and (potentially) biological character of the whole planet. Therefore, if martian organisms exist on the surface of Mars, air-borne dust would be a mechanism for their transport. Notwithstanding breakdown processes that might occur to biological molecules as a result of exposure to the martian surface environment, it is considered that analytical techniques with the necessary sensitivity could be applied to such a sample to bound the occurrence and abundance of biological systems on a planet-wide basis. Limitations of the airfall sample are dilution of biological signal and the uncertainty in context and age of the dust with respect to any biological activity. Evaluation of the biohazard threat of regolith samples from the location to be visited would give greater certainty about biohazard threat in proximity to the human landing site, but as we have no selected landing site for a human mission, achievement of this desirable aim is unlikely to come through the M-2020 mission.

In establishing if there is, or ever was, life on Mars, it is considered that the best-preserved evidence would probably be in a location protected from radiation incident at the surface, potentially at least 2m below the surface. It would need to be established that the regolith sample obtained has a high probability of being sufficiently old to have been protected beyond the timeframe of an obliquity cycle, when redistribution of water at the global scale would have most likely caused biomarkers of martian origin to have been deposited in the regolith material or to have migrated into the sample material. Dust remaining on the surface of the sample tubes or hardware may represent the most pristine samples available as well as the most likely material to be exposed to humans. If possible, the dust can be removed from the hardware/tube exterior and accumulated or the unadulterated hardware/sample tubes can be used for the toxicology assessment (e.g., placed within an occupied animal cage).

Table 6.4 describes the ideal samples types for martian biohazard assessment and Table 6.5 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 6A and move towards determination of whether martian environments contain biological hazards that might have adverse effects on future missions or on humans or other terrestrial species if uncontained martian material were released on Earth.

Table 6.4: Descriptions of ideal sample types for a comprehensive biohazard assessment of the martian
surface.

Sample Type	Justification				
Concentrated airfall dust	The degree of mixing observed for martian dust means that a sample of fine (airfall) dust will be a representation of the geological, chemical and (potentially) biological character of the whole planet. Therefore, if martian organisms exist on the surface of Mars, air-borne dust would be a mechanism for its transport. Notwithstanding breakdown processes that				
	might occur to biological molecules as a result of exposure to the martian surface environment, it is considered that analytical techniques with the necessary sensitivity could be applied to such a sample to bound the occurrence and abundance of biological systems on a planet-wide basis.				
Surface regolith	A limitation of the airfall sample is dilution of biological signal, others include the uncertainty in context and age with respect to any biological activity. Evaluation of the biohazard threat of regolith samples from the location to be visited would give greater certainty about biohazard threat in proximity to the human landing site. The proximity requirement of the sample to the human exploration zone is tbd.				
Subsurface regolith	In establishing if there is, or ever was, life on Mars it is considered that the best preserved evidence would likely be in a location protected from radiation incident at the surface, potentially at least 2m below the surface. It would need to be established that the regolith sample being obtained has a high probability of being old enough (i.e. has been buried at the 2m depth) to have been protected beyond the timeframe of an obliquity cycle, when redistribution of water at the global scale would have most likely caused biomarkers of martian origin to have been deposited in the regolith material.				
Rock cores	As with the subsurface regolith, in establishing if there is, or ever was, life on Mars it is considered that the best preserved evidence would likely be in a location protected from radiation incident at the surface, potentially at least 2m below the surface. It would need to be established that the regolith sample being obtained has a high probability of being old enough (i.e. has been buried at the 2m depth) to have been protected beyond the timeframe of an obliquity cycle, when redistribution of water at the global scale would have most likely caused biomarkers of martian origin to have migrated into the sample material.				
Dust on sample tubes or hardware	The dust remaining on the surface of the sample tubes or hardware may represent the most pristine samples available as well as the most likely material to be exposed to humans. If possible, the dust can be removed from the hardware/tube exterior and accumulated or the unadulterated hardware/sample tubes can be used for the toxicology assessment (e.g. placed within an occupied animal cage).				

Table 6.5: Samples and measurements implied by Investigation Strategy 6A

Samples identified to advance Investigation Strategy 6A:

- Concentrated airfall dust.
- Subsurface regolith, as deep as possible from the same location as the samples for IS 6B.
- Rock cores, as deep as possible from the same location as the samples for IS 6B.
- Dust on surface-exposed sample tubes or hardware.

Measurements identified to advance Investigation Strategy 6A:

- Perform the agreed biohazard assessment protocol, presumably comprising nondestructive characterization (e.g., by CT screening) followed by destructive testing.
- Ecotoxicity Tests.
- Identification of the molecular/genetic material within the returned sample(s) (performed in collaboration with Sub-Objective 2.3).

<u>Investigation Strategy 6B</u>. Geochemical Hazards (human health). Assess risks to crew health and performance and set appropriate permissible exposure limits by characterizing the regolith/dust samples and generating simulants which will determine potential acute toxicity resulting from exposures to martian dust.

Extensive knowledge gained from an understanding of lunar dust toxicity (LADTAG, 2013) is potentially applicable to martian dust. Despite these data, uncertainties exist in setting a martian dust permissible exposure limit, uncertainties that could be directly addressed through return of martian dust samples. Unlike broad toxicological evaluations, permissible exposure limits need to be determined using primary samples. If insufficient quantities of martian regolith samples are available, informal exposure limits may be possible for ocular and dermal contact by utilizing larger size fractions of the primary dust or high-fidelity simulants.

Proper understanding of the inherent toxicological properties of martian dust is crucial to the setting of appropriate crew exposure limits used to control human health and performance risks (because of exposure through inhalation, dermal contact, ocular contact, and ingestion of dust or contaminated food or water.; Cain, 2010; Scheuring et al., 2008; Scully et al., 2015; Lam et al., 2013). The physical and chemical properties and the abundance of trace chemicals contained within the martian dust matrix (e.g., metals and other inorganics such as perchlorates) have been characterized by Mars rover missions, and risks can partially be assessed from these profiles (dependent on assumed exposure route and site-specific factors). However, questions still remain that can only be answered by testing with martian regolith samples, such as the extent to which oxidative properties or other inherent factors would affect toxicity. Taking a similar path to that taken with the assessment of lunar dust (Lam et al. 2013; LADTAG 2013), toxicological testing of returned martian dust would probably consist of the several investigations. Although analysis of a bulk sample is important, different size fractions will be investigated in order to understand the composition and physicochemical properties of the particles most relevant to exposure site (e.g., pulmonary, cardiovascular, ocular, and dermal). Special focus will be given to respirable size fractions ($\leq 10 \ \mu m$ and $\leq 2.5 \ \mu m$ in diameter) and the differentiation of local versus global dust.

Table 6.6 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 6B and move towards assessment of risks to crew health and performance. The studies listed in Table 6.5 will be performed utilizing the samples characterized as part of IS 6A.

Table 6.6: Samples and measurements implied by Investigation Strategy 6B

Samples identified to advance Investigation Strategy 6B:
Concentrated airfall dust, either from a drift deposit or collected from the atmosphere
Near-surface/surface regolith containing dust sized particles
Measurements identified to advance Investigation Strategy 6B:
• Bulk Elemental Composition (EMPA) and mineralogy determination (XRD) to help understand the origin of any toxicity.
• Particle Size Analysis. Determine particle size distribution within the samples as well as confirm size fraction for exposure studies.
• Total Surface Area and Pore Space (BET). Understand the amount of total surface area available for geochemical reactivity and direct interaction with biological systems.
• Morphology (SEM). Analyze the shapes of martian dust grains with a grain size distribution sufficient to assess their potential impact on human soft tissue (especially eyes and lungs)
• Chemical Reactivity (ion chromatography and spectroscopy). Characterize soluble ion concentrations, chemical reactions that can occur, and oxidative potential upon humidification.
• Assess martian dust pulmonary toxicity (adverse impacts to the respiratory system) relative to the known toxicity of lunar dust and well characterized reference dusts (e.g., titanium dioxide
and quartz).
• Assess martian dust ocular hazard (Adverse impact to the eye) using representative unfiltered martian drift surface dust. Particle size is not a practical limitation.

• Assess martian dust dermal hazard (Irritation/Abrasion of skin) using representative unfiltered martian drift surface dust. Particle size is not a practical limitation.

The following two strategies relate to the **<u>safety of engineered systems</u>**, again as outlined in the MEPAG report of 2015: *it is necessary to understand the ways in which the martian environment affects engineered systems*. Successful human missions to the Mars surface requires a functional crew free from debilitating health risks imposed by the martian environment, and with the capability to return to Earth safely.

<u>Investigation Strategy 6C</u>. Geochemical Hazards (Engineering). Assess broader risks to crew health and performance by characterizing the regolith/dust samples and generating simulants which will allow for an array of acute to chronic toxicity testing to be performed.

To ensure crew safety and mission success, spacecraft and equipment designed for future human exploration missions to Mars will undergo rigorous ground testing and evaluation with Mars regolith and with dust simulants on Earth. Crewed systems will be certified to meet new or unique requirements that were not imposed on earlier robotic science missions. For example, spacesuit developers will have to demonstrate suit fabric resistance to martian regolith/dust abrasion damage and ability to remove dust before bringing suits into habitable areas for maintenance. What is more, the scale of human systems—with landers more than 20 times the size of the *Curiosity* rover—may require very large quantities of Mars regolith/dust simulant to support ground testing and certification. Several types of simulants, of varying degrees of fidelity, will be used to evaluate the interaction of the Mars environment with crewed systems. Regolith properties will be important to some evaluations, such as mobile system trafficability; however, dust properties will be much more important because dust will coat virtually all external surfaces, and is more likely to be transported into crew cabins.

Table 6.7 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 6C and move towards assessment of risks to crew health and performance. The studies listed in Table 6.6 will be performed utilizing the samples characterized as part of IS 6A.

 Table 6.7: Samples and measurements implied by Investigation Strategy 6C

Samples identified to advance Investigation Strategy 6C:	
Representative unfiltered martian airfall dust.	
Measurements identified to advance Investigation Strategy 6C:	

- Analyze the particle grain shape, surface area and size distribution to understand how dust will be "kicked up" by large descent engine plumes or large rovers, as well as to validate fluid system component performance, such as filters.
- Abrasivity testing will help evaluation of pressure seal degradation, hatch leakage, optical surface degradation (windows, visors, instruments), damage to protective coatings and rotating equipment (such as bearings or pumps), and wear on spacesuits and flexible insulation materials.
- Determination of electrical and magnetic properties to assess potential problems, such as charged dust particles resulting in static shock equipment damage, as well as to evaluate potential useful properties, such as electrostatic dust cleaning techniques.
- Determination of thermal and optical properties to evaluate dust-coated radiators, solar arrays, electrical cables, and light fixtures.
- Chemical characterization for crop growth experiments (including perchlorate uptake assessment), hardware corrosion assessments, membrane function, and chemical process hardware interactions (such as ISRU or water extraction)
- Surface area analysis to determine how much the sample can adsorb and may be important for developing simulants used in plant growth studies.
- Physical and mechanical properties characterization to assess the interaction of structural elements with the Mars environment.

<u>Investigation Strategy 6D</u>. Characterize the martian regolith for its efficacy as a radiation shield for humans on the surface from a solar particle event. This would include determination of the types and quantity of radiation that can be shielded and the degree to which other biologically relevant particles are formed after passing through the substrate.

