JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. E9, PAGES 22,487–22,506, SEPTEMBER 25TH, 2000

Issues involved in a Martian sample return: Integrity preservation and the Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM) position

Clive R. Neal

Department Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana

Abstract. Returning geological samples from Mars is the next logical step as part of an integrated exploration program and is the critical subsequent stage in the search for evidence of life on the red planet. Analysis of such samples on Earth will generally produce data of superior accuracy and precision than can be accomplished in situ on the Martian surface, and such data will be invaluable in providing ground truth for remotely sensed observations. However, obtaining meaningful data requires that the samples returned to Earth suffer little (or preferably no) compositional or morphological changes during collection on Mars, transit to Earth, entry into Earth's atmosphere, impact on the surface, and long-term curation. This paper presents recommendations from NASA's committee for Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM) for preserving the integrity of Martian samples during a return mission. Potential contaminants include dead bacteria on the outbound spacecraft and materials that come into contact with the samples during collection and storage. Therefore it is recommended that the spacecraft be sterilized and cleaned at least to Pathfinder standards, with the components that interact with the samples having a higher degree of cleanliness. Furthermore, it is recommended that only pure, homogeneous materials should be used for components that come into contact with the samples. The adverse effects of temperature on the samples are explored, and it is demonstrated that heat sterilization or undue temperature increases in transit or reentry have the potential to destroy important mineralogical and geochemical information. Concomitant with this will be degassing of the samples and stable isotopic fractionation. Therefore it is recommended that samples be kept at 240 K or below during transit, reentry, and curation. It is further recommended that heat sterilization not be used, except in extreme circumstances, and other sterilization techniques, such as radiation, be explored. While the purpose of this paper is not to design a sample return mission, the recommendations presented here are intended to act as guidelines for returning Martian samples in their pristine state. In essence, any procedure or piece of equipment that has the potential to compromise the pristinity of Martian samples during the collection, transportation, or curation needs to be fully evaluated by a scientific committee with the requisite expertise prior to implementation. CAPTEM is willing to serve in such a capacity if requested by NASA.

1. Introduction

When the Apollo missions returned geological samples from the Moon, our knowledge regarding lunar origin and evolution took an immense leap forward. By analogy, sample return missions to Mars will greatly enhance our knowledge of the red planet to a degree that is not attainable just by remote sensing or one-way lander (in situ analyses) missions alone. By rational and balanced integration of sample return into future missions the ground truth for remote sensing and robotic exploration will be attained, greatly enhancing the value of the remotely gathered data [e.g., *Jolliff et al*., 2000; *Wood and Boynton*, 2000]. This paper focuses upon the issues surrounding preserving the integrity samples returned from Mars for analysis on Earth; specifically, preservation from initial collection to return to Earth such that the analyses performed will yield data that will provide an unequivocal Martian signature. It is aimed primarily at scientists but also at a broader audience that includes mission planners, engineers, and NASA administrators. The purpose of writing this paper is to bring to the scientific community the recommendations proposed to deal with preserving the integrity of Martian samples. Any comments, suggestions, or revisions that the reader may have to the recommendations defined here can be conveyed to Curation and Analysis Planning Team for Extra Terrestrial Materials (CAPTEM) via the Web or through C. R. Neal.

The value of Apollo and Luna samples in advancing our understanding of the Moon prompted *Johnson Space Center* (*JSC*) [1974] to explore a comparable sample return effort from Mars. Shortly after the data were received from the Viking landers, the U.S. National Academy of Sciences reviewed and endorsed the scientific merits of collecting samples from Mars and returning to Earth for analysis [*Committee on Planetary and Lunar Exploration* (*COMPLEX*), 1977, 1978]. In light of these data, the 1974 JSC report was revised [*JSC*, 1977] and published in amended form by *Bogard et al*. [1979]. The *Space Science Board* (*SSB*) [1988] of the National Academy pub-

Copyright 2000 by the American Geophysical Union.

Paper number 1999JE001185
0148-0227/00/1999JE001185$09.00

lished a revision of the *COMPLEX* [1977, 1978] reports. The National Aeronautics and Space Agency (NASA) *Solar System Exploration Committee* (*SSEC*) [1986, 1988], the *European Science Foundation* (*ESF*) [1986], and the European Space Agency [*Chicarro et al*., 1989] have all published reports endorsing the merits of a Mars sample return effort. *Gooding* [1990] published, through JSC, a document that focused on contamination issues surrounding such returned samples.

In this paper, we build upon previous reports regarding the complexities of returning samples from Mars to Earth for scientific study [*JSC*, 1974; *Gooding*, 1990], and it is a logical expansion of an earlier CAPTEM report (J. Jones and A. Treiman, 1998, available at http://cass.jsc.nasa.gov/captem/mars.html, hereinafter referred to as Jones and Treiman, 1998). It discusses contamination issues within the framework of an Athena-like sampling mission; however, the concepts may be extrapolated to other plausible sampling scenarios and architectures. The paper is intended to complement the recent report of the Mars Sample Handling and Requirements Panel (MSHARP) [*Carr*, 1999]. These previous studies defined the value of analyzing Martian samples on Earth rather than (or in addition to) in situ on Mars as well as the goals of a sample return program. Briefly, the search for evidence of life is a primary objective, but parallel and intimately related goals are determination of the planet's climatic and geological histories.

2. Strategic Decisions for Optimizing Scientific Results From Sample Return Missions

While previous works have defined following the water and the search for life as the primary objectives of any sample return missions, they are dependent on understanding the origin and evolution of Mars and afford a unique opportunity to conduct critical geoscience research. This is the impetus for publishing this paper in a journal for geoscientists. If it appears that "life" issues at times seem to be subordinate to geologic considerations, it is not because they are less important but because this paper primarily addresses the overlap between the two. The following significant questions need to be addressed: (1) What types of samples will be collected to optimize scientific results? (2) How should the samples be collected? (3) What types of sample analyses will be performed? (4) What are the potential sources of contamination during collection, return, and processing/curation on Earth? (5) Will planetary protection requirements and any sterilization protocol(s) compromise the returned samples? (6) What terrestrial materials can be used in handling the Martian samples? (7) What are the preservation issues involved in curating Martian samples on Earth?

Preserving the integrity of these precious samples is paramount in obtaining the optimal scientific return and benefit from any Mars sample return mission. However, although analyses of Martian samples on Earth will be more accurate and precise than if conducted on the surface of Mars, a balance must be struck between analytical exactitude and the likelihood of the samples being compromised during collection, return, and processing, especially due to any sterilization procedures. This "likelihood factor" will be influenced by issues such as the nature of the sample, type of analyses to be performed, budgetary constraints, and mission/engineering limitations (see Jones and Treiman, 1998). While it is recognized that a balance must be made between what is desirable and what is achievable given these issues, this paper focuses upon the issues surrounding the samples themselves. It specifically concentrates on sample preservation from initial collection on Mars to analysis (and curation) on Earth such that the analyses will be performed on pristine, scientifically uncompromised samples.

Table 1. Examples of Sample Types and Expected Information[a]

Sample Type	Information			
	Biogenic	Atmospheric/ Solar Wind	Lithospheric/ Geologic	Resource
Atmosphere	2	4	3	1
Fresh igneous rock	1	1	4	2
Weathered rock	3	4	4	1
Sedimentary rock	4	4	3	4
Soil	4	4	4	4
Deep regolith	4	4	2	4
Ice	4	4	1	4

[a] Numbers represent increasing importance from 1 to 4 with 4 being of highest importance.

3. What Type of Samples Should Be Collected to Optimize Scientific Results?

The announcement that meteorite ALH84001 contains possible evidence of life on Mars [*McKay et al*., 1996] has propelled Martian exploration to the forefront of the public and scientific arenas. Samples returned from Mars will help address the issue of potential life on Mars, either extinct or extant, and will certainly lead to a better understanding of planetary evolution and of the Martian environment through important geoscience research. Table 1 defines the types of samples required to achieve these goals (modified from *Gooding* [1990] and Jones and Treiman, 1998).

Broad-based scientific investigations (biological, chemical, and physical) are required to understand the evolution of Mars and environmental conditions that may have been radically different in the past [e.g., *Squyres et al*., 1987; *Squyres and Kasting*, 1994; *Carr*, 1996] and that may have permitted life to develop [*McKay et al*., 1996; Jones and Treiman, 1998]. Therefore the primary sampling consideration of early sample return missions should be to maximize the diversity of sample types thus allowing these broad-based investigations into the evolution of Mars to proceed (cf. Jones and Treiman, 1998).

3.1. Biogenic Considerations

Fundamental questions that can be addressed by a Mars sample return mission include the following: (1) Was there life on Mars in the past? (2) Is there life on Mars now?

Guidelines for the evaluation of returned samples for biomarkers have been outlined by the Mars Expeditions Strategy Planning Group (MESG) (1996 at http://www.hq.nasa.gov/office/oss/mccleese.htm). This report stated that to achieve widely accepted confirmation of Martian life, all three of the following should be clearly identified and shown to be spatially and temporally correlated within rock samples: (1)

organic chemical signatures that are indicative of life; (2) morphological fossils (or living organisms); and (3) supporting geochemical and/or mineralogical evidence (e.g., clearly biogenic isotopic fractionation patterns or the presence of unequivocal biominerals).

These characteristics can be properly evaluated by returning a variety of Martian samples of sufficient size to Earth for interdisciplinary study in appropriate laboratories. With the possible fossil life signs found associated with carbonate in ALH84001 [*McKay et al*., 1996] and now possibly Nakhla and Shergotty [*McKay et al*., 1999], samples of sedimentary (fluvial, lacustrine, hydrothermal, evaporative) origin will be important in exploring for fossil life forms [e.g., *Farmer*, 1995, 1996, available at http://exobiology.nasa.gov/ssx/Selected_Research/exopaleo_for_mars_05.html]. The present-day Martian surface is hostile to life in that the exposure to extreme UV radiation appears to cause the breakdown of organic molecules (Viking lander experiments did not find complex organic molecules down to the ppb level [*Biemann et al*., 1977]). Therefore samples of the subsurface are probably the best candidates to search for past and present biologic activity. However, *Nealson* [1997a] pointed out that some terrestrial bacteria are extremely UV resistant, noting that on Earth, bacteria tend to be tolerant of extreme conditions and listed guidelines to the "limits of life" to demonstrate that prokaryotic life can survive under extreme conditions on Earth.

3.2. Lithospheric/Geologic Considerations

The following important scientific questions regarding the geology of Mars can be addressed by sample return missions: (1) How did Mars form and how did it evolve? (2) What is/was the volcanic activity of Mars? (3) What influence did planetary differentiation and volcanic processes have on the Martian climate and environment?

Primary igneous material is required to address such questions, and this should be used to determine absolute ages that in turn can be used to calibrate crater count ages. Past episodic volcanism and major impact events may have played key roles in producing or changing Mars' proposed early warm, wet climate and surface geologic conditions. Samples of fine-grained sands (Martian loess) may yield an average crustal composition, while analysis of fresh (unweathered) Martian rocks will give insights into the formation and evolution of Mars. Major geochemical differences exist among the inner planets as demonstrated by lunar sample studies and differences in planetary bulk densities and moments of inertia [*Taylor*, 1982, 1990; *Gooding*, 1990]. Studies of Martian meteorites as well as orbital data suggest that a small metallic core is present [e.g., *Lee and Halliday*, 1996, 1997a, 1997b; *Halliday et al*., 1996], indicating planetary evolution generally similar to that of Earth but possibly not extending to plate tectonics.

3.3. Atmospheric Considerations

Presently, the Martian atmosphere is thinner and of a significantly different composition compared to that of Earth. However, the images returned by the Mariner, Viking, and Mars Global Surveyor missions suggest that the Martian landscape has been sculptured by fluid flow, presumably water [e.g., *Carr*, 1996, and references therein]. The following immediate questions arise: (1) Was the Martian atmosphere thicker (and warmer) in the past? (2) Where is the water now? (3) What is the annual water budget of the atmosphere and how is it generated?

The present-day Martian atmosphere cannot support liquid water. If liquid water is currently present, it is underground, but the physical features demonstrating the presence of surface water at some time during its evolution are vital in arguing for the presence of life on Mars. Martian summer and winter temperatures fluctuate above and below the sublimation temperature of water ice, and around the equator, ice sublimes to be deposited at the poles. Whether this is a diminishing process or whether the ice at the equator is replenished via underground aquifers is not known at present. Samples that would be critical in evaluating the paleoclimatology of Mars would include samples of the present-day Martian atmosphere, sections through ancient lake or river sediments, evaporite deposits, and samples of the ice cap(s) to investigate volatile cycles throughout Martian history. In addition, analysis of weathered materials (secondary minerals) would yield information on the nature of weathering and atmospheric conditions [e.g., *Farquhar et al*., 1999]. Cores of the regolith will be essential for examining the solar wind flux and hypothesized changes in atmospheric density over the time represented by the depth of material sampled. If the atmosphere was thicker earlier in the evolution of Mars, then significant variations in the flux of the solar wind above that occurring naturally should be observed if gardening has not obliterated such signatures and ancient soils exist. Remnants of primary degassing may still reside in the Martian atmosphere, and detailed analysis of atmospheric samples will give an indication of the general type of volatile material incorporated by Mars. Finally, we concur with MSHARP [*Carr*, 1999] in that if analyses are to be conducted on Earth, these samples need to be preserved in their pristine condition during collection, travel back to Earth, and analysis/curation.

4. How Should the Samples Be Collected?

Samples could be collected in a variety of ways: (1) scoop samples (unconsolidated only) and/or (2) exposing fresh material (e.g., drill core samples, consolidated and unconsolidated). As the collected samples will be used to address the considerations outlined in section 3, consideration of the types of samples to be collected is paramount. For example, both regolith and solid rock samples as well as weathered and fresh samples will need to be in the returned cache. When planning the sample acquisition, consideration also needs to be given to actual specimen collection. How this is conducted will impact on the information obtained.

Scoop samples will only essentially collect weathered soil samples. Collection of rock core samples will allow fresh consolidated samples as well as their weathered rinds. Furthermore, a coring device can also be used to collect unconsolidated soil samples. Like MSHARP, CAPTEM endorses the use of the Athena payload drill-coring device as a reason-able method for obtaining fresh, unweathered rock samples. It is further recommended that a variety of sample gathering devices (i.e., scoops plus drills) be mounted on the rover and lander to allow for collection of a diverse sample suite and, more importantly, to allow samples to be collected and returned if any one sampling system fails. While a variety of samples and sample types can be collected, cross contamina-

tion becomes a distinct possibility after collection and during the return to Earth. This can be avoided by a compartmentalized sample container that has individual slots for cores and separate sections for soil samples.

5. What Types of Sample Analyses Will Be Performed?

It is inevitable that advances in analytical techniques and instrumentation will be achieved between now and the return of the first Mars samples. This section is intended to give an idea of the types of analyses and techniques that are currently available in order to achieve the goals of the missions. In section 6 these data will be evaluated in terms of how easily they could be compromised. It is conceivable that the data required for certain aspects of the mission goals will require both technique and hardware development. Such requirements need to be considered in detail so proper preparation for the analysis of the returned samples can begin.

5.1. Biogenic Considerations

In order to test samples for extant life, radiolabeled nutrients may be added to a subsample of the returned material and changes attributable to biologic systems noted. However, with the inconclusive results from the Viking biological experiments [e.g., *Klein*, 1978; *Levin*, 1988], more detailed and sensitive testing is required. Viking biology experiments consisted of (1) labeled release to identify metabolic products; (2) pyrolitic release to look for microorganisms that functioned by photosynthesis, chemotrophy, or organic response to chemicals; and (3) gas exchange to search for living organisms by measuring the change in gas composition in a closed environment [*Klein et al*., 1976; *Levin and Straat*, 1976]. While all gave encouraging results, the data were interpreted as reflecting only unusual surface chemistry, not responses to life [e.g., *Oyama and Bedahl*, 1977; *Klein*, 1978; *Blackburn et al*., 1979; *Bogard et al*., 1979]. No organic molecules were detected, but the presence of a strong oxidant in the Martian soil may have obliterated such molecules [e.g., *Horowitz et al*., 1977; *Biemann et al*., 1977]. *Levin* [1988] suggested that a simple way to demonstrate the presence of living organisms would be to supply the labeled release nutrients separately. *Levin* [1988] concluded that a response from only one isomer, but not its enantiomer, would essentially prove the presence of life. However, as concluded by *Klein* [1998], the surface of the planet is probably too hostile to support a carbon-based biota. This does not preclude the presence of life in subsurface environments nor completely preclude it in surface samples. Indeed, *Clark* [1998] suggested that it was conceivable for organisms (active or dormant) to have adapted and to be present at or near the surface of Mars. While the search for biological "oases" on Mars continues, experiments to investigate extant Martian life in returned samples must be fully evaluated. Such experiments, when conducted on Earth, should be more sensitive and comprehensive than those performed by the Viking landers on the surface of Mars. Conversely, *Zent and McKay* [1994] concluded that it may be impossible to return Martian regolith samples in such a way to preserve them in pristine condition without knowing in advance the nature of the oxidants, as well as their modes of production and loss. This is clearly an example of where interdisciplinary and detailed mission planning and careful construction of in situ and Earth-based experiments are required in the search for extant life.

Identification of Martian organic material could be complicated by the possibility of "false positives" through forward contamination from Earth. Therefore cleanliness of the spacecraft is critical, especially those areas that come into contact with the samples. Another possible complication is the fact that Mars has been subject to continued meteorite impact over its history. Such meteorites can contain significant organic material [e.g., *Engel and Macko*, 1997; *Brearley*, 1999], and trying to unravel truly Martian from meteoritic signatures could be an involved process.

Carbonaceous meteorites contain organic matter that may represent a prebiotic distribution of amino acids [e.g., *Robert and Epstein*, 1982; *Cronin et al*., 1988; *Kerridge*, 1991]. Bombardment of Mars by such meteorites may have imparted a prebiotic amino acid signature that could be included in a sample return and/or provided the starting materials for life to develop. For example, the Murchison meteorite (an organic-rich CM2 carbonaceous chondrite) contains nonprotein amino acids (those that have rarely been associated with life on Earth) and characterized by relatively high concentrations of specific protein amino acids (e.g., glycine, alanine, aspartic acid, and glutamic acid) [*Kvenvolden et al*., 1970, 1971; *Engel and Nagy*, 1982, 1983; *Cronin et al*., 1988]. The amino acids in the Murchison meteorite have been shown to be of extraterrestrial origin through stable isotope analyses [e.g., *Engel and Macko*, 1997]. These amino acids exhibit a small excess of L enantiomers, which is typical of prebiotic amino acids [*Engel and Nagy*, 1982].

In the search for extinct life, two broad investigations can be followed that are similar to those conducted on the Martian meteorites: (1) measurement and characterization of any organic compounds present and (2) search for microfossils and biominerals/molecules (e.g., oxides, phosphates, carbonates) via detailed microscopy and chemical studies.

Although the possibility exists that if life existed on Mars, it may have been very different from that on Earth [cf. *Nealson*, 1997a], we can use the early Earth as a basis upon which to build an analytical and sampling strategy for a Mars mission. This can be done by examining the evidence for bacteria in Precambrian terrestrial rocks [*McKirdy*, 1976; *McKirdy et al*., 1980, 1984; *McKirdy and Hahn*, 1982; *Jackson et al*., 1984; *Crick et al*., 1988]. Ancient Martian organic matter would have probably been altered via diagenesis to products that are stable over geological time (e.g., carbohydrates, nucleic acids, nucleotides, and most proteins [*Ehrlich*, 1990]). However, amino acids, fatty acids, porphyrins, n-alkanes, and isoprenoid hydrocarbons are found in Archean sediments on Earth [e.g., *Hodgson and Whitely*, 1980]. Kerogen is an organic compound stable over geological time. Four types of microbial kerogen are recognized in Precambrian terrestrial rocks, although only types I and II are probably applicable to Mars, as their depositional environments are anoxic to suboxic lacustrine; types III and IV kerogen are attributed to marine environments, although these should not be dismissed if comparisons are to be made [see *Imbus and McKirdy*, 1993]. *Imbus and McKirdy* [1993] also gave a list of potential organic biomarkers found in Precambrian rocks that are potentially relevant to this study. Such biomarkers may be used as a starting point for evaluating Martian samples for extinct life.

For example, *Brocks et al*. [1999] suggested that the presence of cholestane, pristane, and phytane in 2.7-b.y.-old shales from the Pilbra Craton, Australia, was strong evidence of the existence of eukaryotes 0.5 to 1.0 b.y. prior to that indicated by the fossil record. Pristane and phytane are considered to be the breakdown products of the chlorophyll molecule's 20 carbon "tail" (phytol) and thus represent indicators of photosynthesis [e.g., *Ponnamperuma*, 1972].

Stable isotope ratio determinations are important as appreciable fractionations in $^{13}C/^{12}C$ and $^{34}S/^{32}S$ can be used to indicate animal and plant metabolism on Earth and would be expected to indicate the same for Martian samples, depending on the temperature of formation. However, a baseline for stable isotopic analyses of materials from Mars needs to be established in order for relative fractionations to be quantified (see section 5.3). Carbonate and sulfide minerals are known to exist on Mars [e.g., *Gooding et al*., 1988; *Treiman*, 1995; *McKay et al*., 1996], and while the origin of these carbonates and sulfides is still hotly debated [e.g., *Harvey and McSween*, 1996; *Leshin et al*., 1997, 1998; *Valley et al*., 1997; *Treiman and Romanek*, 1998; *Warren*, 1998; *Gibson et al.,* 1996a, 1996b; *Greenwood et al*., 1997; *Shearer et al*., 1996; *Shearer and Papike*, 1996; *Gleason et al*., 1997; *Farquhar et al*., 1999], samples free from shock and terrestrial contamination would clearly aid in determining unequivocal isotopic signatures of biogenic activity. Major and minor element chemistry of the carbonate and sulfide phases will also be critical in evaluating the temperature of formation [cf. *Hutchins and Jakosky*, 1997; *Valley et al*., 1997; *Treiman and Romanek*, 1998].

Investigations of organic compounds (PAHs and amino acids) in conjunction with the above analyses are also required to explore the existence of life on Mars. It is essential to have (at least) a rudimentary understanding of the complexity surrounding the characterization of such organic constituents in any geological sample, not least of which is the problem of organic extraction. For example, *Shock and Schultze* [1990] suggested that the differences in amino acid distributions and abundances reported for the Murchison meteorite were simply due to differences in extraction procedure. Therefore it is important to have a detailed analytical plan in place for the Mars samples prior to their return. Martian samples free from prolonged terrestrial exposure are required in order that any PAH or amino acid signature can be solely attributed to Mars. Present work on ALH84001 debates whether these signatures are due to terrestrial contamination [e.g., *Becker et al*., 1997; *Bada et al*., 1998; *Jull et al*., 1998] or are a product of ancient Martian life [e.g., *Clemett et al*., 1998]. Therefore avoidance of terrestrial organic contamination is critical (see below) for the prevention of false positive signatures of organic life.

Morphological studies will be an integral part of any study of returned Martian samples. Current work on ALH 84001 has produced conflicting views on the nature of oxide crystals in the carbonates of this meteorite. The oxides have been interpreted as being inorganic in origin [e.g., *Bradley et al*., 1996, 1997, 1998; *Sears and Kral*, 1998] or as "bacteriomorphs" (products of bacetrial metabolism [e.g., *McKay et al*., 1996, 1999; *Thomas-Keprta et al*., 1997, 1998]). One of the major objections to the interpretation of these oxide crystals being of bacterial origin was their size (70-300 nm); cells with a volume less than that of a 200-nm sphere would not be viable [*Nealson*, 1997b; *Kerr*, 1998]. *Gillet et al*. [2000] suggested that this objection is not valid for dormant or fossilized bacteria and reported bacteriomorphs (of terrestrial origin) in the Tatahouine diogenite that were of similar size and shape to those in ALH84001. While the current Martian surface environment is inhospitable to carbon-based life, preservation of bacteria from an age when environmental conditions were more favorable for life to develop is certainly possible. Recent studies by *Farmer* [1998], *Farmer and Des Marais* [1999], and *Westall* [1999] have documented the fossilization and preservation of bacteria and have proposed guidelines for the search and recognition of bacteriomorphs.

As with analysis of the returned samples for organic compounds, morphological studies require that terrestrial bacteria not be allowed to contaminate the sample. Recognition of an inactive, but terrestrial bacterium on a returned Martian sample will yield a false positive signature that could, at worst, prevent the release of the samples to the general scientific community. At best, this could delay the release of the samples until radical sterilization has destroyed vital chemical and geological signatures. Stringent cleaning procedures for the spacecraft and meticulous sample handling procedures in the receiving facility are therefore required.

5.2. Geologic/Lithospheric Considerations

It is important to understand the timescale of evolutionary events on Mars, and this will be an integral analytical task when the samples are returned. From the Martian meteorites it is already known that there are old (>4 Ga) and young (< 0.2 Ga) rocks on Mars. Recent photogeologic evidence suggests there may be Martian volcanism as young as 40-100 Ma [*Hartmann et al*., 1999a, 1999b]. Using radiogenic isotope systematics (e.g., Sm-Nd, Rb-Sr, U-Th-Pb, Re-Os, Hf-W, Lu-Hf, or Ar-Ar) of fresh igneous samples will not only yield absolute ages but also will allow an insight into planetary differentiation. Current work on the Martian meteorites attests to the wealth of information that can be obtained regarding planetary processes [e.g., *Papanastassiou and Wasserburg*, 1974; *Nyquist et al*., 1979, 1995, 1998; *Shih et al*., 1982, 1996, 1998; *Jagoutz et al*., 1994, 1999; *Lee and Halliday*, 1996, 1997a, 1997b; *Halliday et al*., 1996; *Borg et al*., 1997, 1998, 2000; *Turner et al*., 1997; *Blichert-Toft et al*., 1999: *Brandon et al*., 2000]. Investigations into Martian differentiation and formation of discrete planetary reservoirs will be aided by oxygen isotopic analyses and by whole rock elemental determinations (both major and trace elements [e.g., *Morgan and Anders*, 1979; *McSween*, 1994; *Kong et al*., 1999; *Neal et al*., 1999a, 1999b, 2000; *Warren et al*., 1999]).

The initial results from Pathfinder indicated that the rocks analyzed by the rover were unexpectedly high in silica and potassium and low in magnesium compared to Martian soils and meteorites. In fact, the analyses suggest that the rocks are quartz normative, similar to terrestrial anorogenic andesites and close to the mean composition of the Earth's crust [*Rieder et al*., 1997; *McSween et al*., 1999; *Kring and Gleason*, 1999]. This suggests a more evolved planet than previously thought and supports the study of *Papanastassiou and Wasserburg* [1974], who demonstrated that Nakhla had a Rb-Sr evolution similar to that of terrestrial mid-ocean ridge basalt (MORB) source. Petrographic study of these "andesites" is needed in order to demonstrate a true igneous affinity, and such analyses will be of use in distinguishing the rocks into igneous, sedimentary, or metamorphic.