Mars' atmosphere and regolith provide some protection from galactic cosmic ray (GCR) and solar irradiation. Studies have shown that additional shielding of common materials such as aluminum or polyethylene does not significantly reduce the GCR exposure (Slaba et al., 2013). A comparison of the attenuation characteristics for different subgroups of martian rocks and the martian regolith indicates that changes in composition have negligible effect on overall shielding properties because of the similarity of their constituents (within 0.5 and 1 %; Kim et. al., 1998). In addition, it is shown that on the martian surface, almost any amount of aluminum shielding increases exposure levels for humans. The increased exposure levels are attributed to neutron production in the shield and martian regolith as well as the electromagnetic cascade induced in the martian atmosphere. This result is significant for optimization of vehicle and shield designs intended for the surface of Mars.

Table 6.8 summarizes the type of samples that should be collected, and the associated measurements required in order to carry out Investigation Strategy 6D and move towards assessment of the efficacy of the martian regolith as a radiation shield for humans on the surface. The studies listed in Table 6.7 will be performed utilizing the samples characterized as part of IS 6A.

 Table 6.8: Samples and measurements implied by Investigation Strategy 6D

Samples ide	patified to	advance	Investigation	Strateav 6D.
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• Representative unfiltered martian airfall dust.

Measurements identified to advance Investigation Strategy 6D:

- Determine the extent of protection that different thickness layers of regolith provide from different types and dosages of radiation
- Determine the extent of damage produced by irradiation of the surface, and assess the potential for biologically-significant species to be produced

7 Objective 7: Evaluate the type and distribution of *in situ* resources to support potential future Mars exploration

UNDERSTAND POTENTIAL IN SITU RESOURCES				
Why is this objective critical?Identifying potential Mars resources, and understanding how they could be utilized, is enable for future exploration				
Which are the most	Regolith of several different kinds, rock with hydrated			
important samples?	minerals, airborne dust			

7.1 Introduction and Current State of Knowledge

Considerable recent planning has focused on the potential importance of Mars *in situ* resources to support future human missions (e.g., Drake et al., 2009; Portree et al., 2011; MEPAG NEX-SAG, 2015; ICE-WG, 2015; Abbud-Madrid et. al., 2016). From the perspective of saving mass on the outbound journey, the single most significant need is for propellant for a Mars Ascent Vehicle (Polsgrove, 2015; see Figure 7.1). A methane - oxygen propellant system was baselined in the Mars Design Reference Architecture (Drake, 2009), partly because of its potential *in situ* availability. By mass, 78 % of that propellant is oxidizer, which is most readily obtained by conversion of the CO₂ that dominates the martian atmosphere into oxygen and CO, which could be used to manufacture methane. Although the martian atmosphere is a crucial resource, for this purpose, measuring its composition more precisely than is already known, by means of analysis of returned samples, is considered not necessary. Some of the notional ISRU concepts that may be involved in future human missions are shown in Figure 7.2.

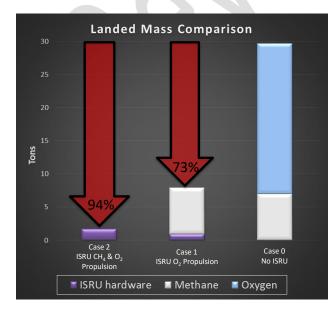


Figure 7.1: Results from an ISRU baseline study (Kleinhenz, 2017) conducted for the Evolvable Mars Campaign showing the benefits of ISRU propellant production. Case 0: the propellant mass needed for a Mars ascent vehicle (Polsgrove, 2015). Case 1: oxygen is produced from the Mars atmosphere and methane is transported from Earth. Case 2: methane and oxygen produced on Mars from the atmosphere and soil water. *In situ* production of the methane fuel requires a source of hydrogen, which can be combined with the carbon from the martian atmosphere. Water is known to be present in significant quantities on Mars and could serve this need. But the interest in water as an *in situ* resource goes well beyond the manufacture of propellant. Water can provide many of the needs of a research station, such as life support, radiation shielding, and agriculture.

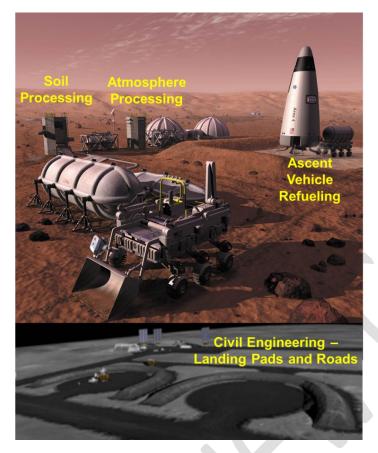


Figure 7.2: Conceptual example of exploration systems using ISRU capabilities.

In situ resource utilization is not limited to propellant and life support production. Local material could also be used as feed stock for construction, including for structures, roads, and additive manufacturing. Native salts (Mg, Ca and Na perchlorates and Ca-Chloride) in the martian regolith could be used as water absorbents for closed loop life support systems or for capture of the limited atmospheric water. Mars regolith could also be used to supplement agriculture (Wheeler, 2004). Hydroponic plant growth requires around 90 kg of fertilizer to provide dietary calories for one person per year (365 days) (Lunn et al., 2017). Nutrients from regolith, nitrates in particular, could be used to reduce terrestrial fertilizers as would recycled waste materials. These *in situ* nutrients could be extracted and incorporated into a fertilizer, or the regolith itself could be enriched into a soil which would provide more buffering to the plant roots.

Water: A planet-wide survey of water resources down to a depth of about 1 m was provided by the Gamma Ray Spectrometer Suite on the Mars Odyssey spacecraft, suggesting that even at the equator, the near-surface regolith contains 3 - 7 % water-equivalent hydrogen (Boynton et al., 2002). However, the GRS pixel size is approximately 400 km, which is not amenable to planning specific engineering implementations. Neutron data collected by the Dynamic Albedo of Neutrons (DAN) instrument along the pathway driven by MSL measures total hydrogen (modeled as "water equivalent hydrogen" or WEH) over a 3 m wide, 60 cm deep footprint. Most of these data are best modelled by a 2-layer structure, where the upper layer is ~ 20 cm thick, and has less hydrogen (average 1.5 - 1.7 % WEH) than the lower layer (average 2.2 - 3.3 % WEH) (Litvak *et al.*, 2014; Mitrofanov *et al.*, 2014). The total amount of H₂O released from samples analyzed by MSL to date has been around 2 wt. % for each sample (values range ~ 1.1 ± 0.5 up to ~2.5 ± 1.6 wt. %; (Vaniman,

2014). The CheMin data from MSL's first three samples show the presence of the hydrated minerals bassanite, akaganeite, and smectite along with an unidentified amorphous component, although with an uncertainty in the concentration of ~ 50 % (Vaniman et al., 2014). Perchlorate was first identified as a significant component of martian regolith (0.4 - 0.6 wt. %) by the *Phoenix* mission (Cull et al., 2010), it was probably seen by *Viking* (Navarro-Gonzalez et al., 2010), and the SAM data indicate the presence of oxychlorine minerals with abundances as high as 1.05 \pm 0.44 wt. % Cl₂O₄ equivalent (Sutter et al, 2017). Some of the water content of the martian regolith may be in the form of perchlorate hydrates. In the Rocknest sample, CheMin did not detect any hydrous crystalline phases, and yet SAM showed water release upon heating (Leshin et al., 2013). Most of that water must therefore be in an X-ray amorphous component. The specifics of the mineralogy make a big difference in understanding the quantity of water that could be expected to be released with temperature in an ISRU recovery operation.

Ice: The presence of water in the form of ice deposits is also of great interest to ISRU. Recent studies have identified substantial ice sheets at depths of ~ 1 m at a latitude of ~55 °N (Dundas et al., 2018). Permafrost also exists at shallower depths and in great quantity, at latitudes higher than ~60 ° (both N and S) (Mellon, 2009). There are some important trade-offs between accessing and utilizing the subsurface ice versus accessing surface hydrated material; these trade-offs are still under engineering evaluation.

Atmosphere: The use of the Mars atmosphere in the production of oxygen is a critical part of ISRU propellant and life support production stategy. While understanding the Mars atmosphere is important, the tehcnologies to preform this processing are well underway. A lot of valuable data will be collected by the MOXIE investigation on the M-2020 mission (Hecht et. al., 2017; McClean et al., 2017).

<u>Other resources</u>: Beyond water, a Mars research station would have needs for local fabrication and production of many materials that could have a local source. One example is concrete for fabrication of building materials, possibly robotically (Lee et al., 2015). Additive manufacturing using local regolith, has also been explored (Jakus et al., 2017) and the idea of refining materials to extract other resource has also been discussed (e.g., regarding lunar regolith; Landis, 2007). These and other uses of *in situ* resources will benefit greatly from laboratory analysis of the composition and morphology of martian rock and regolith.

7.2 Key Open Questions for Objective 7

This objective specifally addresses exploration, where identifying and utilizing Mars resources is an enabling capability, particularly for human exploration. Orbital data and landed surveys have identified useful resources such as water. Yet knowledge is lacking regarding how the resource is bound (eg hydration state for water), the physical and thermophysical properaties of the materials, and what other useful minerologic components may exist.

Table 7.1: Key open questions for Objective 7: Understanding potential in situ Mars resources

KEY OPEN QUESTIONS: O	BJECTIVE 7
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What is the concentration, mineralogic basis, and variation of water in martian surface materials?

What are the physical and thermophysical properties of martian surface materials of relevance to the design of potential future ISRU surface systems?

What is the potential of martian granular material for use for in-situ agriculture?

Contingent on discovering significant concentrations of metals of potential future interest, can we predict the possibility of significant deposits on Mars?

7.3 Why Returned Sample Studies are Important to Objective 7

Any of these *in situ* utilization processes require definition of the resources to influence equipment design and resource budgeting. Prospecting *via* orbital and landed surveys as well as technical demonstrations are necessary. Sample return will play a role in supporting this planning, including ground truthing of orbital surveys. Sample return can provide a more comprehensive picture of the availible resources and their properties. When considering long-term human presence this information becomes more critical to site selection, architecture decisions, and hardware design. Likewise, detailed assays of a returned sample may identify other resources and/or ultization potential not yet considered.

Water resources: The form and concentration of water within the regolith is critical to exploration architecture planning and engineering design. While orbital and landed surveys offer enough information for intial designs and technology demostrations, long term human missions would benefit greatly from more comprehensive information. Sample return would permit chemical and geotechnical characterization of the surface material. This allows for refinement of engineering designs and architecture decisions and enables development of high fidelity simulants for terrestrial tests. Lunar ISRU technology development has benifited from the analysis of samples returned from the Moon. While viable ISRU water resources may exist as either hydrated minerals or as water Ice, the focus on this sample return is the former (Figure 7.3). While water ice samples would equally beneficial, the current Mars-2020 landing sites are with 19°N of the equater, where ice is not present. Therefore, the sample objectives listed here do not encompass ice samples.

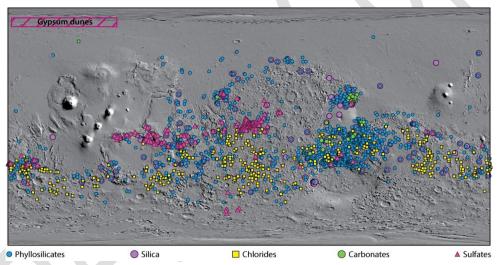


Figure 7.3: A map of aqueous mineral deposits from orbital data (Ehlmann & Edwards, 2014) as potential sources of water for ISRU purposes.