5.3. Atmospheric Considerations

Evidence for atmospheric evolution and climate changes on Mars should be preserved in the stable isotopic signatures of volatile elements in a variety of weathered Martian materials. In addition, the present-day Martian atmospheric composition needs to be further constrained so it can be compared with those determined from weathered materials and potentially act as a baseline standard for stable isotope fractionations to be constrained. Clearly, returning a sample of the present-day Martian atmosphere to Earth untainted presents significant logistical and engineering challenges for Mars sample return missions. Oxygen, carbon, and hydrogen isotope determinations from hydrous and carbonate minerals, water vapor, and carbon dioxide will yield critical information such as (1) estimating the temperatures of formation of the mineral assemblages; (2) determining whether or not the minerals in such rocks or in the bulk soil were formed in equilibrium or if they represent different stages of mineral formation; (3) evaluating the contribution of deep-seated igneous (juvenile?) H_2O to the surface rocks and to the atmosphere (if high-temperature igneous or metamorphic minerals, e.g., micas and amphiboles, are returned from Mars, comparisons with similar assemblages on Earth can be made); (4) using D/H data to help define the total amounts of H_2O and hydrogen loss through hydrodynamic escape from Mars, as well as the degree of isotopic fractionation that accompanied atmospheric escape; (5) using D/H analyses to determine any contribution of deuterium-free solar wind hydrogen to the Martian atmosphere and regolith and to help define the extent of cosmic ray spallation deuterium in the surface minerals; (6) using D/H, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ ratios to trace the hydrologic cycle on Mars and interpreting the mechanisms and temperatures involved in the hydration of primary Martian minerals; and (7) fluid-rock ratios during the formation of altered materials.

Noble gas ratios in the atmosphere are also required in order to better constrain the Viking results, allowing the evaluation of any signatures reflecting planetary degassing, as well as giving a better comparison for trapped gas compositions of (potential) Martian meteorites. Trapped gases have proven invaluable in establishing a Martian origin for the SNC meteorites [e.g., *Pepin*, 1985] and could yield informa-tion regarding the degassing of the planet and atmospheric evolution. Changes in atmospheric density can be evaluated through soil profiles by determining the specific activities of long-lived radionuclides produced by cosmic ray spallation reactions (e.g., ^{14}C, ^{3}He, ^{10}Be, ^{22}Na, ^{26}Al, ^{39}Ar, ^{53}Mn, ^{81}Kr), although such studies will also have to evaluate lateral soil mixing through wind-blown dust. Measurements of these radionuclides at the surface may be able to characterize the spatial and general nature of the cosmic ray flux.

6. What are the Potential Areas of Contamination During Collection, Return, and Processing/Curation on Earth?

There are distinct stages involved in a Mars sample return mission, each of which could introduce contamination or alter the nature of the sample from its original (pristine) Martian state: (1) preparation and acquisition of a sample for loading into a sample return capsule (e.g., chipping, scooping, drilling); (2) loading into and sealing of the sample return capsule; (3) lift-off from Mars; (4) travel to Earth; (5) acquisition at Earth; (6) transfer to quarantine/curation facility; (7) unsealing and processing; and (8) long-term curation.

How will we know if a sample from Mars has been contaminated? *Gooding* [1990] suggested that the Martian meteorite Shergotty be used as a reference composition for Mars samples, but the Martian meteorites have been affected by terrestrial contamination, especially in organic compounds [e.g., *Steele et al*., 1999]. Furthermore, the results from Pathfinder suggest these meteorites may not be representative of rocks at the surface of Mars [*Rieder et al*., 1997; *McSween et al*., 1999], and there is a large compositional variation in the Martian meteorite suite. Again, we concur with MSHARP [*Carr*, 1999] in that it is critical, through careful planning and design, that samples returned from Mars be effectively isolated on the surface of Mars prior to return to Earth. Without knowing the composition of potential contaminants (i.e., spacecraft components), it will be difficult to identify sources and amounts of terrestrial contamination or chemical/physical changes that have affected returned samples since being removed from Mars.

An added complication of returning Martian samples is the potential for the presence of life. The issue of planetary protection, both for Earth and Mars, is where two opposing axioms collide: it is required that any potential biological life forms from Mars not be accidentally introduced on Earth, but any measures implemented to achieve this should not compromise the integrity (pristinity) of the returned samples. Furthermore, parts of the spacecraft sample collection devices and containers that come into direct contact with the samples need to be sterile and free of organic materials. MSHARP [*Carr*, 1999] has recommended that the spacecraft be cleaned to at least Pathfinder standards (12 spores m^{-2} and $< 2.4 \times 10^4$ total) with the components coming into contact with the samples being cleaned to a higher standard. We endorse this as a minimum recommendation as it is an essential step to ensure that the chemical and biological signatures contained in the samples are truly Martian in character and false positive signatures of organic life are prevented.

6.1. Importance of Temperature and Pressure

Figure 1 delineates the critical temperature milestones for potential changes in Mars samples [e.g., *Gooding*, 1990]. The effects of temperature and pressure on the integrity of returned samples are intimately related. For example, preservation of Martian water ice without sublimation, melting, or isotopic exchange is critical for investigating hydrologic cycling. Liquid water may facilitate relatively rapid isotopic and geochemical transport and exchange, thus altering the geochemical signatures of any returned sample, as well as facilitating sample cross contamination. Changes in critical biogenic parameters can also occur. Furthermore, degradation of certain biogeochemical compounds begins at 253-263 K [*Gooding*, 1990], and there is evidence for measurable reaction rates of enzymes at ~250 K [*Franks*, 1982]. Salt minerals may undergo stable isotope exchange at subfreezing temperatures, and while oxygen isotope exchange may be sluggish, hydrogen exchange could be significant (~10‰) over a period of months [*Kyser*, 1987]. If temperature is raised above the freezing point of water, carbon isotope exchange reactions could be significant for CO_2-CO_3^{2-} in aqueous solutions [e.g., *Emrich et al*., 1970; *Kyser*, 1987], with a fractionation factor of 1.009 at 293 K ($20^{O}C$). Above 373 K, oxygen isotope exchange rates in clay

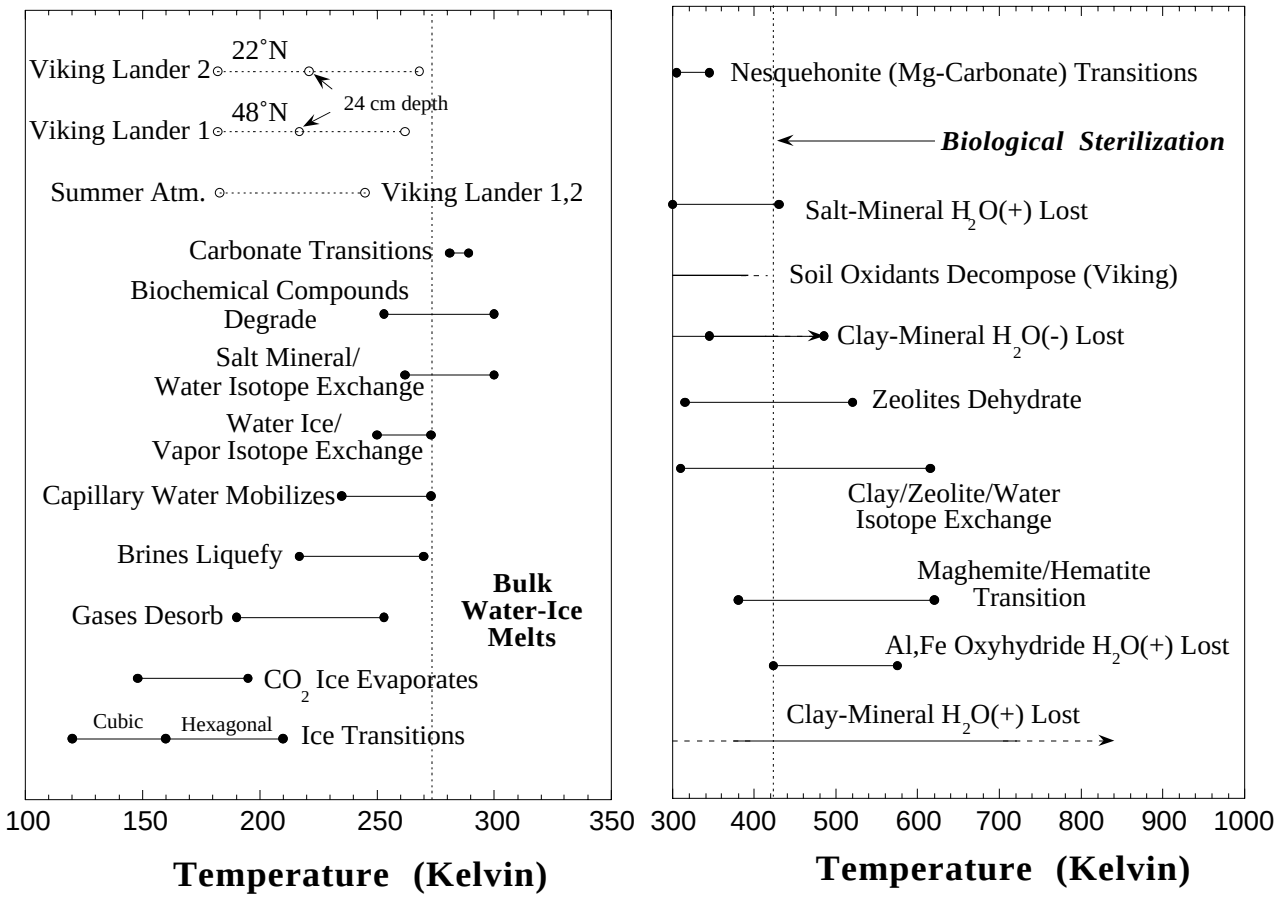

Figure 1. Potential temperature effects on Martian samples. Soil and summer surface atmosphere temperature ranges from the two Viking landers are also shown.

minerals and related silicates are significant [*O'Neil*, 1987]. Above 280-290 K, any vaterite (low-temperature polymorph of $CaCO_3$) would irreversibly invert to calcite, possibly obliterating evidence of carbonate formation mechanisms on Mars [*Gooding*, 1990].

Cole and Ohmoto [1986] published the results of theoretical calculations and a compilation of experimental data from the literature that documented diffusion rates and isotope exchange for a variety of minerals. For example, diffusion rates at 573 K (300°C) would be of the order of 3×10^{-7} cm^2 yr^{-1} for anhydrous minerals. Such rates maybe several orders of magnitude larger for hydrous minerals, especially those with open crystal structures, such as clays. The presence of a fluid again enhances these diffusion rates, but most isotopic exchange in mineral-fluid disequilibrium systems is controlled by surface reactions [e.g., *O'Neil and Taylor*, 1967; *Giletti*, 1985]. *Cole and Ohmoto* [1986, equation 32] derived a rate model for isotopic surface exchange using experimental data and concluded that below 300°C, a hierarchy of surface exchange rates existed in the approximate order:

Ba-Sr carbonates > Ba-Ca sulfates > Ca-Mg carbonates

and

Na/K feldspars ≥ kaolinite > quartz > paragonite > pyroxenes.

These exchange rates are quantified as between 1×10^{-10} and 1×10^{-6} mol m^{-2} s^{-1} at 300°C and between 1×10^{-11} and 1×10^{-7} mol m^{-2} s^{-1} at 100°C. Clearly, over extended time periods, once the connection to Mars ambient conditions has been broken, such as orbiting Mars and the trip back to Earth, there is time for significant isotopic exchange to occur. This is particularly problematic if any water ice melts, providing a ready reservoir for isotopic exchange.

Raising the temperature above the freezing point of water would start to significantly change the pressure in any sample container through the release of gases either by mineral breakdown or evaporation (Table 2). The trace oxygen-rich compound(s) discovered by the gas exchange experiments on the Viking lander [*Oyama and Berdahl*, 1977] would irreversibly decompose by reaction with any available water to liberate oxygen between 273 and 300 K (but note that these are minor components). The Viking lander biology experiments [*Klein*, 1978] demonstrated an irreversible decline in reactivity of the oxidants in Martian sediments upon heating over the 320-400 K range. It is evident that the stable isotope compositions (H, O, C, S) can potentially be altered from the initial pristine Martian signatures, thus reducing the value of these samples for investigating both extinct and extant biogenic activity, climatic change, and carbonate/sulfate formation. In addition, certain organic compounds produced from the decay of microbial matter can be mobilized at relatively low temperatures (Table 3).

Clays are a particularly important group of minerals that

Table 2. Volatile-Release Temperatures of Geologic Materials Heated 10 K min^{-1} Under 1 atm of Dry Nitrogen[a]

Mineral	Chemical Formula	Temperature of Initial Decrepitation[b], K
	$Fe_2(SO_4)_3 \cdot nH_2O$	373 (H_2O)
	$FeSO_4 \cdot 7H_2O$	373 (H_2O)
	$MgSO_4 \cdot 7H_2O$	373 (H_2O)
Gypsum	$CaSO_4 \cdot 2H_2O$	383 (H_2O)
Goethite	FeO(OH)	493-513 (H_2O)
Dickite	$Al_2Si_2O_5(OH)_4$	673 (H_2O)
Diaspore	AlO(OH)	673 (H_2O)
Magnesite	$MgCO_3$	703 (CO_2)
Kaolinite	$(Al_2Si_2O_5(OH)_4$	713 (H_2O)
Siderite	$FeCO_3$	738 (CO_2)
Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	848 (H_2O)
	$FeSO_4 \cdot 7H_2O$	873 (SO_2)
	$Fe_2(SO_4)_3 \cdot nH_2O$	873 (SO_2)
Dolomite	$CaMg(CO_3)_2$	903 (CO_2)
Calcite	$CaCO_3$	933 (CO_2)
	$MgSO_4 \cdot 7H_2O$	1143 (SO_2)

[a]Adapted from *Kotra et al*. [1982] and *Gooding* [1990].
[b]Gaseous species given in parentheses.

will, if present, yield significant information about Mars. It has been suggested by some that Martian soils contain smectitic clays (cf. S. Guggenheim, presentation for Mars 2003 Science Working Group Meeting held May 12 and 13, 1999. Arcadia, California, for the Mars 03/05 Sample Return Project).

Table 3. Melting and Boiling Points of Organic Compounds Representative of Prebiotic and Bacterial Activity[a]

Compound	Formula	Melting Point, K	Boiling Point, K
Methane	CH_4	90.4	111.3
Ethane	CH_3CH_3	101	188.4
Propane	$CH_3CH_2CH_3$	85.9	230.8
Butane	C_4H_{10}	138	272.5
Pentane	$CH_3(CH_2)_3CH_3$	143.3	309.1
Hexane	C_6H_{14}	179	241.3
Benzene	C_6H_6	278.5	353.1
Heptane	C_7H_{16}	183.5	371.6
Toluene	$C_6H_5CH_3$	178	383.6
Octane	$CH_3(CH_2)_6CH_3$	216.2	398.6
Ethylbenzene	$C_6H_5CH_2CH_3$	178	409.2
Adenine	$C_{10}H_{13}N_5O_4$	508	---
Xylene	$(CH_3)_2C_6H_4$	247.8	417.4
Glycine	$H_2NCH_2CO_2H$	535[b]	---
Alanine	$CH_3CH(NH_2)CO_2H$	433.5[c]	---
Aspartic acid	$HO_2CCH_2CH(NH_2)CO_2H$	542	---
Glutamic acid	$HO_2CCH_2CH_2CH(NH_2)CO_2H$	448[c]	---
Aminobutyric acid	$C_2H_5CHNH_2CO_2H$	sublimes	565-577
Valine	$(CH_3)_2CHCH(NH_2)CO_2H$	571	sublimes
Serine	$HOCH_2CH(NH_2)CO_2H$	501	decomposes
Threonine	$CH_3CH(OH)CH(NH_2)CO_2H$	503	decomposes
Isoleucine	$C_2H_5CH(CH_3)CH(NH_2)CO_2H$	566	sublimes
Leucine	$(CH_3)_2CHCH_2CH(NH_2)CO_2H$	566	sublimes
Heptadecane	$CH_3(CH_2)_{15}CH_3$	295	576
Octadecane	$CH_3(CH_2)_{16}CH_3$	301	581
Cholestane	$C_{27}H_{48}$	353	523
Pristane	$C_{18}H_X$	nd	nd
Phytane	$C_{20}H_Y$	nd	nd

[a]Data from *Weast* [1988]; nd, no data.
[b]Decomposition temperature.
[c]Sublimation temperature.

These phyllosilicates contain structural and adsorbed water and can readily fit inorganic cations, H_2O (potentially yielding information on the Martian water budget), and organic molecules (with implications for life) between the structural layers. Clays have been shown to be particularly sensitive to temperature fluctuations, showing significant compositional varia-tions as a result of subtle variations in temperature [e.g., *Guggenheim and Koster van Groos*, 1999]. The stability of interlayer water in clays is affected by the water fugacity [e.g., *Guggenhein and Koster van Groos*, 1992]. Dehydration of water absorbed on the clay surfaces as well as interlayer H_2O has been demonstrated to occur at <373 K (<100°C), sometimes as low as <323 K (<50°C) [*Guggenheim and Koster van Groos*, 1999]. Clearly, important climatic information can be recorded by clays but is easily lost if temperatures are raised much above 273 K.

The atmosphere of Mars is dominated by CO_2, rather than N_2 and O_2, as it is on Earth (Table 4). *Hess et al*. [1980] reported Martian atmospheric pressure variations of between 6.5 and 10.0 mbar. The pressure difference has implications for preserving the pristinity of atmospheric samples. *Fanale and Cannon* [1979] demonstrated that the amount of absorbed CO_2 on Martian analogue samples increased through decreasing temperature. *Gooding* [1990] argued that any returned samples should be kept below 230 K in order to minimize the release of absorbed CO_2 and to make the effect of H_2O desorption negligible (note that MSHARP, through *Carr* [1999], recommended 240 K). While the low temperature increases stable isotope fractionation factors, it also decreases reaction rates. The other alternative proposed by *Gooding* [1990] was to degas the samples prior to sealing them in containers. The latter option would certainly alter the samples, destroying biological, sedimentological, and climatic information and is not recommended.

The above discussion demonstrates the importance of temperature control on both pressure and mineral/compound stability and composition. *Gooding* [1990] emphasized the importance of headspace gas pressure in the sample return container. Indeed, it may be desirable to analyze headspace gases upon the initial opening of the sample container in order to get a better understanding of atmospheric composition and/or

Table 4. Near-Surface Atmospheric Compositions (Volume Basis) on Mars[a] and Earth

Gas	Mars, %	Earth, %	Estimated Leakage Rate,[b] cm^3 STP
CO_2	95.3	0.03	Negligible
N_2	2.7	78.1	7×10^{-4}
Ar	1.6	0.93	9×10^{-6}
O_2	0.13	21.0	2×10^{-4}
H_2O	0.03[c]	0.8[d]	-----
CO	0.07	< 1 ppm	-----
O_3	0.03 ppm	< 0.1 ppm	-----
Ne	2.5 ppm	1800 ppm	2×10^{-8}
Kr	0.3 ppm	100 ppm	-----
Xe	0.08 ppm	8 ppm	8×10^{-11}

[a]Mars data are from *Owen et al*. [1977] and *Gooding* [1990].
[b]Estimated contamination from Earth's atmosphere for leakage into a 1000 cm^3 Mars sample container at a rate of 10^{-9} cm^3 STP s^{-1} for 10 days [*Bogard et al*., 1979].
[c]Typical value, known to vary.
[d]50% relative humidity at 298 K.

understand sample degassing during the return to Earth by comparison with the Viking data. *Gooding* [1990] recommended that headspace pressure be $<1 \times 10^5$ Pa for unweathered igneous rocks and $<1 \times 10^3$ Pa for weathered materials, soil, sediment, and deep regolith samples. The headspace pressure could be controlled by temperature. Therefore we support the recommendation of MSHARP and thereby those of *Gooding* [1990] regarding headspace pressure that the samples should be kept at or below 240 K and that the sample containers should be sealed on the surface of Mars. Efficient seals are required not only from a planetary protection perspective but from a scientific viewpoint also. For example, a poorly sealed container could allow the samples to degas while in space, altering the chemical and isotopic signatures of the samples. As noted above, this can have profound implications for expanding our knowledge of Martian climate and water budget.

Finally, once on Earth, contamination from terrestrial gases at a higher temperature than on Mars could facilitate isotopic exchange, thus further masking the Martian signature of these samples. Perhaps the most profound outcome of a poor sample container seal is the contamination of the samples by terrestrial bacteria once back on Earth, thus yielding a false positive indication of life on Mars.

6.2. Collection of Samples

In this discussion it is assumed that any sample return mission will include a rover-mounted drilling/coring device that will have a maximum depth penetration of 5 cm (but extracts this in two 2.5 cm core lengths) and a diameter of 8 mm [cf. *Arvidson et al.*, 2000]. The rover will also contain a scooping device to sample the regolith. The lander will contain a drill that can penetrate 0.5 m into the regolith. The cores will be stored in a container for the return to Earth. Many of the points discussed here are also pertinent for other sample collection mechanisms, such as scoop and grab samples. Collection of fresh rock samples in this way will be the most invasive method, and it can potentially cause substantial contamination from the abrasion of the coring device and from terrestrial bio-organic material if the device has not been cleaned thoroughly. Therefore a number of factors will be considered when evaluating rock coring via the rover: (1) drilling rate (heating through friction), (2) sample-sample contact (cross contamination), (3) inorganic trace element contamination, and (4) use of Teflon and organic contamination.

6.2.1. Drilling rate. The drilling rate will be dependent on power supply and the type of motor used to drive the drill bit. In all probability these will be optimized to be the most economical such that there should not be appreciable heating of the rock sample during coring. However, only small temperature increases have the potential to radically alter the chemical and physical composition of certain types of sample (e.g., Figure 1). It is recommended that a clear understanding of how the drill will operate be acquired through proficient testing of the drill system prior to assembly of the spacecraft.

6.2.2. Sample-sample contact. Sample-sample contact is a critical issue especially for scoop or grab samples as these will be of nonuniform size and therefore difficult to package. If a variety of samples are collected (i.e., cores and scoop), we strongly recommend that they not just be placed in a single container. The optimal design would be to have the cores separate from each other and the sample container be designed to have a separate compartment(s) for the scoop/grab sample(s). For the rock cores these will be of uniform size and relatively easier to handle. If it is assumed that the sample container will have 5-cm-long slots for rover core samples, then two cores may need to be put in the same sample slot. Should samples from different rocks be mixed? These could abrade and incur cross contamination during rover motions, lift off, and impact on Earth (see section 6.3). Should cores from the same rock be put on top of one another as the deepest (freshest) surface of the second core would then be in contact with weathered outer surface of the first core? Sample contamination, whether from other samples, the drill bit, or the spacecraft, is an issue that can be addressed by experiments (with subsequent geochemical analyses) centered on (1) drilling of different rock types by the corer without cleaning of the drill bit between samples and (2) putting two 2.5-cm cores of different rock types in a tube and subjecting them to movement and stress that may be encountered during the return to Earth. Clearly, it would be unacceptable to only half fill each sample slot (as only half the mass could be returned), except in rare cases where a special feature, such as a weathered surface may need to be preserved.

We recommend that each rock selected for sampling have two or four cores extracted (5-10 g per rock). Essential geoscience studies can be conducted with samples as small as 5 g, as demonstrated by analysis of lunar samples and rare meteorites. The minimum amount of sample necessary is dependent on the grain size of the rock; 5 g may be adequate for fine-grained rocks (which includes most Martian meteorites), but more is required for representative whole rock analyses of coarser rocks (e.g., ALH84001 and some Apollo Lunar Highland rocks). Even for fine-grained rocks, 5 g will leave little or no reserve material for future studies once planetary protection studies, organic and inorganic chemical analyses, and mineralogic-petrologic studies have been completed. Therefore we suggest 5 g per rock be a recommended minimum mass. We strongly urge, where possible, to double this mass up to a total of ~10 g (approximately equivalent to four cores per rock). This differs from the recommendation of MSHARP [*Carr*, 1999], which advocates that only a single core be taken from each of as many rocks as possible, as this would be difficult to execute given the limited time available for sampling once the mission has landed.

Unlike MSHARP, we do not feel that it desirable to mix lithologies within the same sample container unless absolutely necessary. This recommendation is made for the following reasons: (1) Assuming a rover-based coring mechanism, between every other 2.5-cm core, no travel time is necessary so drilling/sampling time (dependent on the life of the batteries) is maximized along with sample return (through optimal use of the sample container). (2) A significant portion of this sample could be used up in planetary protection experiments upon return, so it is most desirable to bring back the largest sample mass as possible but without compromising these samples by cross contamination. (3) As sample masses of individual rocks will be relatively larger, a portion can be placed on reserve for future analyses. However, we recognize that once a mission is underway, real-time decisions on sampling and sample storage will have to be made in order to maximize both the amount and diversity of samples collected.

Regolith samples will be collected by the scoop on the rover and the lander-mounted drill. While the lander drill will penetrate up to 0.5 m, the material sampled, at least in the top few centimeters, will be disturbed and contaminated by rocket exhaust. Therefore regolith sampling by the rover scoop

should be undertaken well away from this disturbed and contaminated area. Regolith samples thus collected should then be isolated from each other and the rock cores in the sample container.

6.2.3. Trace element contamination. If it is again assumed that fresh samples will be collected by a rover-based coring device [cf. *Squyres et al*., 1998; *Arvidson et al*., 2000], contamination of the Mars samples will be affected by contact with the drill bit and core housing (rover and lander drills), the push rod, the "Sheath" at the front end of the analytical instruments, the wire brush for drill bit cleaning, the scoop on the rover, and the sample container.

It is accepted that materials that offer the best drilling performance (centimeters per watt hour) should be chosen for the construction of the drill bit and will probably be tungsten carbide possibly coated with silicon nitride.

Tungsten carbide contamination of a rock sample could seriously affect the analysis of W, C, platinum group elements, Co, Zr, Nb, Hf, Ta [cf. *Jain and Neal*, 1997] and also W-Hf, Lu-Hf, + Re-Os isotope determinations, although actual tests are needed to evaluate the significance of this. Use of silicon nitride may give an overestimation of silica content, a parameter that has gained significance from the Pathfinder results [*Rieder et al*., 1997; *McSween et al*., 1999; *Kring and Gleason*, 1999] in understanding the evolution of Mars. In addition, it may also disturb the isotopic composition of any N-bearing compounds (e.g., nitrates). Recent inovations suggest that the drill bit could be fashioned from synthetic diamond or natural cleavage-free diamond [*Myrick et al*., 2000]. If such a drill bit is used, its carbon isotope composition must be well known in order to assess any contribution of the drill bit to the carbon isotope budget of the rock sample through abrasion. This could affect the interpretation of biotic and prebiotic signatures.

The wear on the drill bit can be assessed on the surface through force/torque required to drill, current sensing (centimeters per watt hour), and visual inspection of the drill bit. We reinforce the recommendation of MSHARP that there should be no artificial tracer placed in the drill bit because the deliberate contamination by addition of tracers could interfere with data interpretation. Therefore contamination needs to be understood through (1) drilling experiments on rocks of different lithologies and permeabilities (it is recommended that rocks of different permeabilities need to be drilled in order to assess contaminant penetration into the interior of the core); (2) analysis of the drill bit used in these experiments (it is recommended that as many elements as possible should be quantified for these materials and by different analytical techniques.); and (3) manufacturing of spare final drill bits (both rover and lander drills), push rod, sheaths, and wire brushes, as well as sample container material when the final parts are made so their composition, as well as any elemental zonation in these materials, can be determined.