<u>Atmospheric resources</u>: Characterizing the Mars atmosphere is not explicitly including in these objectives. Instruments already available on Mars 2020 will adequately cover this without the need for samples. However, characterization of the dust would be of value to enable better predictions of lifetime, performance, and risk factors for candidate mechanical systems.

Other resources: Beyond water, local resources may have application to construction, additive manufacturing, and agricultural uses. Understanding the feasibility and value of these applications would benefit from laboratory analysis of the composition and morphology of martian rock and regolith.

7.4 Sample Investigation Strategies to achieve Objective 7

In support of this objective, we recognize four significant returned sample investigation strategies, which are listed below in Table 7.2. One is to measure the concentration and

mineralogical state of water in certain carefully selected samples. A second is to understand the physical attributes of martian surface materials, so that engineered systems could be designed to interact with them properly (note that this overlaps significantly with one of the investigation strategies within Objective 6). The third is to assess quantitatively the potential of martian granular material for use in possible future on-Mars agriculture. There are important subtleties related to the presence or absence of specific beneficial or deleterious components to agriculture, especially those that are water soluble. The fourth strategy, related to potential martian ore deposits, is completely contingent on encountering and collecting samples with high concentrations of potentially useful commodities. It is important to note that carrying out these strategies would not be enough to complete the objective of evaluating the potential for successful martian ISRU operations. Substantial *in situ* exploration is also required. For example, sample analysis by itself can give highly precise and accurate estimates of concentration/quality, but it cannot be used to estimate quantity. Thus, we view these strategies as necessary but not sufficient to complete the larger objective, at least for certain resources of interest.

Table 7.2: Summary of sample-related investigation strategies to constrain the potential usefulness of martian*in situ* resources for future human explorers.

Investigation Strategies (IS) for Objective 7						
7	ISRU	Evaluate the type and distribution of <i>in situ</i> resources to support potential future Mars Exploration.				
IS 7A	 Determine the concentration, mineralogic basis, and variation of water in martian IS 7A surface materials and identify associated chemical constituents that may negatively impact potential end-use processes of this water. 					
IS 7B	Characterize the physical and thermophysical properties of martian surface materials to influence the design of potential future ISRU surface systems and to develop high-fidelity simulant material for use in ISRU engineering test beds.					
IS 7C	Identify components in martian granular material that may be beneficial or detrimental to its use for <i>in situ</i> agriculture.					
IS 7D	Contingent on discovering significant concentrations of natural metallic resources, characterize the source materials to enable predictions of where and how such deposits may be concentrated on Mars.					

<u>Investigation Strategy 7A:</u> Determine the concentration, mineralogic basis, and variation of water in martian surface materials and identify associated chemical constituents that may negatively impact potential end-use processes of this water.

In situ utilization processes require definition of the resources to influence equipment design and resource budgeting. Namely the form and concentration of water within the regolith is critical to this process. Resource sites with higher water content may drive the location of ISRU processes. With the focus on hydrated minerals for this sample opportunity (as opposed to subsurface ice), understanding the minerology will inform decisions about resource availability and possible byproducts. The water release profile upon heating (which stems from the hydration state and the type of hydrated minerals) is a critical engineering trade regarding heat input and the power profile of the hardware needed (Kleinhenz, 2017). Potential contaminants that could release upon this heating could impact downstream systems, such as electrolysis, and necessitate the need for additional hardware to mitigate this.

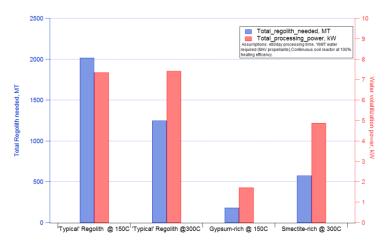


Figure 7.4: An engineering trade showing the processing temperature and quantity of regolith needed to extract water from potential Mars aqueous minerals as defined in the MWIP study (Abbud-Madrid et. al., 2016).

The goal of the samples requested is to understand the water potential. "Typical" surface regolith is likely to be of lower yield but more readily available. Consolidated material with a high water content may be more difficult to obtain and process, but offer reduced processing power and capacity. A shallow subsurface sample of 'typical' regolith may offer a higher water yield. MSL DAN and REMS *in situ* results at Gale suggest the existence of an upper drier layer, 20 cm thick, involved in the water interchange with the atmosphere (with average 1.5 - 1.7 % WEH) and a lower layer below 20 cm with higher water content (average 2.2 - 3.3 % WEH) (Litvak et al., 2014; Mitrofanov et al., 2014; Martin-Torres et al., 2015). Orbital observations (Mitrofanov et al., 2004) also suggest a top dry layer of 2 % water by mass overlying a wet layer with around 16 % water by mass in some regions near the equator. Assuming *Viking 1* rocky sand, the thermal skin depth would be approximately 8 cm for the diurnal period and 2 m for the annual period (Patton et al., 2013). We recognize the potential challenges of obtaining a subsurface sample with the Mars 2020 mission. If the rover can get to depths greater than 8 cm, this would be still be a meaningful gradient for Earth analysis.

Table 7.3: Samples and measurements implied by Investigation Strategy 7A. Samples are listed in approximate priority order

Samples identified to advance Investigation Strategy 7A:

- A "typical" regolith surface sample representative of abundant loose material
- A subsurface regolith sample from the same location as above that accesses material isolated from diurnal heat cycling
- At least one core sample of a sedimentary rock that displays the strongest signature of hydration in the landing zone

Note: The above three samples are identical to those requested for Investigation Strategy 7B. There is potential we can use the same sample for both purposes (as long as we do the measurements in the correct order).

• An additional regolith or rock samples to better constrain more fully the range or variability of water contents in the landing zone.

Measurements identified to advance Investigation Strategy 7A:

- Identify hydrated minerals and hydration states in multiple samples of martian regolith (to facilitate comparison between different regolith types) and in rock samples.
- Characterize the water release profile of these samples with temperature and identify associated contaminants released. Contaminants of particular interest are chlorides and perchlorates which are potential contaminants for water use (propellant production, life support), but are a potentially useful resource for closed loop life support applications.
- Sample probes of at least the depth of the thermal skin depth at sample location, whereby the temperature will remain roughly constant, to characterize the depth of the present day active water layer (absorption and desorption on diurnal/seasonal time scales).

<u>Investigation Strategy 7B:</u> Characterize the physical and thermophysical properties of martian surface materials to influence the design of potential future ISRU surface systems and to develop high-fidelity simulant material for use in ISRU engineering test beds.

The selection of technologies and techniques used to acquire and process the surface material will be highly dependent on the material properties themselves. All of this property information can feed directly into ISRU system models to influence engineering design and can be used to generate/select high fidelity simulant materials for use in hardware test programs.

Knowledge of physical properties will influence the selection of things like digging/excavation equipment (implement, force/energy required, life-span of hardware, etc.) as well as material transfer equipment (gravity fed or mechanical conveyance, sizing, etc.). Reactor systems to extract water will also be dependent on physical and thermophyscial properties. Thermal management and energy requirements are highly reliant on knowing thermal properties, while physical properties, such as particle size, will influence reaction mechanics. Knowledge of the surface fines or airborne dust components will impact filtration design, which is critical for seals and fluid lines as well as any catalyst materials (e.g., electrolysis or water purification units).

The most recent ISRU study focused on using the easyily accessible granular surface material (Kleinhenz, 2017), which likely to have a low water yield. Consolidated material with potentially higher water content may require more robust excavation and comminution equipment. However, engineering studies and models to trade this against the potential for higher water yield require specific geotechnical information of both the consolidated material as well as the granular surface material.

Samples are requested to help bound the range of these properties. The three required samples are identical to those requested in Investigation Strategy 7A. Understanding the potential water yield of a resource along with its physical properties enables important engineering trades.

Table 7.4: Samples and measurements implied by Investigation Strategy 7B. Samples are listed in approximate priority order

Samples identified to advance Investigation Strategy 7B:

- A "typical" regolith surface sample representative of abundant loose material.
- A subsurface regolith sample from the same location as the above that accesses material isolated from diurnal heat cycling.
- At least one core sample of a sedimentary rock interpreted to have a high concentration of hydrated minerals.

Note: The above 3 samples are identical to those requested in Investigation Strategy 7A. There is potential we can use the same material for both purposes (as long as we do the measurement in the correct order).

• An airborne dust sample preferably collected on a filter material to analyze airborne dust properties and its potential interactions with filter material.

Measurements identified to advance Investigation Strategy 7B:

- For martian regolith, characterize the geotechnical properties as regolith particle size distribution and shape, densities, and strength/cohesion properties. This information will influence simulant design and material handling technology (e.g., excavation & transfer).
- For (hydrated) rock samples, characterize the strength and other properties to understand excavation and comminution of rock materials.
- Characterize the thermal properties of the samples to understand heat transfer for resource extraction and system thermal management purposes.
- Analyze regolith properties that may be important for its use in construction applications including as a potential building or shielding material, or as a feed stock for additive manufacturing processes.
- Measure grain size distribution in regolith sample that are comprised of airfall dust in order to understand how small particles might damage catalyst function.

<u>Investigation Strategy 7C</u>: Identify components in martian granular material that may be beneficial or detrimental to its use for in situ agriculture. (Also of interest to Objective #6)

Having multiple regolith samples for basic elemental analysis, and more traditional "soils" type analyses would be invaluable for understanding the needs of future martian agriculture. This could include analyses of the mineral composition, cation exchange capacity (CEC), water holding and so called matric potential, osmotic potential (from soluble compounds / salts), porosity, and more (Thompson and Troeh, 1978). Of course, these must all be taken in the context that the martian regolith is mixture of broken and weathered rock, and not a true "soil" (as that term is used connection with terrestrial agriculture), with organic matter, clay, silts, an active microbiome, and more. Elements essential for plants include (in approximate descending order of need): N, K, Ca, Mg, S, P, Fe, Mn, B, Cl, Zn, Cu, and Mo (Epstein, 1972; Hoagland, 1938). Some other elements can help some plants according to some authors, such as Si, Ni, Co (for N-fixing plants), Na for some halophytes, and perhaps a few others in very small quantities (Epstein, 1972). On the other hand, high levels of some soluble elements, especially transition metals (e.g., Zn, Mn, Cu, Cr, Ni) (Moore, 2017) can often be toxic to plants, as can high levels Na or B or soluble Al. In addition to the straight elemental composition, the compounds and minerals that contain these elements will be important to understand, since these will determine the availability as plant nutrients either through dissolution by water or through microbial processes (Figure 7.5).



Figure 7.5: Seedlings grown in regolith simulant amended soil as part of current NASA sponsored activites.

Basaltic sand dunes are very common on the martian surface and represent a likely candidate for future martian agriculture due to the fertility of basaltic soils on Earth. Initial analyses by the MSL rover of basaltic dunes in Gale crater suggests these materials could be a good source of K, Ca, Mg, Fe, Mn, P, Zn, and Cu; however, they might be depleted in Cl, S, and N (Ehlmann et al.,

2017). Fine-grained bright dune materials on Mars have been shown to contain Cl, S, and N and therefore might be good sources for these elements for agriculture.

Table 7.5: Samples and measurements implied by Investigation Strategy 7C. Samples are listed in approximate priority order.

Samples identified to advance Investigation Strategy 7C:

- A sample of sand-sized basaltic dune material
- One sample of bright fine-grained dune material.
- An additional regolith sample from one or both of the locations specified above. *Measurements identified to advance Investigation Strategy 7C:*
- Identify minerals that are high in elements typically used in fertilizer (N, P, K) in multiple samples of martian regolith (to facilitate comparison between different regolith types).
- Identify compounds that could potentially be damaging to food crop production processes.
- Characterize the presence of metals that may be important for soil microbial metabolism.

<u>Investigation Strategy 7D:</u> Contingent on discovering significant concentrations of natural metallic resources, characterize the source materials to enable predictions of where and how such deposits may be concentrated on Mars.

Because of their rarity, metal resources are arguably one of the two most highly valued resources for modern human civilization (energy resources being the other). As such, they always command extra attention when discovered, either deliberately or accidentally. Ore-forming processes on Earth happen when certain elements are segregated from others, typically either by differential transport or precipitation mechanisms. Once these mechanisms are understood, experts in mineral exploration can predict the location, grade, and mechanical consistency of natural concentrations (and hopefully, these concentrations exceed the definition of "ore"). In the exploration process, it is quite common to have low-grade halos of different kinds of minerals/elements around high-grade deposits—anomalous samples therefore can serve as important signposts.

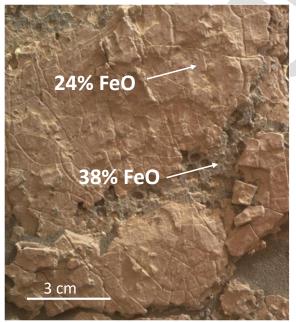


Figure 7.6: Example of anomalous iron detection. MAHLI image of the APXS targets "Morancy Stream" which has 38% FeO and "Morancy Stream Offset" (MSO) which has 24% FeO, acquired on Sol 1668 of the *Curiosity* rover mission. *Image credit NASA/JPL/Caltech/MSSS*

On Mars we do not know that ore-forming processes took place the same way they did on Earth. However, because of the potential future value to the very long-range exploration/habitation of Mars, if samples with high concentrations of possible future martian commodities are encountered, they should be sampled and studied in detail on Earth. The focus is on those metals considered to be the basic building blocks of technology and commerce (Figure 7.6). Note, however, that we view this as being dependent on **samples of opportunity**. The chance of encountering something significant is considered to be low, so it is not justified to have the rover spend a portion of its limited lifetime searching for this. However, if something meaningful is encountered, it could well be worth sampling.

 Table 7.6: Samples and measurements implied by Investigation Strategy 7D

Samples identified to advance Investigation Strategy 7D:

• One sample of the anomalous material.

• Additional samples of rock units nearby to better understand potential ore-forming processes Measurements identified to advance Investigation Strategy 7D:

• Identify minerals that are high in metals (Fe, Ni, Al, Cu, Cr, Au, PGM (Platinum Group Metals), KREEP (Potassium, Rare Earth Elements, Phosphorus)) in multiple samples of martian regolith (to facilitate comparison between different regolith types).

8 Discussion

8.1 Will the Samples to be Collected by M-2020 be Worth Returning?

Can these objectives be achieved with the samples to be collected by M-2020 and by a potential retrieval mission?

The most important message in this analysis is that the details of the science that can be achieved are quite dependent on the samples that are made available to the sample analysts on Earth. Although sample suites and sample context are important, there are multiple ways to put together the collection to achieve the objectives. The M-2020 rover is expected to be able to collect approximately 20 samples within its prime mission, and in our view, a carefully chosen set of 20 samples is enough to put together the necessary suites and individual samples to achieve the objectives we have proposed. These objectives can be more confidently achieved with a full set of 31 samples, representing broader diversity, and that would presumably require that M-2020 continue its sampling operations into the extended mission phase.

- Objective 1. All of the candidate landing sites for M-2020 have evidence for at least one of the four ancient geologic environments known from Earth analog studies to have high habitability potential AND high potential for the preservation of biosignatures. We want to analyze samples from these environments to understand their geologic processes, and we need this foundation to carry out the detailed investigations associated with astrobiology and geochronology. It is possible/likely that more than one of these environments is represented at each site. For example, all of these sites have been exposed to weathering, the key attribute of Sub-Objective 1.4, and all have likely been exposed to ancient martian groundwater, the key attribute of Sub-objective 1.3. The fifth geologic environment, igneous terrane, may or may not be accessible in outcrop at all of these sites. However, as pointed out in Section 1.5, most of our scientific objectives related to igneous rocks do not require outcrop-sourced samples (i.e., in situ), but can make use of transported samples (i.e., ex situ), and our Mars lander and rover experience to date suggests that such samples exist essentially everywhere on Mars. It is also important to note that the landing sites under current consideration are being compared based on what can be seen from orbit, but as has been shown by Sojourner, Opportunity, Spirit, and Curiosity, it is commonplace to discover things on the ground that were not visible from orbit. Thus, aspects of many or all of the five high-priority geologic environments may end up in the sample collection.
- **Objective 2.** Given the samples collected as a part of Objective 1, it would certainly be possible to use them to improve our understanding of Mars' biological potential. This objective is quite technical in nature, and is highly dependent on complex sample

preparation, high-precision, low-detection limit analyses, and stringent contamination control procedures—this is ideally suited to returned sample analysis.

- **Objective 3.** We would very much like to date one or more ancient surfaces that have a defined cratering density. All martian landing sites offer cratered surfaces, and all of the landing sites under consideration by M-2020 are very old (Hesperian or Noachian). However, interpreting crater density can be complicated by the nature of the substrate, the possibility of resurfacing, and the effect of secondary craters, all of which can be interrogated by rovers and returned samples. In addition to that, however, each of the landing sites presents the opportunity to date the products of important martian geologic processes.
- **Objective 4.** The essential strategies for this objective relate to collecting samples of solid materials that have equilibrated with the ancient martian atmosphere, and/or contain trapped gaseous/fluid inclusions of that atmosphere, AND making measurements on one or more dedicated samples of the modern martian atmosphere. A feature in common across all the candidate landing sites is that there is abundant regolith and evidence at each for ancient water/atmosphere-rock interactions. However, M-2020 is not designed to collect an atmospheric sample. This should be adopted as a requirement on the sample retrieval mission.
- **Objective 5.** Understanding Mars as a system requires the collection of very old rocks, including at least some igneous rocks, and rocks (either sedimentary or igneous) that can be used to test models of the history of the martian magnetic field. All of the current candidate landing sites are in Mars' ancient geological terrane, although we cannot presently be sure that they will be suitable for paleomagnetic measurements.
- **Objective 6.** The primary samples of interest for understanding risks to possible future human missions to the martian surface are different kinds of granular materials, including regolith and airfall dust. It is certain that M-2020 will be able to acquire these.
- **Objective 7.** For the purpose of ISRU, we are primarily interested in water-bearing mineral samples, and in regolith. M-2020 will also be able to acquire these.
- **Finding:** If the Mars 2020 rover acquires a scientifically well-chosen set of samples, with sufficient geological diversity, and if those samples were returned to Earth, then major progress can be expected on all seven of the objectives proposed in this study, regardless of the final choice of landing site. The specifics of which parts of Objective 1 could be achieved would be different at each of the final three candidate landing sites, but some combination of critically important progress could be made at any of them.

To answer the question in the heading of this section: YES

8.2 Summary of Sample Types of Interest for Returned Sample Analysis.

A compilation of sample types described in the various sections of this report results in Table 8.1 for the rock samples and Table 8.2 for the granular material. In the case of the rock samples, the columns of Table 8.1 are organized by geological category, the first five of which are keyed to the geological environments being targeted. Since we do not yet know which landing site the M-2020 sample-collecting rover will be sent to, nor where within the landing ellipse the actual landing will be, the sequence by which the samples described in these tables will collected is indeterminate. However, we do know the three landing sites under discussion, and are confident that regardless of where M-2020 starts its traverse, the rover will be able to collect at least a subset of the desired materials. It is our hope that the M-2020 science team will plan the productive lifetime of the rover to acquire as many of the kinds of samples described in these tables as possible.

Note that we cannot expect that M-2020 will be able to collect all the samples. Constraints will include topographic limitations on traverse planning, limitations on the geology available for sampling, a fixed and limited number of sample tubes, etc. Not forgetting, of course, that M-2020

has its own set of science and engineering objectives apart from sample collection and caching. A sample collection that justifies return, therefore, is not one that includes every sample described in these tables, but one that includes a reasonable subset (recognizing, of course, that what is reasonable to some people may not be reasonable to others). The authors of this report would especially like to see a minimum "returnable" sample collection be defined as one that allows at least some progress on each of the seven objectives proposed in this report. As sample collection and retrieval scenarios are further defined, clearly this will need more discussion.

General Geological Category						
Callingantan	l budu a th a much	Deep sub-	Cub activ	1	Volatile-	Other
Sedimentary	Hydrothermal	surface	Sub-aerial	Igneous	Bearing	
A suite of sedimentary rocks representative of the stratigraphic section.	A suite of hydrothermal samples and/or altered host rocks representing decreasing paleo- temperature with distance (e.g., proximal to distal) from a hydrothermal vent	Mineralized fractures or ridges, diagenetic concretions, zones with color change indicating leaching and/or cements and should be sampled along with adjacent host rock.	A suite of rocks or soils/paleosols representative of the range of depth and weathering, from most-altered to least- altered/unaltered parent material.	A suite of igneous rocks as diverse in composition and texture as possible	Sedimentary rocks and regolith of known age containing clays or other hydrated minerals, in particular minerals that contain structural volatiles (carbonates, sulfates, sulfates, chlorides, perchlorates).	Oriented samples of igneous or sedimentary rocks
A suite of sedimentary rocks showing a range of lithification intensity and style.	A suite of hydrothermally generated deposits and/or hydrothermally altered host rocks representative of the range of chemistry and mineralogy within an ancient hydrothermal system.	Cross sectionally arranged samples from altered zones. Key phases include Fe and Mn oxides, phyllosilicates, silica, sulfates, carbonates, and other salts. Goal is to use samples to track fluid chemistry change with system time- evolution or distance.	Mineral deposits (e.g., iron oxides, salts, carbonates) precipitated in chemical gradients (e.g., springs) or due to evaporation (e.g., ephemeral ponds), especially those with evidence for long-term buildup.	A suite of ancient rocks that are the most likely candidates for the original crust of Mars, including those subjected to the least amount of apparent aqueous alteration	Dry, clay-free dune material to study adsorption and dry implantation processes of atmospheric species in contrast to S8.	Samples, including impact melts, taken from individual craters amenable for age dating.
Rocks of any type that show a range of weathering styles and weathering intensity, including weathering rinds, if present.	Hydrothermally generated/altered rocks sampling interbedding, cross-cutting and/or overgrowth relationships from different stratal positions within the hydrothermal system		Rocks with precipitated coatings or rinds.	Igneous samples from an extensive lava flow in the >3.5 Ga and <1 Ga age ranges from surfaces for which well determined cratering statistics have been established	Any rock of known age containing minerals with trapped fluid inclusions.	Breccias associated with large basin- forming impacts

 Table 8.1: Summary of rock samples desired/required to achieve the objectives of Mars Sample Return

Pre-decisional – For planning and discussion purposes only.