6.2.4. Use of Teflon and organic contamination. Use of plastics could cause severe problems with regard to organic contamination during sample collection. Use of unplasticized fluorocarbon Teflon (PFA, FEP [*Townsend*, 1990]) as the sample holder sleeve material needs to be fully evaluated. Will Teflon be inert under the conditions of space and unshielded from cosmic/solar radiation? If it breaks down, will the products be recognizable? Will static buildup cause dust to adhere to the sample holder that could cause problems of cross contamination but also may prevent insertion of core samples into the sleeves? Will it become brittle and prevent sample insertion? If any other plastics are used, similar sorts of questions must be asked and the purest forms should be used (see section 6.6). CAPTEM recommends that if Teflon is to be used, PFA or FEP should be used as a baked on coat on the metal of the sample container, rather than a separate insert, as this reduces the possibility that the sleeve could come loose, preventing sample insertion. The use of Teflon in this way will provide some degree of cushioning for the samples and reduce abrasion of the container. In addition, Teflon could also provide a mechanism for returning and preserving the pristinity of an atmospheric sample if seals of sufficiently low leak rate can be manufactured and tested within budgetary and time constraints.

6.3. Caching of Samples and Return to Earth

The samples returned should contain, as far as is feasible, unadulterated Martian signatures. Table 5 highlights the preservation hazards for these samples. Contamination of the samples can begin during collection, but the sample container design is critical for (1) preventing sample/container interactions and sample cross contamination; (2) planetary protection issues; and (3) terrestrial contamination of the samples.

Requirements of the Mars sample container and the return spacecraft are as follows: isolation of the samples from microbial, dust, gaseous, and radiative contamination on the surface of Mars; protection of the physical and chemical integrity of the samples; and that both the sample container and spacecraft should not induce changes in properties of the samples (e.g., induced magnetization, chemical contamination).

The ideal situation would be to hermetically seal the samples in the sample container after the last sample has been cached such that they are isolated in all respects. This would remove the need for sterilization on the Martian surface that is essentially unverifiable and potentially very damaging to sample integrity. Seal materials will need to be chosen carefully after the experience with the Apollo samples. For example, *Allton* [1989] reported that a seal composed of an indium-silver alloy was used as a seal material in boxes containing lunar samples. The results of subsequent analyses for In and Ag in at least some lunar samples are often questioned because of this. However, if such In-Ag seals are gas tight, the potential contamination may be a trade-off worth making if a pristine Martian atmospheric sample can be returned.

The seal used on Mars would need to be gas tight, impact proof, and act as a biogenic barrier (both to prevent Martian contamination of Earth and vice versa). Use of High Efficiency Particulate Air (HEPA) filters has proven effective in effectively isolating contained samples from biologic contamination [e.g., *Brunkhorst et al*., 1999]. If the sample container design achieved these goals, the samples could be isolated on Earth and studied for signs of life.

It is recommended that to the extent feasible, any exposure of the cached samples to temperatures significantly higher (during the return to Earth) than the ambient Mars surface temperature be avoided. Ideally, the samples should be kept below 240 K in order to approximate the temperature at which they were collected. This may be difficult during reentry and impact on Earth. Any rise in temperature will result in evolution of gases, isotopic exchange, and degradation of sample pristinity (see Figure 1). If temperature and pressure are controlled in the sample container so that gases emanating from

Table 5. Preservation Hazards and Recommendations for Martian Samples

Hazard	Definition	Recommendation
Contamination	addition of extraneous solid, liquid, or gaseous matter that would complicate, compromise, or preclude measurement of natural (Martian) chemical, biologic, or isotopic compositions of a sample	effective sample isolation on the Martian surface (rock and regolith sample). <1% of each element/compound in the Viking atmospheric analyses (atmospheric sample)
Temperature	increases producing decrepitation of solids, evaporation or desorption of volatile elements or compounds, or chemical/ isotope exchange reactions among sample components	≤240 K for all samples
Pressure	increase/decrease in confining (headspace) gas pressure that would lead to desorption or surface displacement of volatile elements or compounds, or solid-gas reactions	$<1\times10^5$ Pa for unweathered igneous samples $<1\times10^3$ Pa for weathered rocks, soil, sediment, deep regolith
Ionizing radiation	bombardment of a sample by protons, neutrons, alpha or beta particles, or photons (including X rays or gamma rays) that would produce radiation damage or obscure the record of radiation exposure on Mars	minimum shielding of 5 g cm^{-2}
Magnetic fields	exposure to magnetic lines of force that would obscure natural remnant magnetism in a sample or introduce artifacts	fields affecting the samples should be $<5.7\times10^{-5}$ T (1 Earth field)
Acceleration and shock	mechanical disturbances that would alter/obscure natural physical attributes of a sample (e.g., porosity, grain shapes, particle size distributions, degree of induration, layered sequences)	<2000 *g* for <1 ms (igneous rocks) <<2000 *g* for <1 ms (sedimentary rocks)
Sample/ container interactions	degassing of materials that could induce isotopic exchange with the samples; physical breakdown of part or all of the container, while unlikely, causing mixing of terrestrial and Martian materials; physical abrasion of the sample against the container that could also introduce terrestrial contamination	isolation of individual samples (cores, scoop, etc.); sample container to be made out of inert, homogeneous material; lining of the container with an inert, synthetic material (i.e., Teflon) to reduce abrasion by having a cushion between the sample and container

the samples are kept to a minimum, the only cross contamination possible is from mechanical breaking and mixing. This is especially critical for unconsolidated and weathered soil samples. Soil samples could mix with core material if the latter is disaggregated and mixed during lift off from Mars, movement during transit, and landing on Earth. Therefore we reemphasize our recommendation that the sample container have separate sections for cores and regolith samples.

The sample container and spacecraft should not generate magnetic fields that would adversely affect the samples by superimposing a different magnetic signature on them. *Gooding* [1990] argued that the samples should not be subject to magnetic field greater than that of Earth (5.7×10^{-5} T), and we see no reason to change this. Additionally, the possibility of induced magnetization may be greatly reduced if the samples are kept below 273 K (see Figure 1).

During transit between the surface of Mars and Earth, the samples will be subjected to unwanted doses of cosmic radiation (galactic and solar cosmic rays) that could affect the radiation record preserved in the Mars samples. *Gooding* [1990] argued for a baseline shielding value of 5 g cm^{-2} on the basis of two major concerns: (1) Naturally well-shielded samples taken from depth on Mars (e.g., > 10 cm) will be exposed to high doses of galactic cosmic rays upon excavation. (2) All Martian samples, regardless of depths of origins, will be exposed to high doses of solar cosmic rays (or their secondary products) after lift off from Mars.

The baseline shielding figure was proposed because there is a significant drop off in solar cosmic ray penetration above these values [e.g., *Arvidson et al*., 1981; *Reedy et al*., 1983].

Upon return to Earth, the samples will experience temperature rise, the effects of which are discussed above. Also shock from the impact could disaggregate and mix the samples and/or adversely affect any remnant magnetism. Clearly, the design of the sample container and return capsule is extremely important.

Gooding [1990] undertook empirical calculations to model shock and stress affects on a variety of assumed Martian geological samples using

$$S = 98.1\ N_g\ d^{2/3},$$

where S (Pa) is stress, N_g is the "g" number of acceleration (N_g = 0.385 at the Martian surface), and d is the specific gravity of the sample. Stresses have been computed for a number of igneous (gabbro, basalt, andesite) and sedimentary (shale, sandstone, limestone) for up to 20 g (Figure 2). *Gooding* [1990] concluded that unit-mass samples of drift or "crusty/cloddy" material would fail at stresses exceeding g of ~7-11. Average blocky material should be resistant to stress-induced failure at all accelerations g < 35 for a specific gravity of 2. It would appear from Figure 3 that coherent samples, if they were col-

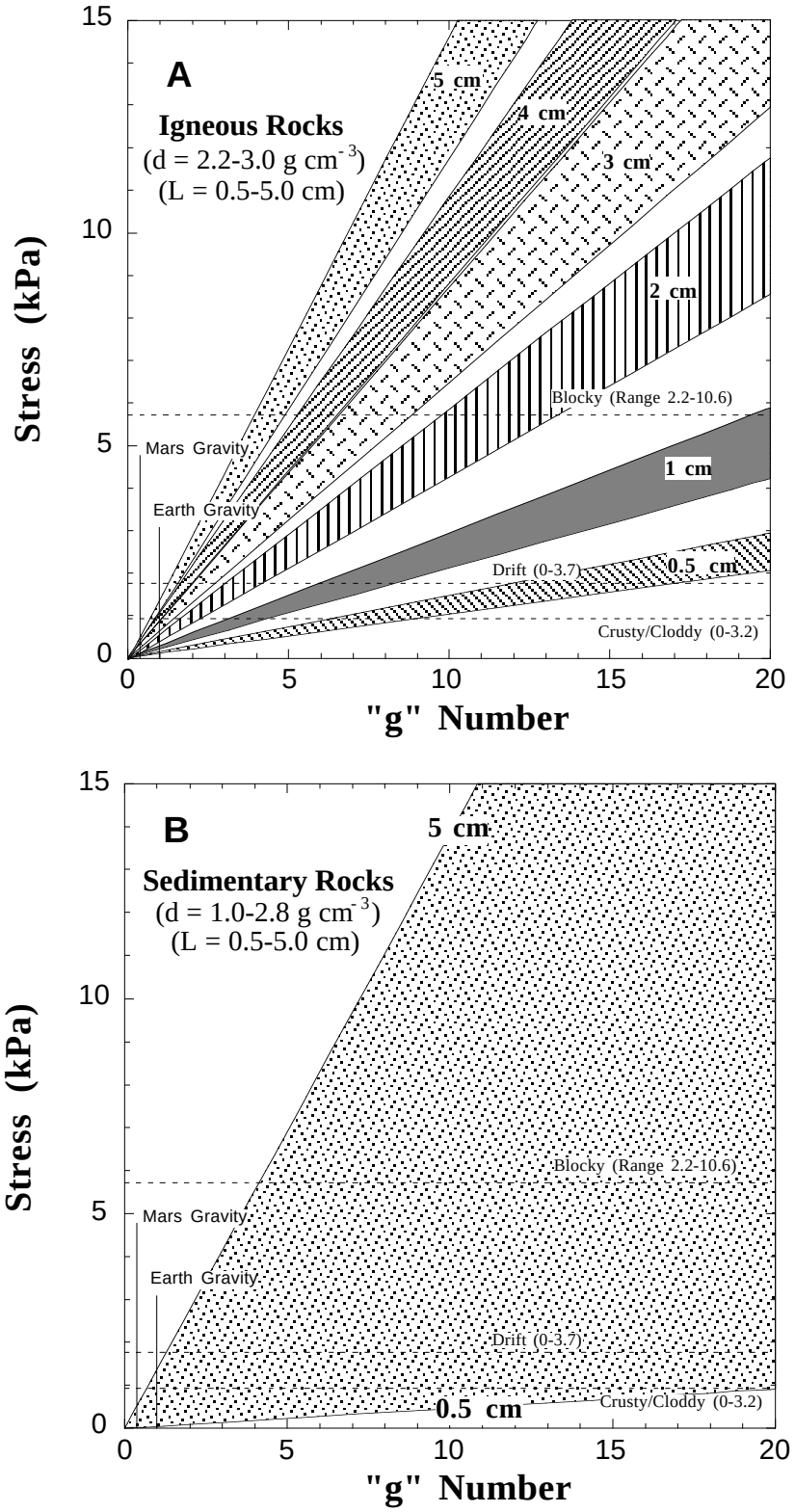

Figure 2. Acceleration force milestones for Martian samples collected as cubes of 1-cm dimensions. Positively sloping straight lines represent stress calculated as a function of "*g*" number (where 1 g = 981 cm s^{-2}) for igneous (basalt, gabbro, andesite) and sedimentary (shale, sandstone, limestone) materials (data from *Touloukian et al*. [1981]). The lines represent stress experienced by a bulk 1-g sample as a force normal to the face of a cube. The horizontal lines show average values of the strengths of blocky, crusty/cloddy, and drift material at the Viking lander sites as estimated by *Moore* [1987]. Modified from *Gooding* [1990].

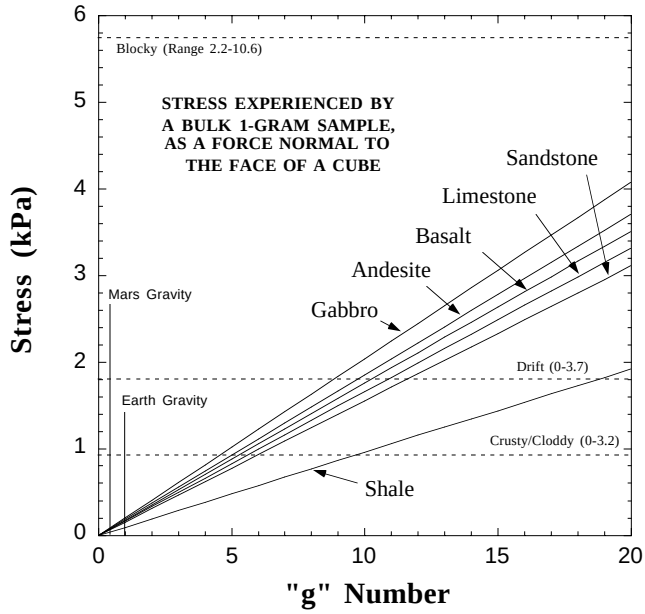

Figure 3. Acceleration force milestones for Martian samples collected as cores of varying length and 1-cm diameter. Stresses calculated as a function of *g* number (as in Figure 2) for igneous (basalt, gabbro, andesite, granite) and sedimentary (shale, siltstone, sandstone, limestone) materials (data from *Touloukian et al*. [1981]). The stress is the compression imposed on the base of a core sample that hits the surface of Earth with its long axis perpendicular to the surface. The lengths refer to length of samples assuming a 1-cm diameter. The sedimentary rocks produce only one field because of the wide range of specific gravities (1-2.8) used in the calculations results fields for specific core lengths with much overlap. The horizontal lines show average values of the strengths of blocky, crusty/cloddy, and drift material at the Viking lander sites as estimated by *Moore* [1987].

lected as cubes of 1-cm dimensions, would survive impact on Earth.