Sedimentary rocks with a variety of grain compositions.	A suite of hydrothermally generated/altered rocks representative of the range of rocks fitting hypothesized age model within the potential hydrothermal system.	Rocks formed under a variety of redox conditions, and especially those with evidence for sedimentation or mineral precipitation under reducing conditions.	Basalts and highly fractionated rocks are especially informative.	Highly shocked rock containing impact melt pockets or veins, where the timing of the shock event is known.	Any rock of known age containing minerals with trapped fluid inclusions.
Relatively coarse- grained clastic sedimentary rocks. Most valuable would be rocks for which at least some of the sedimentary grains are multi-mineralic (i.e. small rocks), and which could be studied independently.	Rocks, especially clays, that potentially show evidence of late- stage diagenetic processes such as hydrothermal alteration, superimposed on the hydrothermal system		An ultramafic igneous rock within a basaltic igneous host rock that could represent a potential mantle or lower crustal xenolith.		Highly shocked rock containing impact melt pockets or veins, where the timing of the shock event is known.
A suite of sedimentary rocks representative of stratigraphy within an ancient stream channel.					Hydrothermally altered impact breccia or in- place rocks modified by impact-induced hydrothermal activity; any impactite or heavily shocked rock of any type
Sample(s) of lithified aeolian sedimentary rock (at different stratigraphic horizons).					

Table 8.2: Summary of granular material samples desired/required to achieve the objectives of MSR

General Intended Purpose				
Sedimentary System Volatiles Environmental Hazards		ISRU		
Modern regolith, especially if locally derived.	Dust and soil/ sediments including a perchlorate- bearing sample	Concentrated airfall dust	Modern regolith, especially if locally derived.	
Sample of modern aeolian sediment from the surface.		Subsurface regolith, as deep as possible	A subsurface regolith sample from the same location as a 'typical' regolith surface sample that accesses material isolated from diurnal heat cycling	
		Dust on the surface exposed sample tubes or hardware	Dust and soil/ sediments including a perchlorate-bearing sample	
		Near-surface/surface regolith containing dust sized particles	Sample of modern aeolian sediment from the surface.	
		We also need to remove sample and measurement number references to present as a bulleted list to fit with the other objectives	martian airfall dust	

8.3 Some Proposals for the Downstream Missions of the MSR campaign

Our analysis also has identified some issues at different levels of priority that affect the downstream missions that will retrieve the samples and return them to Earth. These include the following:

- Paleomagnetic measurements on returned samples are an important part of Objective 5, and a key sample quality criterion is ensuring that exposure to magnetic fields remains below 200 μT. Laboratory measurements of the magnetic field in drill actuators and the RIMFAX antenna on the M-2020 rover conducted by the Project fall well below this limit, so the decision was made not to include a magnetic witness blank in the sample containers. However, it is possible that the sample return missions could potentially expose the samples to higher magnetic fields and thus reduce the likelihood of making measurements of remanent magnetization in ancient martian samples. It would be highly valuable to include a magnetic witness blank in the OS.
- As discussed above under Objective 4, one or more samples of modern atmospheric gas that is significantly larger than the rock/regolith sample tubes would be scientifically quite valuable. The M-2020 mission is not designed to collect such samples. Our analysis indicates samples taken at two different points in the Mars year for assessment of seasonal variability are of high priority to science. It should be possible to accommodate such atmospheric samples in the OS for return to Earth.
- As discussed above under Objective 6, there are questions about whether the sizing of the regolith/dust samples to be collected by M-2020 is sufficient to generate confident answers. If it were possible to be able to collect additional regolith or dust sample mass from the SRL mission (perhaps as a contingency sample), it would be very valuable.
- Other issues relating to exposure of the sample tubes to high temperatures and/or pressures during return to Earth may be identified, once the mineralogy and nature of the cached samples is known.

Finding 5: The retrieval missions of the MSR Campaign should (1) minimize stray magnetic fields to which the samples will be exposed and carry a magnetic witness plate to record exposure, (2) collect and return atmospheric gas sample(s), and (3) collect additional dust and/or regolith sample mass if possible.

8.4 Planning for the management of the samples should they be transported to Earth.

From this analysis, it would be possible to:

- compile a matrix of the analytical instruments/facilities and which investigations would require or desire them,
- evaluate which measurements or investigations can be carried out using sterilized samples this may become an important input into planning for the activities that must be carried out in containment,
- reconsider the amount of sample mass needed for each of the measurements, which may be an early input into a sample management plan, including sample sub-division strategies, and sample allocation plans,
- reconsider how much of the sample collection would be allocated for scientific research "immediately", vs. how much sample mass should be retained in pristine state for the benefit of future researchers.

8.5 Concluding Comments

We conclude that most/all of the seven objectives could be achieved if the Mars 2020 rover acquires, as expected, a scientifically well-chosen set of samples, and if those samples were returned to Earth. There are, of course, dependencies on the range of diversity within the sample collection (which will in turn be affected by several other unknowns, including how many samples are in the collection). With regards to Objective 1, the specific geologic processes it will be possible to characterize will depend on the selected landing site, and thus this represents a pivotal choice. However, it is evident that at least one of the critical sub-objectives of Objective 1, and likely more than one, would be possible with the Mars 2020 rover sample acquisition and caching activities, given the range of possible landing/sampling sites now under consideration.

We note that, as demonstrated by the Apollo lunar samples (e.g., Crawford, 2012), returned martian samples will be a resource for current and future generations of planetary scientists. Such samples offer not only the advantages of myriad laboratory analytical techniques, but also the promise of advances in analysis technologies that will postdate sample return.

We conclude that it is important for the sample retrieval missions to proceed as soon as possible after M-2020 has collected and cached the samples, both on scientific and on technical grounds. Scientifically, the exploration of Mars is a complex iteration of discovery and discovery response. There is more than one way to unravel the scientific puzzle that is Mars, but since results from earlier missions inform results from later missions, logical sequential relationships are important. It is widely accepted within the science community (e.g., witness the recent Decadal Survey) that the definitive answers from returned Mars samples is the most important next thing. The potentially groundbreaking discoveries from MSR will assuredly generate fundamental knowledge and capabilities that will have long-lasting implications for both science and engineering. Second, the retrieval missions will either require, or will greatly benefit from, existing Mars orbital telecommunications infrastructure. That infrastructure is aging, and the longer we wait to implement a sample return campaign, the higher the risk. While there are plans for refreshing this aging telecoms structure, it is by no means assured that the level of capability necessary to manage the risks of MSR will be available to ensure campaign success. Finally, there are potential negative effects to having the samples sitting un-retrieved on the martain surface for a very long time. These could include having them be in a somewhat different thermal environment, which may trigger temperature-dependent reactions between the various components of the samples. Fortunately, rocks and minerals are relatively stable entities, so this is believed to be a relatively minor concern, and time frames up to a decade or more have previously been deemed to be acceptable—however, for samples of this quality and cost we want the best we can get.

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International Mars Sample Return Conference, April 25-27, 2018, in Berlin, Germany (https://atpi.eventsair.com/QuickEventWebsitePortal/2nd-international-conference-on-marssample-return/home). Included within that activity, a number of abstracts based on the content of this report were published. Some of these abstracts were presented at the conference as oral talks, and some were presented in poster format. Regardless of the mode of presentation, we greatly valued the feedback received from the community, and it has been carefully considered and incorporated into the final version of this document. In addition, the analysis of Objective 7 (ISRU) was presented for discussion at the Space Resources Roundtable on June 13, 2018 (see https://www.csmspace.com/events/srr/)--again, feedback received has been incorporated. Finally, a high-level summary was presented to MEPAG at a virtual meeting on June 25, 2018 for broader community discussion/feedback.

A parallel PPT file to accompany this report has been prepared, and it may be accessed at TBD. In case of discrepancies between the PPT and text versions of this analysis, the text version (this document) should be interpreted as superior.

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APPENDIX 1: iMOST Terms of Reference

<u>HISTORICAL NOTE</u>: This Terms of Reference document was prepared at the time NASA, ESA, and IMEWG were in the early stages of planning the The **2nd International Mars Sample Return Conference**, which was subsequently held April 25-27, 2018 in Berlin. One of the purposes of the study described below was to generate sample-related information as input to that conference. All of the documentation of the Berlin conference is archived at the following web site: <u>https://atpi.eventsair.com/QuickEventWebsitePortal/2nd-international-conference-on-marssample-return/home</u>. The committee that carried out this Terms of Reference adopted the name International MSR Objectives/ Samples Team (iMOST), and the members of this committee are listed below in Appendix 2.

Introduction

The analysis of samples returned from Mars is of interest to the international Mars exploration community. IMEWG (International Mars Exploration Working Group) is currently exploring options to involve the international community in the conduct of sample collection and the analysis of the returned samples. The sample-caching rover is an essential component of the Mars Sample Return campaign, so the existence of the Mars 2020 mission constitutes a critical opportunity to make progress on MSR. The Mars 2020 samples, when returned, would provide the basis for performing a variety of Earth-based experiments including ones related to the search for signs of life.

In mid-2017, NASA opened the possibility of a MSR campaign in the next decade, available to potential participation of the international space community. The possibilities presented are currently being evaluated by IMEWG. As part of this evaluation, IMEWG is chartering the International MSR Objectives/Samples Team (iMOST) to characterize the kinds of samples that would be needed to achieve the MSR scientific objectives, and the types of measurements that would need to be made on those samples once returned to Earth.

IMEWG is currently planning a major conference on Mars Sample Return in April 2018, and it is expected that this charter group will deliver a draft report at the meeting. The April conference will be sponsored primarily by ESA and on the 10th anniversary year of IMEWG's first MSR conference, which was held in 2008.

There are two main reasons why an updated analysis of the science potential of MSR is now appropriate:

- 1. The last major analysis of the specific scientific objectives of MSR, and how they translate to sample types and sample quantities was the MEPAG E2E-iSAG (End-to-End International Science Analysis Group) analysis carried out in 2010-11 (and published in early 2012). Since then, there have been advances on different fronts that may change our perception of the scientific priorities for MSR:
 - The number of Mars meteorites in our collections on Earth has now grown to over 100 (this number was 55 in 2011), and includes one brecciated sample that has a different age from all the other martian meteorites, and is thus presumably representative of a different region of Mars.
 - The Curiosity rover landed on Mars (Aug. 2012), and has operated successfully for more than 5 years. Its suite of instruments has recognized a different chemistry for the martian surface with its identification of abundant perchlorates. In addition, scientific output from the wealth of data returned by orbiter missions since 2011, such as NASA's Mars Reconnaissance Orbiter and Mars Odyssey, as well as ESA's Mars Express, has been fundamentally important in shaping and improving our understanding of the martian surface.

- Research on terrestrial analogs, especially in the general field of astrobiology, has blossomed. We have a better understanding of the relationship of life to its environment, and of changes with time.
- There have been substantial improvements in our ability to handle and analyze very small samples. A highly visible example is the work that has been done on the Hayabusa samples (JAXA), and the associated instrumentation developments around the world.
- 2. As part of the planning for the investigation of the samples after they arrive on Earth, we need a systematic analysis of which measurements would need to be made on the samples in order to achieve the diverse scientific objectives of MSR. This information can be used to derive an instrument list and the logical progression of analyses. This is key input into planning for the sample receiving facility, for one or more curation facilities, and for certain key operational decisions.

Assumptions

We request that this study be constrained by the following assumptions:

- 1. The starting point for evaluating MSR science objectives will be the MEPAG E2E-iSAG (2011) analysis and the subsequent derivative work by the Returned Sample Science Board (RSSB), soon to be published.
- 2. In order to be specific, samples to be considered for this study will be limited to rock and regolith samples able to be collected and cached by the Mars 2020 rover, and an atmospheric gas sample that could be collected by the retrieval mission. Rock and regolith investigations will be limited to those that can be achieved using samples of the size and quality that can be collected using the Mars-2020 sampling system.

Requested Deliverables

- 1. A reviewable draft report, in both text- and PPT-format is requested by April 1, 2018. It is assumed that one or more presentations on this material will be given at the April MSR Conference, and that the committee will consider any feedback received as they prepare the final version of the report. This report will contain:
 - a) An updated, consensus list of the potential science objectives of MSR, identifying those achievable based on the above assumptions (recognizing that sample-related science objectives are site-dependent, yet most of the objectives can be met at any one landing site). However the first sample return campaign is implemented, and whichever objectives are achieved, the remaining objectives may thereby form the basis for future sample returns.
 - b) A list of options and priorities for contingency samples that could increase or secure science return.
 - c) An analysis of the kinds of samples required/desired to achieve the various scientific objectives.
 - d) An evaluation of the specific Earth-based measurements that would need to be made on candidate samples to achieve the objectives.
 - e) An analysis of the possible design of sample suites that may enhance our ability to achieve the scientific objectives of MSR, and that could be considered by the M-2020 science team as they plan sample collection traverses.
- 2. A final version of the report is requested by July 1, 2018 (two months after the end of the MSR Conference), incorporating feedback from the Conference. It is hoped that the final version of the report will be submitted for publication in one of the professional journals. This report may not contain any material that is proprietary or sensitive—we need to be able to use it in open forum, such as the COSPAR Assembly in July 2018
- 3. If time permits, a reference table of the instruments and associated sample preparation equipment necessary to achieve the scientific objectives of MSR. The list may, in part, be dependent on the types of samples delivered to Earth, and in part be contingent on advances in analytical techniques, thus cannot be more than a working draft, but would provide a useful framework for planning the post-receipt period.

It is possible that an extension into follow-up activities may be requested after the April MSR Conference.

Team, logistics

- Steering of the science team's work shall be performed by a leadership team, which shall include NASA and ESA representatives and the co-chairs of the science team
- It is expected that the science team will be configured with appropriate intellectual, international, organizational, and gender diversity.
- The logistics for the team will be managed by the Mars Program Office, at JPL, and may be supported as needed by participating organizations.
- Other than planning for a single face-to-face meeting of the leadership team, it is expected that all of the team's work will be carried out using e-mail and teleconference processes.

Michael Meyer, David Parker, and Jim Watzin, on behalf of IMEWG

November 9, 2017

APPENDIX 2: iMOST Team Roster and Affiliations

Name	Institution	Nation represented
Co-Chairs:		
Beaty, David	JPL/Caltech	US
Grady, Monica	Open University	UK
McSween, Hap	Univ. of Tennessee	US
Sefton-Nash, Elliot	ESTEC	ESA
Facilitation:		
Carrier, Brandi	JPL/Caltech	US
Team Members:		
Altieri, Francesca	IAPS – INAF	Italy
Amelin, Yuri	Australian National University	Australia
Ammannito, Eleonora	ASI	Italy
Anand, Mahesh	Open University	UK
Benning, Liane	German Research Center for Geosciences	Germany
Bishop, Janice	SETI Institute	US
Borg, Lars	Lawrence Livermore Lab	US
Boucher, Dale	Deltion Innovations	Canada
Brucato, John R.	OA-Arcetri	Italy
Busemann, Henner	ETH Zurich	Switzerland
Campbell, Kathy	University of Auckland	New Zealand
Carrier, Brandi	JPL/Caltech	US
Czaja, Andy	Univ. of Cincinnati	US
Debaille, Vinciane	Universite Libre de Bruxelles	Belgium
Des Marais, Dave	NASA ARC	US
Dixon, Mike	University of Guelph	Canada
Ehlmann, Bethany	California Institute of Technology	US
Farmer, Jack	Arizona State University	US
Fernandez-Remolar, David	Luleå University of Technology	Sweden
Filiberto, Justin	Southern Illinois University	US
Fogarty, Jennifer	NASA JSC	US
Glavin, Danny	NASA GSFC	US
Goreva, Yulia	JPL/Caltech	US
Hallis, Lydia	Glasgow University	UK
Harrington, Andrea	NASA JSC	US
Hausrath, Libby	Univ. of Nevada, Las Vegas	US
Herd, Chris	Univ. of Alberta	Canada
Horgan, Briony	Purdue University	US
Humayun, Munir	Florida State Univ	US
Kleine, Thorsten	University of Muenster	Germany
Kleinhenz, Julie	NASA Glenn	US
Mangold, Nicolas	University of Nantes-LPG	France
Mackelprang, Rachel	Cal State-Northridge	US
Mayhew, Lisa	Univ. Colorado	US
McCubbin, Francis	NASA JSC	US
McCoy, Torin	NASA JSC	US
McLennan, Scott	Stony Brook Univ.	US
Moser, Desmond	Western University	Canada
Moynier, Frederic	Paris Institute of Earth Physics	France
Mustard, Jack	Brown University	US
Niles, Paul	NASA JSC	US

Ori, Gian G.	Int. Research Sch. of Planet. Sci.	Italy
	Universita d'Annunzio	
Raulin, Francois	University of Paris (UPEC)	France
Rettberg, Petra	German Aerospace Center (DLR)	Germany
Rucker, Michelle	NASA JSC	US
Schmitz, Nicole	German Aerospace Center (DLR)	Germany
Schwenzer, Susanne	Open University	UK
Sephton, Mark	Imperial College	UK
Shaheen, Robina	University of California San Diego	US
Sharp, Zachary	University of New Mexico	US
Shuster, David	University of California Berkeley	US
Siljestrom, Sandra	Research Institutes of Sweden, Stockholm	Sweden
Smith, Caroline	Natural History Museum, London	UK
Spry, Andy	SETI Institute	US
Steele, Andrew	Carnegie Institution of Washington	US
Swindle, Tim	Universitiy of Arizona	US
ten Kate, Inge Loes	Utrecht University	NL
Tosca, Nick	Oxford University	UK
Usui, Tomo	Tokyo Institue of Technology	Japan
Van Kranendonk, Martin	UNSW Sydney	Australia
Wadhwa, Mini	Arizona State University	US
Weiss, Ben	MIT	US
Werner, Stephanie	University of Oslo	Norway
Westall, Frances	CNRS-Orleans	France
Wheeler, Ray	NASA KSC	US
Zipfel, Jutta	Senckenberg Research Inst, Frankfurt	Germany
Zorzano, Maria Paz	Centro de Astrobiologia	Spain

APPENDIX 3: Expected Size and Quality of the Samples to be Collected by Mars-2020

Over approximately the last 4 years, sample quality standards have been established by several different methods to ensure that the MSR samples will be able to address the planned scientific objectives, within the necessary constraints of mission design and cost (Beaty et al., 2014; Liu, et al., 2014a, b; Carrier et al., 2017b). Some of these standards were formulated for the M-2020 Project by the Returned Sample Science Board (RSSB), a group chartered in mid-2015 by NASA to represent the sample scientific community who will study the returned samples, and others were formulated by predecessors of the RSSB (and the RSSB never found a reason to modify the specifications) (Beaty et al., 2014, RSSB 2016a, b, 2018b, c). Table A3.1 summarizes the full set of sample quality requirements compiled by RSSB (2018b), and which are described below.

Sample Quality Parameter	Recommended Requirement
Biologic Contamination	<1 viable terrestrial organism per tube
Organic Contamination	Tier 1 compounds <1 ppb Tier 2 compounds <10 ppb TOC <40 ppb
Inorganic Contamination	Zr, Nb, Ta, La, Ce, Eu, Gd, Li, B, Cs, Sc, Mn, Y, Mg, Zn, Ni, Co, Cl, Br, P, S <1% K, Rb, Sr, Sm, Nd, U, Th, Re, Os, Lu, Hf, W <0.1% Pb <2 ng/g
Magnetics	Exposure to <0.5 mT Shock pressure <0.1GPa Orientation to half-cone uncertainty of <5°
Fracturing	Size distribution in a single core of <20% by mass in pieces $\leq 2 \text{ mm}$, and >70% by mass in pieces with largest dimension >10 mm
Internal Movement	Minimize by preloading tubes compatible with X-ray CT imaging of core before removal
Temperature	<60 °C required, <40 °C desired
Cross-Contamination	<150 mg per samples tube
Sealing	<1% water, translated to He leak rate for 20 years
Radiation	<100 krad over 20 years

 Table A3.1: Campaign-Level Science Requirements for Mars Samples

Earth-sourced contamination: Minimizing Earth-sourced contamination is critically important for geochemistry, isotope geochronology, andastrobiology investigations. Mars-sourced contaminants will be monitored by witness blanks.

Organic compounds: The limits for Earth-sourced organic carbon in/on the samples originated from a nearly year-long study by a science/Planetary Protection team (OCP) carried out in 2014 (2). Their final recommendation was organized into three components: <1 ppb Tier 1 compounds (organic compounds that would be deliberately evaluated in returned samples as input to life-related interpretations), <10 ppb other C-compounds (everything that is not on the Tier 1 list), and <40 ppb total organic carbon (TOC).

Inorganic elements: The key input for this originated at the "Workshop on MSR Sample Quality", Mar. 16, 2014 (a pre-LPSC workshop), in part aided by a pre-RSSB focus group. It was recognized

that for most kinds of elemental geochemistry studies, the data do not matter beyond two significant figures. Thus, for the following elements: Zr, Nb, Ta, La, Ce, Eu, Gd, Li, B, Cs, Sc, Mn, Y, Mg, Zn, Ni, Co, Cl, Br, P and S, agreement was reached to limit Earth-sourced inorganic contamination to ≤ 1 % of the concentration in martian meteorites (and Tissint was later chosen as the reference). However, this accuracy is not sufficient for geochronology studies, such that for the primary parent-daughter pairs (K, Rb, Sr, Sm, Nd, U, Th, Re, Os, Lu, Hf and W) a constraint of ≤ 0.1 % was adopted (it was subsequently recognized that W may be subject to unavoidable contamination from the WC cutters in the drill bits). Several elements required to build the spacecraft (e.g., Ti, Al, Fe) were left unconstrained. Pb contamination was identified as being of interest at a very low level (~ 0.1 % of the concentration in martian meteorites), to allow for U-Th-Pb geochronology, although this is a notoriously difficult contaminant to deal with on Earth. Initial element lists developed above were refined in a 2014 GSA poster (Liu et al., 2014a).