As core samples are to be returned, the effect of elongation and compression at the base of these samples can be estimated using

$$S = 98.1\ N_g\ d\ L,$$

where L is the length of the core assuming a 1-cm diameter. However, if two 2.5-cm cores are in the same sample slot and have a specific gravity of 2.2-3.0 g cm^{-3} (Figure 3), the compression stress experienced at the base of this 5-cm-long core exceeds the upper limit of the estimated strengths of Martian "blocky" material [*Moore*, 1987] at an acceleration of only g = 7. Therefore the integrity of the sample is threatened. Cushioning of the individual sample holders with a contained deformable material should be investigated.

Recent impact experiments at JPL (J. Crisp, presentation for Mars 2003 Science Working Group Meeting held May 12 and 13, 1999, Arcadia, California, for the Mars 03/05 Sample Return Project, 1999) demonstrated that failure of the returned samples will depend on the length of the core, its density, and its orientation when it strikes Earth's surface. In these experiments, half of the rock cores were impacted on their bases with the other half being impacted on their side, with a peak g force of ~1800 for ~0.5 ms. Thirty-six rock cores were tested (18 parallel and 18 perpendicular to the impact direction) consisting of chalk, limestone, and basalt. The results (Figure 4) indicated that over half sustained no damage. Only six samples sustained minor to major damage, the majority of these being the softer chalk samples. The conclusion was that if the Mars rock cores were subjected to ≤ 2000 g for short periods (i.e., <1 ms), very little scientific information would be lost, although further experiments are required. Soil and fragile rock samples may require lower impact energies in order to survive.

Fragile samples can survive impacts on Earth. For example, the L4 chondrite meteorite Bjurbole [*Hughes*, 1978a, 1978b] is known for its fragility and friability. *Hughes* [1978a, p. 392] disaggregated 4 g of this meteorite "gently and with extreme care using very light pressure from small dental picks and chisels and with a pestle and mortar, only very weak force being applied with the pestle." This meteorite survived impact despite its fragility.

6.4. What Terrestrial Materials Can Be Used in Handling the Martian Samples?

Any material from Earth that comes into contact with the returned samples is a potential contaminant. Not only will such materials need to be cleaned to a higher degree than that for Pathfinder (see above and *Carr* [1999]), it is recommended that their compositions be quantified. For example, the drill bit used to collect the core samples will be tungsten carbide. This material can also contain other trace elements (see above and *Jain and Neal* [1997]). If the composition of the drill bit is known, the amount of contamination can at least be semiquantitatively assessed. This assessment would be easier if materials used were pure or, if this is not possible, compositionally homo-geneous. Therefore CAPTEM recommends that as far as possible within mission/curation constraints, only pure, homogeneous materials be used for components that come into

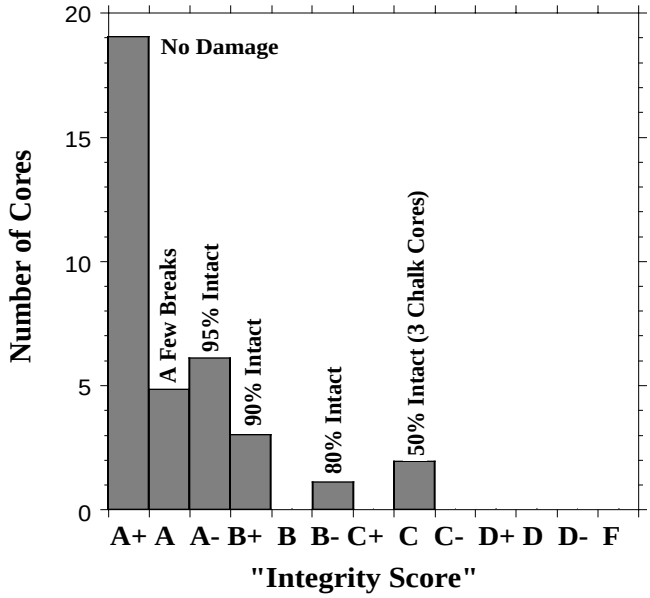

Figure 4. Results of the Jet Propulsion Laboratory impact tests on rock core samples (basalt, limestone, chalk). Adapted from J. Crisp (unpublished data, 1999).

contact with the samples. Even then, major and trace element compositions and organic content should be quantified independently of manufacturers' analyses. Examples of materials that would impart minimal contamination to the samples are aluminum, stainless steel, unplasticized Teflon (compare PFA and FEP), and titanium. The aluminum should be low in zinc (i.e., not the 7000 series alloys); the 6061 alloys (i.e., alloyed with Mg and Si) are acceptable. Stainless steel should be low sulfur, contain no molybdenum, and be compatible with electropolishing and passivating in nitric acid. There is a wide variety of titanium alloys, and careful consideration should be given to the minor and trace constituents in conjunction with the required physical and metallurgical properties. Unplasticized Teflon would impart organic contamination recognizable as nonbiogenic.

Townsend [1990] considered the types of materials that would be suitable in a Mars sample receiving facility. The recommendations from this study are reiterated and modified here in order to emphasize the fact that terrestrial contamination of the Mars samples needs to be minimized not only during collection and return but also during long-term curation.

1. The materials used to construct tools, equipment, containers, and environmental cabinets for the handling, processing and storage of Mars samples should be limited to stainless steel, aluminum, and unplasticized Teflon (compare PFA and FEP). These have proven most effective in the long-term curation of the Apollo samples.

2. All materials that the samples come into contact with should be sterilized, cleaned and packaged according to approved cleaning procedures (e.g., JSC 03243), and introduced to the containment area only through a strerilized transfer lock.

3. Undesirable contaminants are generally any terrestrial materials. It is suggested that a workshop be convened to consider contaminants that should be avoided. In order to give the reader an idea of what these contaminants may be, the following is an example list generated from the bias of the author: organic compounds, microorganisms (living or dead), Pb, U, Th, Li, Be, B, K, Rb, Sr, noble metals, noble gases, and rare earth elements.

4. Long-term storage should be under an inert gas and at temperatures below 240 K. Pure nitrogen would be the leading option, but if measuring the nitrogen isotopic composition of returned Martian samples is a priority, careful consideration of this issue is required.

CAPTEM further recommends that during the manufacturing stage of the components (whether for spacecraft or the receiving/curation facility), they be analyzed using at least two different analytical techniques. In addition, an understanding, prior to launch, of outgassing potential under vacuum will be invaluable. This will either demonstrate the purity of the substance and/or allow us to understand the nature of potential contamination through quantifying the impurities present.

7. Sterilization Issues

Planetary protection is divided into forward (contamination of Mars by terrestrial materials) and backward (contamination of Earth with Martian materials) phases [e.g., *DeVincenzi et al*., 1990, 1996, 1998]. *DeVincenzi et al*. [1998] presented a comprehensive review of the history of planetary protection and important research areas that need to be explored prior to defining requirements for a Mars sample return mission.

A major complication to the search for life on Mars would be if terrestrial microbes survived the round trip [e.g., *Mitchell and Ellis*, 1972; *Exobiology Program Office*, 1995]. Therefore sterilization and cleaning of outbound components is critical. Just as critical are checks to ensure that sterilization is complete, and this is where witness plates will be invaluable. Use of witness plates may also prove to be critical in assessing contamination, and their usefulness has been detailed by *Carr* [1999]. A summary of their uses is presented here: (1) inclusion of all plates through the cleaning/sterilization prior to launch, (2) removal of some just prior to launch as a record of forward contamination, (3) seal some plates just prior to arrival at Mars to record any "transit" contamination, and (4) keeping some witness plates open during sample acquisition and sealing them prior to loading in the Mars ascent vehicle.

We recognize that engineering constraints will probably dictate the exact use of witness plates, but we support the recommendation of MSHARP that use of these plates is vital for monitoring and understanding sample contamination. A possible scenario involves pure silica witness plates inserted in three of the core slots immediately after construction of the sample container. All three would go through sterilization procedures and one "plate" removed immediately afterward and evaluated for both organic and inorganic contents. The second witness plate would be removed immediately prior to launch. The third witness plate would be removed with the Mars samples upon return to Earth.

While the probability of the returned samples containing viable organisms cannot be demonstrated to be zero [cf. *Clark*, 1998], it is considered to be extremely low [*National Research Council*, 1997; *SSB,* 1998; (MESG*,* 1996, available at http://www.hq.nasa.gov/office/oss/mccleese.htm)]. In order to build public confidence that contamination from the samples will not be a threat would require sufficient isolation and testing procedures for life signs once on Earth. We agree with MSHARP [*Carr*, 1999] that sealing the Mars samples in a sterile and clean container and returning it to Earth can effectively isolate the samples on the Martian surface. Effective and robust containment systems can be built using multiple seals and HEPA filters (or their equivalents [e.g., *Brunkhorst et al*., 1999]). Upon arrival, the sample container should be conveyed to a level 4-type biologic containment facility (of the kind used to contain the most toxic and dangerous terrestrial viruses such as Ebola, Lassa Fever, or Marburg, but one that is also designed to protect the sample against contamination). The sample container should be opened in the controlled environment of this level 4-type facility and tested for life signs and quarantined until deemed safe. Specifying the modifications required for the "level 4-type" biologic containment facility, and the testing procedures that need to be developed is beyond the scope of this contribution but requires detailed study.

Whether some of the sample is sterilized for other types of examination can be decided after initial testing for organic material and viable organisms. The public should be assured that these precautions are as stringent as those used for the most dangerous biological agents on Earth. The Apollo capsule-type design has been used safely for many types of return vehicles by the U.S. and Russian civil and military space programs, and this design can be made to withstand impact and remain intact.

Table 6. Effects of Dry Heat Sterilization (150°C) on Returned Martian Samples

Science Lost or Impaired	Science Retained
Desorption of gases from mineral grains (atmospheric information	inorganic chemistry (major and trace elements)
Identity of oxidant(s) in the Martian soil	long-lived radiogenic isotope ratios (e.g., Sm-Nd, Rb-Sr, Lu-Hf, Re-Os) etc.
Decomposition of heat-sensitive minerals (ice, zeolites, salts, some carbonates)	textures of igneous (and metamorphic) rocks
Erasure of natural radiation records and annealing of radiation damage	mineralogy of igneous (and metamorphic) rocks
Alteration of stable isotope signatures through increased exchange reactions	
Resetting of mineral thermometers	
Destruction of some fluid inclusions	
Degradation of biochemical compounds	
Textural information of evaporites and possible sedimentary rocks	
Mineralogy of evaporites and possible sedimentary rocks	

Certification of the sample as "safe" will probably be determined by the Planetary Protection office or equivalent. CAPTEM suggests that if samples contain no organic carbon or any demonstrably viable organisms or morphological evidence thereof, they pose no threat from a planetary protection perspective and sterilization will not be required. After study by the Preliminary Examination Team (see MSHARP [*Carr*, 1999]), such samples should be released forthwith to the scientific community. If signs of life are found, sterilization of the samples will be required prior to release to the scientific community for detailed analysis. However, the scientific community wants the samples in pristine condition in order to extract the most science from them regarding Mars. The current NASA Management Instruction on Planetary Protection (NASA Directive NMI 8020.7D) states "The conduct of scientific investigations of possible extraterrestrial life forms, precursors, and remnants must not be jeopardized. In addition, the Earth must be protected from the potential hazard posed by extraterrestrial matter carried by a spacecraft returning from another planet."

Potential sterilization procedures involve chemicals, heat, or radiation. The effects of temperature sterilization techniques on the integrity of returned samples have been indirectly outlined by *Gooding* [1990] and are summarized in Figure 1. While high-temperature signatures may remain unaffected (e.g., Rb-Sr, Sm-Nd isotopes, major and trace element zonation), low-temperature signatures may be altered or obliterated (Table 6). For example, extended heating at >423 K could cause significant annealing of cosmic ray- or fission-induced nuclear particle tracks or from radiation-induced thermoluminescence [*JSC*, 1974, 1977; *Gooding*, 1990, and references therein]. Such sterilization may not only destroy important chemical signatures but may also compromise morphological evidence [e.g., *Hochstein et al*., 1974]. Furthermore, any fluid inclusions present could be severely compromised, or resetting of mineral thermometers could occur [*Gooding*, 1990]. Loss of volatiles would undoubtedly occur as well as isotopic exchange. Perhaps the most important sample property potentially affected by heat sterilization is the extent of oxidation and the intrinsic oxygen fugacity of Martian materials. *Gooding* [1990] noted that heating in a vacuum would still entail a change in oxidation state through the loss of hydrogen and suggested heating the samples in a gold-lined vacuum chamber to prevent H loss. We argue against this because it would compromise a number of important geochemical analyses.

Involvement of chemicals in the sterilization of returned samples would also affect the isotope composition the samples as well as facilitate reactions with the lower-temperature components. In addition, the use of chemicals in sterilization necessitates the de facto introduction of terrestrial contamination that will compromise not only biological signatures but chemical and isotopic signatures as well (e.g., peroxide, ozone). Use of radioactivity is currently being explored as a sterilizing agent for Mars samples [*Allen et al*., 1999]. Subjecting the samples to high doses of gamma radiation will not result in the changes associated with heating or chemical sterilization agents. Use of gamma rays may have an effect on the exposure ages and cosmic radiation history of returned samples. However, this procedure leaves the sample relatively unchanged compared to the use of heat and chemicals [*Allen et al*., 1999]. CAPTEM recommends that chemical sterilization not be used on the returned samples and heat only be used under extreme circumstances. CAPTEM further recommends that the efficiency and effects of high doses of gamma radiation as a sterilization medium on geological samples be fully explored and optimized and suggests that this be the sterilization process used on the Martian samples.

8. What Are the Preservation Issues Involved in Curating Martian Samples on Earth?

While many lessons learned from Apollo sample returns can be applied in the collection, preservation, and curation of Mars samples [i.e., *Allton*, 1998], there are distinctions between the two planetary bodies that need to be highlighted that will require different procedures to be defined.

1. Mars has a distinct atmosphere, and while this is of lower pressure than that on Earth, it is much higher than that of the Moon. This atmosphere, which may have been thicker and wetter in the past, is of sufficient pressure to facilitate stable isotope exchange with Martian rocks and soils.

2. Viking lander and Pathfinder experiments demonstrated the existence of chemical weathering affecting the soil and rocks. Weathered products will be the most reactive and presumably in equilibrium with the Martian atmosphere. If equilibrium is not maintained, records of current climate (from surface material) and past climate (samples from depth) will be lost or at least degraded.

3. Representative sampling of Mars will necessarily include the atmosphere. Returning a sample of the Martian atmosphere will bring challenges for curation: the Martian atmosphere is of different composition and at a lower pressure than that of Earth. Maintaining the pristinity of such a sample will require the development of new facilities and procedures.

Curation of Martian samples on Earth will utilize procedures and protocols developed for lunar samples, cosmic dust, and meteorites that will preserve the integrity and pristinity of returned samples [cf. *Townsend*, 1990]. However, while an exhaustive discussion of curatorial procedures is outside the scope of this paper, CAPTEM recommends that a thorough review of these procedures and protocols should be conducted (and amended accordingly) prior to the return of the samples. New ones can then be formulated to address the unique challenges of long-term Mars sample curation/preservation. For example, the need to keep bio-organic contamination out of the sample containers and the curation facility will require an examination of air filtration requirements and protocols. Storage facilities will need to be designed for these samples that should be at or below 240 K and under an inert atmosphere (e.g., nitrogen). It is encouraging to see work beginning on this vital part of Mars sample return endeavors [e.g., *Lussier et al*., 2000; *Allen et al.*, 2000].

9. Summary

Further expansion of our understanding of Mars will be greatly enhanced by returning Martian samples to Earth for detailed analysis as part of an integrated exploration program. This is, by analogy with our investigation of the Moon, the critical next step in our exploration of the red planet. Essential in this venture will be the preservation of pristine Martian signatures contained in these samples, particularly those indicative of life (either extinct or extant). Therefore spacecraft sterilization takes on added importance to prevent forward contamination of the samples, as do planetary protection issues for Earth. In addition, once on Earth, contamination of the samples will need to be prevented both in the short (reentry and impact on Earth) and long terms (processing and curation).

Compromising the integrity of the returned samples, whether physically, chemically, or biologically, can be avoided through planning and organization. This document makes a number of recommendations to this end, while recognizing that budgetary and engineering constraints as well as mission parameters may require modification of these. In dealing with pristinity issues, a sample return mission can be divided into several categories.

9.1. General

Any procedure or piece of equipment that can impact (contaminate) the collection, transportation, or curation of returned Mars samples needs to be fully evaluated by a scientific committee, prior to implementation, that has expertise in extraterrestrial sample analysis, curation, and preservation. CAPTEM is willing to serve in such a capacity if requested by NASA.

9.2. Spacecraft

Transportation of organic material from Earth to Mars may result in bio-organic contamination of the returned samples resulting in false positives when the samples are examined for life signs. In turn, this may cause unnecessary delays in releasing the samples to the scientific community. Therefore, after sterilization of the spacecraft the dead bacteria, etc., need to be removed. It is recommended that the spacecraft be sterilized and cleaned at least to Pathfinder standards, with the components that come into contact with the samples having a higher degree of cleanliness. The use of witness plates to monitor contamination of the spacecraft during construction and exposure on the Martian surface is recommended as they could prove to be very useful in documenting forward contamination.

9.3. The Samples

It is desirable that as diverse a suite of samples as possible should be returned in order to conduct broad-based investigations into Martian evolution (Jones and Treiman, 1998). If analyses are to be conducted on Earth, it is highly desirable that these samples be preserved in their pristine condition during collection, travel back to Earth and analysis/curation. CAPTEM supports the recommendation of the Mars Sample Handling and Requirements Panel (MSHARP [*Carr*, 1999]) that the samples should be kept or below 240 K (or as close to this as possible) and that the sample container should be isolated on the surface of Mars.

9.4. Sample Collection

Contamination of samples is possible from contact with any of the rover components, ranging from in situ analytical instruments to the wheels and contact with parts of drilling or caching mechanisms. CAPTEM endorses the use of a coring system to acquire fresh, unweathered samples. However, of all the potential sources of contamination during sample collection, contamination from the coring device, which will probably be tungsten carbide, is likely to be geochemically the most pervasive. Contamination of the samples via the drill bit could potentially compromise trace element (e.g., Zr, Nb, Co, Hf, W, C, platinum group elements) and isotopic (e.g., W-Hf, Lu-Hf, Re-Os, Pt-Os) analyses. It is recommended that drill bit contamination be thoroughly investigated through experiments on Earth. In addition, the composition of the drill bits should be characterized with detailed chemical and isotopic analysis. These recommendations could also be applied to any lander-based drill. It is further recommended that a variety of sample gathering devices (i.e., a scoop plus the drills) be flown on the rover and lander to allow the collection of a diverse suite of samples and, most importantly, to enable the return of samples if any one sample collection system fails.

9.5. Sample Containment

As the samples will be contained for a relatively long time (months to years), the container should not compromise sample integrity. Unlike MSHARP [*Carr*, 1999], CAPTEM does not feel that it is desirable to mix lithologies within the same sample container unless absolutely necessary. Therefore we recommend that the container be constructed out of the purest

materials possible, allow for no cross contamination between potentially diverse samples, keep rock cores separate from each other and from unconsolidated regolith samples, and be isolated on the surface of Mars. Rover-collected regolith samples should be kept separate from the lander-based drill regolith sample as the latter will have been contaminated with and disturbed by rocket exhaust.

9.6. Sterilization

While the probability of the returned samples containing viable organisms cannot be demonstrated to be zero, it is considered to be extremely low [*National Research Council*, 1997; *SSB*, 1998; (MESG, 1996, available at http://www.hq.nasa.gov/office/oss/mccleese.htm)]. If steriliz-ation is required, we recommend that heat and chemicals not be used, as these methods severely compromise sample integrity. While important information is retained at moderate sterilization temperatures (~150°C), a significant amount is lost regarding biologic and environmental evolution (Table 6). The preferred sterilization method is one of high dose (i.e., 3×10^{7}-10^{8} rads [*Allen et al*., 1999]) gamma radiation. Further experimentation into this technique is required. Certification of the sample as "safe" will probably be determined by the Planetary Protection office or equivalent. However, CAPTEM suggests that if samples contain no organic carbon or any demonstrably viable organisms or morphological evidence thereof, they pose no threat from a planetary protection perspective, and sterilization will not be required. After study by the Preliminary Examination Team (see MSHARP [*Carr*, 1999]), such samples should be released forthwith to the scientific community.

9.7. Materials

Materials used in spacecraft construction (i.e., those that will come into contact with the samples) should be fully characterized and a database created during the manufacturing stage of the components (whether for spacecraft or the receiving/curation facility). These materials should be analyzed for organic and inorganic constituents using at least two different analytical techniques. This will either demonstrate the purity of the substance or allow an understanding of the nature of potential contamination through quantifying the impurities present. CAPTEM endorses the recommendation of MSHARP [*Carr*, 1999] in that there should be no artificial tracer placed in the drill bit because the deliberate contamination through the addition of tracers will potentially interfere with data interpretation. As far as possible within mission/curation constraints, only pure, homogeneous materials should be used for components that come into contact with the samples. Materials that would be acceptable from a sample contamination standpoint are (1) low-Zn aluminum (i.e., not the 7000 series alloys), the 6061 alloys (i.e., alloyed with Mg and Si) are acceptable; (2) low-sulfur stainless steel that contains no molybdenum and is compatible with electropolishing and passivating in nitric acid; (3) titanium alloys as pure as feasible given the required physical and metallurgical properties; (4) unplasticized Teflon (PFA or FEP) that would impart organic contamination recognizable as nonbiogenic; and (5) tungsten carbide or diamond used for the drill bits pure as possible; if the former is used it should have a pure matrix (e.g., Co), and sample contamination documented through drilling experiments on Earth.

9.8. Curation

Long-term curation of Martian samples on Earth will utilize procedures and protocols developed for lunar samples, cosmic dust, and meteorites in order to preserve the integrity and pristinity of returned samples. We recommend that a thorough review of these procedures and protocols be conducted (and amended accordingly) prior to the return of the samples and new ones formulated to address the unique challenges of long-term Mars sample curation/preservation. For example, it is emphasized that storage of the samples should be at or below 240 K and under a very pure, inert atmosphere (e.g., nitrogen) for long-term preservation of low-temperature chemical signatures and prevention of isotopic exchange. The need to keep bio-organic contamination out of both the sample containers and curation facility will require an examination of air filtration requirements and protocols. Maintaining the pristinity of a sample of Martian atmosphere, which is of different composition and at a lower pressure than that of Earth, will require the development of new facilities and procedures.

Acknowledgments. Insightful comments from Dimitri Papanastassiou and Glenn MacPherson, as well as thoughtful and comprehensive reviews by Larry Nyquist and an anonymous reviewer have greatly improved this manuscript. Joy Crisp is thanked for supplying information regarding planetary protection and sample integrity experiments. This paper was supported through NASA grant NAG5-8099. CAPTEM reports to the Discipline Scientist for the NASA Cosmochemistry Program, Joseph Boyce. Among CAPTEM's duties is representing the interests and needs of scientists who study extraterrestrial samples to other constituencies in NASA, including program and mission designers. Membership of CAPTEM at the time of writing this paper was: J. Papike, Chair (University of New Mexico), D. Ming, Secretary (NASA, Johnson Space Center), D. DesMarais (NASA, Ames Research Center), B. Jolliff (Washington University, St. Louis), J. Jones (NASA, Johnson Space Center), L. Leshin (Arizona State University), C. Neal (University of Notre Dame), G. Ryder (Lunar & Planetary Institute), A. Treiman, (Lunar & Planetary Institute). CAPTEM's Web address is http://cass.jsc.nasa.gov/captem/.

References

Allen, C.C., C.B. Agee, R. Beer, and B.L. Cooper, Clean and cold sample curation, in *Concepts and Approaches for Mars Exploration, Lunar and Planet. Inst. Contrib. No. 1062*, p. 3, Houston, Tex., 2000.

Allen, C.C., et al., Effects of sterilizing doses of gamma radiation on Mars analog rocks and minerals, *J. Geophys. Res., 104*, 27,043-27,066, 1999.

Allton, J.H., Catalog of Apollo lunar surface geological sampling tools and containers, *Rep. JSC-23454,* 97 pp., NASA Johnson Space Center, Houston, Tex., 1989.

Allton, J.H., Lessons learned during Apollo lunar sample quarantine and sample curation, in *Proceedings, Mars Sample Quarantine Protocol Workshop, June 4-6*, 1997, edited by D.L. DeVincenzi, pp. 13-15, NASA Ames, Moffat Field, Calif., 1998.

Arvidson, R.E., C.M. Hohenberg, and J.R. Schirk, Long-term characterization of the Martian atmosphere and soil from cosmic ray effects in returned samples, *Icarus*, *45*, 250-262, 1981.

Arvidson, R.E., S. Squyres, E. Baumgartner, L. Dorsky, and P. Schenker, Rover trials for mars sample return mission prove successful, *Eos Trans. AGU*, *81*, 65, 72, 2000.

Bada, J.L., D.P. Glavin, G.D. McDonald, and L. Becker, A search for endogenous amino acids in Martian meteorite ALH84001, *Science, 279*, 362-365, 1998.

Becker, L., D.P. Glavin, and J.L. Bada, Polycyclic aromatic hydrocarbons (PAHs) in Antarctic Martian meteorites, carbonaceous chondrites and polar ice, *Geochim. Cosmochim. Acta*, *61*, 475-481, 1997.

Biemann, K., et al., The search for organic substances and inorganic volatile compounds in the surface of Mars, *J. Geophys. Res*., *82*, 4641-4658, 1977.

Blackburn, T.R., H.D. Holland, and G.P. Ceasar, Viking gas exchange reaction: Simulation on UV-irradiated manganese dioxide substrate, *J. Geophys. Res., 84*, 8391-8394, 1979.

Blichert-Toft, J., J.D. Gleason, P. Télouk, and F. Albarede, The Lu-Hf isotope geochemistry of shergottites and the evolution of the Martian mantle-crust system, *Earth Planet. Sci. Lett., 173*, 25-39, 1999.

Bogard, D.D., M.B. Duke, E.K. Gibson, J.W. Minear, L.E. Nyquist, and W.C. Phinney, Consideration of sample return and the exploration strategy for Mars, *NASA Tech. Memo., TM-58213*, 91 pp., 1979.

Borg, L.E., L.E. Nyquist, L.A. Taylor, H. Wiesmann, and C.-Y. Shih, Constraints on Martian differentiation processes from Rb-Sr and Sm-Nd isotopic analyses of the basaltic shergottite QUE 94201, *Geochim. Cosmochim. Acta, 61*, 4915-4931, 1997.