Magnetics: A pre-RSSB magnetics focus group, led by B. Weiss in 2014, conducted a study to assess the requirements for magnetics measurements on one or more returned samples. These include limitations on exposure to a spacecraft magnetic fields (< 0.5 mT), shock intensity during launch and landing (< 0.1 GPa), and accuracy to which orientation should be determined with respect to their pre-sampling positions on the Martian surface based on a surface features (to within 5°). Furthemore, to ensure that paleomagnetic directional measurements can be oriented with respect to absolute Martian geographic coordinates at the time the magnetization was acquired by the samples, their parent rocks should be in-place bedrock or at least blocks with paleohorizontal indicators (i.e., bedding planes, flow-top features, vesicularity or crystal size gradients, and/or stratified grain size sorting) (RSSB, 2016; Weiss et al., 2018).

On the basis of magnetic field measurements around the Mars 2020 testbed drill, the M-2020 project accepted a requirement that the drilled cores will not experience fields exceeding the 0.5 mT requirement. This ensures that most ferromagnetic grains in the samples will not be remagnetized by spacecraft fields.

Mechanical Integrity and Internal Movement: The fracturing of a rock sample does not directly affect its scientific utility, as long as the pieces stay together (after all, once the MSR samples arrive at Earth, they will be deliberately broken into small pieces for the purpose of sample allocation). Although this was discussed at the 2014 Sample Quality Workshop, a viable approach to structuring a meaningful and achievable requirement was not identified at the time. Through discussions between the Mars-2020 project scientist and a pre-RSSB focus group, agreement was reached on a size-frequency distribution, which would have enough large pieces (> 70 %) to support the high-priority preparation of polished thin sections, enough medium-sized pieces (> 20 %) for many kinds of geochemical investigations and would minimize the quantity of "fines" (< 10 %), which are far less useful. Note that since different rocks have different strength, it was necessary to define this requirement with respect to a reference rock, which was selected to be a specific variant of the Bishop Tuff.

The movement of fragments of a rock relative to each other in the core is generally considered to be more damaging to science than fracturing itself. A fractured rock can be reconstructed if the pieces are still together. However, it was found to be impossible to write defensible requirements relating to distances or angles of movement of the multiple particles relative to each other. An alternate approach of minimizing the free volume inside the sample tubes was adopted—this would have the indirect effect of minimizing movement. In addition, the material of the tubes was chosen in part to allow X-ray CT scanning before opening, which may assist in understanding fragmentation, internal rotations and displacements.

Temperature: The RSSB conducted an intensive analysis of temperature constraints for 11 investigations where thermal excursions could affect the outcome. A maximum temperature of 60 °C (20 ° above ambient temperature) was determined for samples within core tubes on the martian

surface and during recovery on Earth. Lower temperatures of 40 – 50 °C are desirable for investigations of organic matter, amorphous materials, hydrated sulfates and zeolites, and these lower temperatures can be satisfied for landing sites in the northern hemisphere without additional effort (Beaty et al., 2016). Temperature excursions during drilling can be mitigated by duty cycling. In response to this study, M-2020 Project engineers modified the core tube design to achieve this temperature constraint at all the putative Mars landing sites.

Mars-sourced contamination: Because the Mars-2020 rover will reuse drill bits, and not have the ability to clean between their sampling uses, cross contamination between Mars samples is inevitable. This was discussed at the 2014 Sample Quality Workshop, and agreement was reached that for most of the kinds of scientific questions of MSR, and for a series of samples that come from a single type of geologic terrane, a cross contamination limit of 1% would be compatible with most kinds of geochemistry studies.

Sealing: Volatiles in the sample, either bound in minerals, or adsorbed on mineral surfaces, may be released during storage of core tubes on the martian surface. Sealing of the tubes is critical to retain volatiles, so that the original volatile inventory will be measured and the original states of volatiles can be calculated from thermodynamic considerations and from atmospheric samples that will be obtained as part of the follow-on retrieval mission. The tubes will also contain some headspace atmospheric gas. The limit is based on the leak rate for He for a 20-year residence on Mars.

Radiation: A radiation limit of 100 krad was proposed--this is approximately the natural dose the samples would receive if they spent 20 years in Mars orbit. Additional sample irradiation beyond that is in general considered undesirable, although this is a relatively low dose and specific adverse effects caused by exceeding it by a small amount have not been identified.



Figure A3. 1: A returnable Mars-2020 sample tube assembly with illustration of a collected core. On the left is the interface with the drill, on the right is the hermetic seal. Total length of the tube is ~15 cm. The sample cavity is ~13 mm x 100 mm.

Mars-2020 Sample Caching Capabilities: The rover's drill will use rotary motion with or without percussion to penetrate martian rock surface to collect samples directly into clean sample tubes. Each collected core is 13 mm in diameter and 60 mm long, amounting to an average of 10-15 grams of martian material per tube (Figure A3.1). After imaging and evaluating the volume of collected material, each tube will be hermetically sealed for eventual deposit in cache depots on the martian surface.

Mars-2020 will carry total of 43 tubes, of which 5 (witness blank tubes) will be flown pre-loaded with a range of witness materials designed to accumulate molecular and particulate contaminants. These witness tubes will be sealed, cached on the martian surface, and potentially returned to Earth together with the martian samples for analysis in terrestrial laboratories. Witness blanks are an important part of the Mars-2020 proposed strategy to provide a mechanism for characterization of the round-trip terrestrial contamination. Round-trip blanks/controls are widely accepted by the science community as a good method to mitigate the fact that terrestrial contaminants at low levels cannot be eliminated entirely from the hardware. Characterization of the molecular and particulate contamination captured by the witness blanks is necessary for distinguishing Earth-sourced contaminants from the martian signal.

Besides core samples, Mars-2020 will collect regolith samples using a specially designed bit (Figure A3.2). This regolith bit has a closed end and openings on the side. Using the drill, the bit will be slowly spun down into the martian soil, producing an inward cascade of the particles <2mm in diameter. Inverting the drill will pour the collected material into the sample tube and, subsequently, hermetically sealed as all other samples.

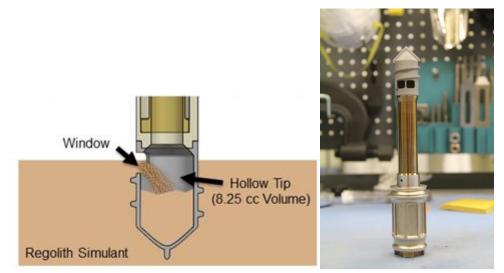


Figure A3.2: Left-Artist's rendition of the M-2020 regolith drill bit collecting granular material as it rotates just below the martian surface. Right-After collection the drill bit and attached sample tube are carefully reoriented to allow the sample to move from the drill bit into the sample tube.

APPENDIX 4: Glossary of Acronyms

ALH	Allan Hills
AMS	Accelerator Mass Spectrometry
APXS	Alpha Particle X-Ray Spectrometer, an instrument carried on both the MER and MSL missions
CEC	Cation Exchange Capacity
CHEMIN	Chemistry and Mineralogy instrument, an instrument on the MSL mission
CONICET	Consejo Nacional de Investigaciones Científicas y Técnicas
COSPAR	Committee on Space Research
CRISM	Compact Reconnaissance Imaging Spectrometer for Mars, an instrument on the MRO mission
СТ	Computerised Tomography
DAN	Dynamic Albedo of Neutrons, an instrument on the MSL mission
E2E-	End-to-End International Science Analysis Group
iSAG	
Eh	Redox potential
EMPA	Electron Microprobe Analysis
EPS	Exopolymeric Substance
ESA	European Space Agency
ExoMars	A Mars rover mission scheduled for launch in 2020
FTIR	Fourier Transform-Infrared Spectroscopy
GCR	Galactic Cosmic Rays
GS-MS	Gas Chromatography-Mass Spectrometry
(GC-MS)	
iMARS	International Mars Architecture for the Return of Samples, a planning committee chartered by
	IMEWG that was active in 2007-08.
IMEWG	International Mars Exploration Working Group
iMOST	International Mars Sample Return Objectives and Samples Team, a planning committee
IS	chartered by IMEWG that was active in 2017-18.
ISRU	Investigation Strategy In Situ Resource Utilisation
JAXA	
JAAA JPL	Japan Aerospace Exploration Agency
	Jet Propulsion Laboratory
KREEP	Potassium, Rare Earth Element and Phosphorus
LA-MS	Laser Ablation-Mass Spectrometry
LIBS	Laser-Induced Breakdown Spectroscopy
M-2020	Mars 2020, a Mars rover mission scheduled for launch in 2020
	Mars Hand Lens Imager, an instrument on the MSL mission
MAVEN	Mars Atmosphere and Volatile Evolution, a Mars orbiter mission launched in 2013
MEPAG	Mars Exploration Program Analysis Group
MEX	Mars Express, a Mars orbiter mission launched in 2003
MGS	Mars Global Surveyor, a Mars orbiter mission launched in 1996
MRO	Mars Reconnaissance Orbiter, a Mars orbiter mission launched in 2005
MS MSP	Mass Spectrometry Mars Sample Beturn
MSR	Mars Sample Return
MSL	Mars Science Laboratory, a Mars rover mission launched in 2011
MWIP	Mars Water ISRU Planning, a planning committee chartered by NASA that was active in 2016.
NASA	National Aeronautical and Space Administration
	National Research Council, an organization within the U.S. National Academy of Science
NWA	Northwest Africa, a designation used for many Mars meteorites

OCP PBS PGM PIXL PP REE REMS RIMFAX	Organic Contamination Panel, a planning committee chartered by NASA that was active in 2014 Potential Biosignature Platinum Group Metals Planetary Instrument for X-ray Lithochemistry, an instrument on the M-2020 mission Planetary Protection Rare Earth Elements Rover Environmental Monitoring Station, an instrument on the MSL mission Radar Imager for Mars' Subsurface Experiment, an instrument on the M-2020 mission
RSL	Recurring Slope Lineae
RSSB	Returned Sample Science Board
SAM	Sample Analysis at Mars, an instrument on the MSL mission
SDT	Sample Definition Team
SEM	Scanning Electron Microscopy
SSB	Space Studies Board, a standing committee of the U.S. National Academy of Science
STEM	Scanning Transmission Electron Microscopy
TES	Thermal Emission Spectroscopy
TGO	Trace Gas Orbiter, a Mars orbiter mission launched in 2016
TIMS	Thermal Ionisation Mass Spectrometry
TLS	Tunable Laser Spectrometer, an instrument on the MSL mission
тос	Total Organic Carbon
WEH	Water-equivalent Hydrogen
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

APPENDIX 5: Glossary of Definitions of Terms

Note that some partial-acronyms, i.e. phrases including acronyms, are listed here. In general, some key mineral group names are listed, but specific phases are not.

Acetyl-CoA pathway – Set of biochemical reactions used by some bacteria and archaea called acetogens. Also known as the Wood–Ljungdahl pathway.

Aeolian – Pertaining to a process or feature formed by the movement of an atmosphere interacting with a bodies' surface.

Allogenic – Originated from eroded ancient crust.

Alteration halo – A border of minerals produced by hydrothermal alteration in the rock surrounding a vein.

Amazonian – Most recent martian geologic epoch, dominated by hyperarid, cold conditions and low meteorite and asteroid impact rates. Generally accepted to span from 3.0Ga to present day. *Anaerobic* – Relating to or requiring an absence of free oxygen.

Anhedral – [Of rocks] to have no defined crystal faces, or cross-section shape in thin section. **Authigenic** – In situ newly formed minerals in a deposit by various chemical reactions.

Breccia – Rock comprised of angular fragments of stones cemented by finer calcareous material. **CheMin** – Chemistry and Mineralogy X-diffraction instrument aboard NASA's Mars Science Laboratory Rover.

Chemosynthetic pathways – Use of energy released by inorganic chemical reactions for nutrition. *Chemolithotroph* – Organism that uses inorganic reduced compounds for energy.

Chemotrophic – [of organisms] to obtain energy by the oxidation of electron donors.

Clastic – A type of sedimentary rock or sediment. Clastic rocks are accumulations of transported weathering debris that have been lithified.

Concretion – Feature formed when water carries dissolved minerals through sediments or porous rocks and minerals precipitate such that surrounding sediments are incorporated or replaced.

Conglomerate – Clastic sedimentary rock containing rounded clasts > 2 mm diameter. Inter-clast space is generally filled with smaller particles and/or a calcite or quartz cement.

Cosmogenic nuclides – Nuclides (isotopes) created when high-energy cosmic rays interact with nuclei, causing nucleons to be expelled.

Crystal mold – Diagnostically-shaped cavity left in rock after dissolution of a crystal of a specific mineral phase.

Deltaic - Of or like a river delta.

Diagenesis – Process of sediment modification post-deposition, including cementation, compaction, leaching and replacement, but excluding weathering and metamorphism.

Epithermal – [of mineral veins and ore deposits] Deposited from warm waters at shallow depth at relatively low temperature and pressure (compared to the higher pressure and temperatures in hypothermal and mesothermal environments).

Evaporites – Water-soluble mineral sediment that results from concentration and crystallization by evaporation from an aqueous solution.

Facies – The character of a rock expressed by its formation, composition, and fossil content. **Filamentous** – of a slender object or fibre, particular those found in plant or animal structures. **Feldspar** – Mineral in the feldspar group (KAlSi₃O₈ – NaAlSi₃O₈ – CaAl₂Si₂O₈) of rock-forming

tectosilicate minerals. Feldspars are ~41 wt. % of the Earth's continental crust. Feldspar-bearing rocks are said to be Feldspathic.

Fractional Crystallisation – The removal of early formed crystals from an originally homogeneous magma (for example, by gravity settling) so that these crystals are prevented from further reaction with the residual melt. The composition of the remaining melt becomes relatively depleted in some components and enriched in others, resulting in the precipitation of a sequence of different minerals.

Fumarole – Volcanic vent from which gases emerge.

Geochronology – Study of age determination of rocks, fossils and sediments using stable- or radioisotope ratios for relative and absolute dating, respectively.

Hesperian – Middle martian geologic epoch characterized by volcanic activity and catastrophic flooding events. Broadly accepted to span 3.7-3Ga.

Hydraulic fracturing – Fracturing of rock by a pressurized fluid.

Inorganic carbon – the boundary between "organic" and "inorganic" carbon is ambiguous, and no single definition is broadly accepted. Here we use 'inorganic' to refer primarily to materials comprised of oxygen and carbon. Examples include gaseous CO and CO_2 , dissolved CO_3^{2-} and HCO_3^{-} , and carbonate minerals such as calcite and dolomite. Many definitions of inorganic carbon also include metal and metalloid carbides, cyanides, and elemental carbon, although for clarity we refer here to such materials specifically by name rather than as inorganic carbon.

Ion microprobe – Analytical instrument that applies a stable and focused beam of charged particles to a sample such that the elemental composition of the sample can be determined via analysis of the emitted X-rays (if the primary beam is electrons), or of the secondary beam of material sputtered from the target (if the primary beam is ions).

Isotopes – Atoms of the same element having a different number of neutrons, and hence mass. They are chemically identical and form the same compounds, phases, etc, but the mass difference causes them to react at subtly different rates. Radioactive versus stable isotopes (¹⁴C vs ¹³C, ³H vs ²H) are frequently distinguished, and the relative abundance of certain isotopes (in organic matter, primarily ²H, ¹³C, ¹⁵N, ¹⁸O, and ³⁴S) are frequently used to distinguish between materials of terrestrial versus extraterrestrial origin.

Isotopic fractionation – any chemical, physical or biological process that alters the relative abundance of isotopes in a material. An example is the depletion of ²H and ¹⁸O in water vapor evaporating from a liquid. Many natural processes have characteristic isotopic fractionations, e.g. fixation of CO₂ in the photosynthesis. The loss of radioactive isotopes (e.g., ¹⁴C or ³H) due to decay is not typically regarded as fractionation as it occurs regardless of physical or chemical processes. *Lacustrine* – Relating to lake environments.

Lagerstätte – Sedimentary deposit that exhibits extraordinary fossils with exceptional preservation, possibly including preserved soft tissues.

Laminations – Thin layering in sedimentary rocks.

Laser Ablation [Mass Spectrometry] – Analysis technique that uses laser illumination of a sample to ablate material such that the fine ablation products can then be analysed in a mass spectrometer. *Leaching* – Removal of soluble substances and colloids from upper soil layers by downward percolating precipitation.

Macromolecular organic carbon – complex, high molecular weight, organic carbon compounds which are formed by polymerization or cross-linking of smaller subunits. Organic macromolecules include ordered biopolymers such as proteins, DNA, polysaccharides, and lignin; synthetic polymers including polyester, polytetrafluoroethylene (Teflon), and silicone; and irregular geopolymers such as humic acids, asphaltenes, and kerogen.

Mafic – Of a silicate mineral or igneous rock that is rich in magnesium and iron (a portmanteau of magnesium and ferric). Most mafic minerals are dark in color, and common rock-forming mafic minerals include olivine, pyroxene, amphibole, and biotite. Common mafic rocks include basalt, diabase and gabbro.

Matric potential – Component of water potential due to the adhesion of water molecules to nondissolved structures of the system, i.e. the matrix, such as plasma membranes or soil particles. *Meteoric* – [of water] derived from precipitation.

Methanogen – Organism that produces CH₄ as a result of its metabolism.

Mössbauer spectroscopy – Analysis technique usitilising the nearly recoil-free, resonant absorption and emission of gamma rays in solids.

Noachian – Early martian geologic epoch characterized by a higher impact flux, and evidence for abundant surface water. Broadly accepted to span 4.1-3.7Ga.

Olivine – Magnesium iron mineral group with the general formula $(Mg^{2+}, Fe^{2+})_2 SiO_4$. It is nesosilicate, or orthosilicate. Mg-rich olivine crystallizes from magma that is rich in magnesium and low in silica. Olivine occurs in both mafic and ultramafic igneous rocks and as a primary mineral in certain metamorphic rocks.

Opaline-silica – A form of hydrated silica that can be formed in hydrothermal settings, and on Earth can have bio-mediated formation.

Organic carbon – for the purposes of this report, any carbonaceous substance that is not inorganic. Typical definitions include the presence of covalent C-C and/or C-H bonds, average oxidation state < 4, yielding CO₂ upon combustion, and others. All of these definitions comprise (different) subsets of the broader definition that we adopt here. Examples include formic acid, ethanol, glucose, hydrocarbons including methane, lipids, amino acids, purines, pyrimidines, urea,

chlorofluorocarbons, Teflon, dimethylsilicone, etc. The term organic carbon does not imply formation by a biological process.

Organic particulates – macromolecular organic material that can be captured by sieving filters (for example > 1 Im particulates).

Osmotic potential – The potential of water molecules to move from a hypotonic solution (more water, less solutes) to a hypertonic solution (less water, more solutes) across a semi permeable membrane.

Ostwalkd ripening – The change of an inhomogeneous structure over time such that small crystals or particles dissolve and redeposit onto larger crystals or particles.

Paleoclimate – Historial climate recorded in sediments.

Paleosol – A stratum formed as a soil in a past geologic age.

Paragenetic sequence – Chronologically ordered set of mineral phases formed successively from a starting chemical equilibrium.

Phase assemblage – A set of co-existing minerals. Meaning is on emphasis of their co-mediated genesis.

Phyllosilicates – A major rock-forming mineral group formed of sheets of Si₂O₅ tetrahedra. Also known as clay minerals. All are hydrated and thus their existence indicates the presence of water in their formative environment.

Pre-biotic chemistry – Organic or inorganic chemistry occurring naturally before the advent of life on the Earth.

Penecontemporaneous – Of a process occurring immediately the deposition of a stratum. **Planetesimals** – Solid object arising during the accumulation of planets whose internal strength is dominated by self-gravity and whose orbital dynamics is not significantly affected by gas drag.

Playa – [of deposits or environment] flat land mediated by saturation followed by dessication. Playa deposits may contain evaporite minerals or geologic textures resulting from many of these cycles.

Phototrophic – [of an organism] obtaining energy from sunlight to synthesize organic compounds for nutrition.

Phylogenetic – Pertaining to evolutionary relationships between biological entities.

Provenance – [of a lithology] the original composition of the igneous, metamorphic, or sedimentary source rocks.

Pyroxene – Group of common rock forming minerals with a structure defined by single chains of silica tetrahedra (inosilicates). Pyroxenes have the general formula [X][Y](Si,Al)₂O₆.

Radiolysis – The dissociation of molecules by ionizing radiation.

Raman spectroscopy – Measurement of wavelength and intensity of inelastically scattered light from molecules. Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.

Regolith (the reason for this is that there is more than one definition of regolith, and its relationship to the lay term "soil" is confusing).

Sabkha – Area of coastal flats subject to periodic flooding and evaporation, resulting in accumulation of aeolian clays, evaporites, and salts.

Saltation – Transport of solid particles over a surface due to forces imparted by a turbulent fluid. *Shergottite* – Meteorite belonging to a group defined by the type-specimen Shergotty, which fell in India in 1865. It is composed mostly of pyroxene, solidified from a martian magma at ~4.1 Ga, but was subsequently aqueously altered.

Siliceous – [Of rocks] having silica, SiO₂, as the principle component.

Sinter (geologic material) – The product of natural fusing processes, using heat and pressure and chemistry, that do not require melting.

Stratigraphic – Relating to layering in sedimentary rocks.

Stromatolite – Rocks formed by fossilized bacteria and their products. These are associated with early forms of life on Earth.

Subaerial, subaqueous, subglacial – Refer to processes occurring within and mediated by the atmosphere, water, or ice, respectively.

Synchrotron – Ring-based particle accelerator producing X-rays used for analysis, including to identify mineral phases in geologic materials by X-ray diffraction.

Taphonomy – Study of the fossilization process.

Tephra – Rock fragments and particulates erupted by volcanic processes.

Thermal skin depth – The distance δ , over which the effect of a thermal wave of period, P, reduces by a factor of 1/e. Given by: $\delta = (\kappa P / \rho c \pi)^{1/2}$, where κ is the thermal conductivity, ρ is the density and c is the specific heat capacity.

Travertine – Form of limestone precipitated from mineral-rich water.

Ultramafic – Igneous and meta-igneous rocks with a very low silica content (< 45%). Composed of usually > 90% mafic minerals. Earth's mantle is composed of ultramafic rocks.

Volcaniclastic – Term used to describe all particles originating from volcanic eruptive processes. *Vug* – Cavity in a rock formed by tectonic processes. Can be filled with secondary minerals.

Weathering rind – Discolored, chemically altered, outer zone or layer of a discrete rock fragment formed by the processes of weathering.