Borg, L.E., L.E. Nyquist, and H. Wiesmann, Rb-Sr isotopic systematics of the lherzolitic shergottite LEW88516, *Lunar Planet. Sci.* [CD-ROM], *XXIX*, abstract 1233, 1998.

Borg, L.E., L.E. Nyquist, H. Wiesmann, Y. Reese, and J.J. Papike, Sr-Nd isotopic systematics of Martian meteorite DaG476 *Lunar Planet. Sci.* [CD-ROM], *XXXI*, abstract 1036, 2000.

Bradley, J.P., R.P. Harvey, and H.Y. McSween, Jr., Magnetite whiskers and platelets in ALH 84001 Martian meteorite: Evidence of vapor phase growth, *Geochim. Cosmochim. Acta 60*, 5149-5155, 1996.

Bradley, J.P., R.P. Harvey, and H.Y. McSween Jr., No "nanofossils" in Martian meteorite, *Nature 390*, 454-455, 1997.

Bradley, J.P., R.P. Harvey, and H.Y. McSween Jr., Epitaxial growth of nanophase magnetite in Martian meteorite ALH 84001: Implications for biogenic processes., *Meteorit. Planet. Sci*., *33*, 765-773, 1998.

Brandon, A.D., R.J. Walker, J.W. Morgan, and G.G. Goles, Re-Os isotopic evidence for early differentiation of the Martian mantle, *Lunar Planet. Sci.* [CD-ROM], *XXXI*, abstract 1676, 2000.

Brearley, A.J., Origin of graphitic carbon and pentlandite in matrix olivines in the Allende meteorite, *Science, 285*, 1380-1382, 1999.

Brocks, J.J., G.A. Logan, R. Buick, and R.E. Summons, Archean molecular fossils and the early rise of eukaryotes, *Science, 285*, 1033-1036, 1999.

Brunkhorst, J.M., J.M. Choi, H.J. Davis, and W. Ho, Biological barriers for Mars mission, *Lunar Planet. Sci.* [CD-ROM], *XXX*, abstract 1654, 1999.

Carr, M.H., *Water on Mars*, 229 pp., Oxford Univ. Press, New York, 1996.

Carr, M.H., Mars Sample Handling and Requirements Panel (MSHARP) final report, *NASA Tech. Memo.*, TM-1999-209145, 47 pp., 1999.

Chicarro, A.F., G.E.N. Scoon, and M. Coradini, Mission to Mars: Report of the Mars Exploration Study Team, *Eur. Space Agency Spec. Publ.*, *ESA SP-1117,* 138 pp., 1989.

Clark, B.C., Surviving the limits to life at the surface of Mars, *J. Geophys. Res., 103*, 28,545-28,555, 1998.

Clemett, S.J., M.T. Dulay, J.S. Gilette, X.D.F. Chillier, T.B. Mahajan, and R.N. Zare, Evidence for the extraterrestrial origin of polycyclic aromatic hydrocarbons (PAHs) in the Martian meteorite ALH 84001, *Faraday Discuss. R. Soc. Chem.*, *109*, 97-110, 1998.

Cole, D.R. and H. Ohmoto, Kinetics of isotopic exchange at elevated temperatures and pressures, in *Stable Isotopes in High Temperature Geological Processes, Rev. Mineral.*, vol. 16, edited by J.W. Valley, H.P. Taylor Jr., and J.R. O'Neill, pp. 41-87, Mineral. Soc. of Am., Washington, D.C., 1986.

Committee on Planetary and Lunar Exploration (COMPLEX), Post Viking biological investigations of Mars, 26 pp., Space Sci. Board, Natl. Acad. of Sci., Washington, D.C., 1977.

Committee on Planetary and Lunar Exploration (COMPLEX), Strategy for the exploration of the inner planets: 1977-1987, 97 pp., Space Sci. Board, Natl. Acad. of Sci., Washington, D.C., 1978.

Crick, I.H., C.J. Boreham, A.C. Cook, and T.G. Powell, Petroleum geology and geochemistry of Middle Proterozoic McArthur Basin, northern Australia, II, Assessment of source rock potential, *AAPG Bull*., *72*, 1495-1514, 1988.

Cronin, J.R., S. Pizzarello, and D.P. Cruikshank, Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets, in *Meteorites and the Early Solar System,* edited by J.F. Kerridge and M.S. Matthews, pp. 819-857, Univ. of Ariz. Press, Tucson, 1988.

DeVincenzi, D.L., H.P. Klein, and J.R. Bagby, Planetary protection issues and future Mars missions, *NASA Conf. Publ., 10086*, 28 pp., 1990.

DeVincenzi, D.L., P. Stabekis, and J. Barrengoltz, Refinement of planetary protection policy for Mars missions, *Adv. Space Res*., *18*, 311-316, 1996.

DeVincenzi, D.L., M.S. Race, and H.P. Klein, Planetary protection, sample return missions and Mars exploration: History, status, and future needs, *J. Geophys. Res., 103*, 28,577-28,585, 1998.

Ehrlich, H.L., *Geomicrobiology,* 2nd ed., rev. and expanded, 646 pp., Marcel Dekker, New York, 1990.

Emrich, K., D.H. Ehhalt, and J.C. Vogel, Carbon isotope fractionation during the precipitation of calcium carbonate, *Earth Planet. Sci. Lett., 8*, 363-371, 1970.

Engel, M.H., and S.A. Macko, Isotopic evidence for extraterrestrial non-recemic amino acids in the Murchison meteorite, *Nature, 389*, 265-268, 1997.

Engel, M.H., and B. Nagy, Distribution and enantiomeric composition of amino acids in fossils, *Nature, 323*, 531-533, 1982.

Engel, M.H., and B. Nagy, Author's reply, *Nature, 301*, 496-497, 1983.

European Science Foundation (ESF), Report on the exploration of Mars, 12 pp., Strasbourg, France, Sept. 1986.

Exobiology Program Office, An exobiological strategy for Mars exploration, *NASA Spec. Publ., SP-530*, 56 pp., 1995.

Fanale, F.P. and W.A. Cannon, Mars: CO_2 adsorption and capillary condensation on clays: Significance for volatile storage and atmospheric history, *J. Geophys. Res*., *84*, 8404-8414, 1979.

Farmer, J.D., Mars exopaleontology, *Palaios, 10*, 197-198, 1995.

Farmer, J.D., Optimization of an '05 sample return for Mars exopaleontology, 13 pp., NASA Exobiology Program, NASA Ames Res. Cent., Moffett Field, Calif., 1996.

Farmer, J.D., Thermophiles, early biosphere evolution, and the origin of life on Earth: Implications for the exobiological investigation of Mars, *J. Geophys. Res., 103*, 28,457-28,461, 1998.

Farmer, J.D., and D.J. Des Marais, Exploring for a record of ancient Martian life, *J. Geophys. Res., 104*, 26,977-26,995, 1999.

Farquhar, J., M.H. Thiemens, and T.L. Jackson, $\Delta^{17}O$ anomalies in carbonate from Nakhla and Lafayette and $\Delta^{33}S$ anomalies in sulfur from Makhla: Implications for atmospheric chemical interactions with the Martian regolith, *Lunar Planet. Sci*. [CD ROM], *XXX* abstract 1675, 1999.

Franks, F., The properties of aqueous solutions at subzero temperatures, in *Water. A Comprehensive Treatise*, vol. 7, *Water and Aqueous Solutions at Subzero Temperatures*, edited by F. Franks, pp. 215-338, Plenum, New York, 1982.

Gibson, E.K., D.S. McKay, K. Thomas-Keprta, and C.S. Romanek, Evaluating the evidence for past life on mars, *Science, 274*, 2119-2124, 1996a.

Gibson, E.K., D.S. McKay, K. Thomas-Keprta, and C.S. Romanek, Technical comment, *Science, 274*, 2125, 1996b.

Giletti, B.J., The nature of oxygen transport within minerals in the presence of hydrothermal water and the role of diffusion, *Chem. Geol., 53*, 197-206, 1985.

Gillet, P., J.A. Barrat, T. Heulin, W. Achouak, M. Lesourd, F. Guyot, and K. Banzerara, Bacteria in the Tatahouine meteorite: Nanometric-scale life in rocks, *Earth Planet. Sci. Lett., 175*, 161-167, 2000.

Gleason, J.D., D.A Kring, D.H. Hill, and W.V. Boynton, Petrography and bulk chemistry of Martian orthopyroxenite ALH84001: Implications for the origin of secondary carbonates, *Geochim. Cosmochim. Acta, 61*, 3503-3512, 1997.

Gooding, J.L., Scientific guidelines for the preservation of samples collected from Mars, *NASA Tech. Memo., TM-4184*, 32 pp., 1990.

Gooding, J.L., S.J. Wentworth, and M.E. Zolensky, Calcium carbonate and sulfate of possible extraterrestrial origin in the EETA79001 meteorite, *Geochim. Cosmochim. Acta, 52*, 909-915, 1988.

Greenwood, J.P., L.R. Riciputi, and H.Y. McSween Jr., Sulfide isotopic composition in shergottites and ALH84001, and possible implications for life on Mars, *Geochim. Cosmochim. Acta, 61*, 4449-4453, 1997.

Guggenhein, S., and A.F. Koster van Groos, High-pressure differential thermal analysis (HP-DTA), I, Dehydration reactions at elevated pressures in phyllosilicates, *J. Therm. Anal., 38*, 1701-1728, 1992.

Guggenhein, S., and A.F. Koster van Groos, Thermal analytical techniques applied to the Clay Minerals Society (CMS) source clays, in *Source Clays Handbook*, pp. 91-115, Clay Miner. Soc., Boulder, Colo., 1999.

Halliday, A.N., M. Rehkämper, D.-C. Lee, and W. Yi, Early evolution of the Earth and Moon: New constraints from Hf-W isotope geochemistry, *Earth Planet. Sci. Lett*., *142*, 75-89, 1996.

Hartmann, W.K., D.C. Berman, G.A. Esquerdo, and A.S. McEwen, Recent Martian volcanism: New evidence from Mars Global Surveyor, *Lunar Planet. Sci.* [CD ROM], *XXX,* abstract 1270, 1999a.

Hartmann, W.K., M. Malin, A. McEwen, M. Carr, L. Soderlom, P. Thomas, E. Danielson, P. James, and J. Veverka, Evidence for recent volcanism on Mars from crater counts, *Nature, 397*, 586-589, 1999b.

Harvey, R.P., and H.Y. McSween Jr., A possible high-temperature origin for the carbonates in the Martian meteorite ALH84001, *Nature, 382*, 49-51, 1996.

Hess, S.L., J.A. Ryan, J.E. Tillman, R.M. Henry, and C.B. Levoy, The

annual cycle of pressure on Mars measured by Viking Landers 1 and 2, *Geophys. Res. Lett*., *7*, 197-200, 1980.

Hochstein, L.I., K.A. Kvenolden, and D.E. Philpott, The effect of sterilization on biological, organic chemical, and morphological information in natural samples, internal document, NASA Ames Res. Cent., Moffett Field, Calif., 1974.

Hodgson, G.W., and C.G.Whitely, The universe of porphyrins, in *Biogeochemistry of Ancient and Modern Environments*, edited by P.A. Trudinger, M.R. Walter, and B.J. Ralph, pp. 35-44, Springer-Verlag, New York, 1980.

Horowitz, N.H., G.L. Hobby, and G.S. Hubbard, Viking on Mars: The carbon assimilation experiment, *J. Geophys. Res., 82*, 4659-4662, 1977.

Hughes, D.W., A disaggregation and thin section analysis of the size and mass distribution of the chondrules in the Bjurböle and Chainpur meteorites, *Earth Planet. Sci. Lett*. *38*, 391-396, 1978a.

Hughes, D.W., Chondrule mass distribution and the Rosin and Weibull statistical functions, *Earth Planet. Sci. Lett*. *39*, 371-376, 1978b.

Hutchins, K.S., and B.M. Jakosky, Carbonates in Martian meteorite ALH84001: A planetary perspective on formation temperature, *Geophys. Res. Lett., 24*, 819-822, 1997.

Imbus, S.W., and D.M. McKirdy, Organic geochemistry of Precambrian sedimentary rocks, in *Organic Geochemistry, Principles and Applications*, edited by M.H. Engel and S.A. Macko, pp. 657-684, Plenum, New York, 1993.

Jackson, K.S., D.M. McKirdy, and J.A. Dechelman, Hydrocarbon generation in the Amadeus Basin, central Australia, *APEA J., 24*, 42-65, 1984.

Jagoutz, E., A. Sorowka, J.D. Vogel, and H. Wänke, ALH84001: Alien or progenitor of the SNC family?, *Meteoritics, 29*, 478-489, 1994.

Jagoutz, E., O. Bogdanovski, N. Krestina, and R. Jotter, DaG: A new age in the SNC family, or the first gathering of relatives, *Lunar Planet. Sci.* [CD ROM], *XXX,* abstract 1808, 1999.

Jain, J.C., and C.R. Neal, Problems associated with ICP-MS analysis of niobium and tantalum in tungsten-carbide-milled rock powders, paper presented at 43rd International Conference on Analytical Science and Spectroscopy, McGill Univ., Montreal, Canada, 1997.

Johnson Space Center (JSC), On the petrological, geochemical, and geophysical characterization of a returned Mars surface sample and the impact of biological sterilization on the analyses, report, 318 pp., NASA Johnson Space Cent., Houston, Tex., 1974.

Johnson Space Center (JSC), Consideration of sample return and the exploration strategy for Mars, report, 76 pp., Lunar and Planet. Sci. Div., NASA Johnson Space Cent., Houston, Tex., 1977.

Jolliff, B.L., et al., A balanced model for exploration of the terrestrial planets: Lessons learned from the Lunar experience, in *Concepts and Approaches for Mars Exploration, Lunar and Planet. Inst. Contrib. No. 1062*, pp. 162-163, Houston, Tex., 2000.

Jull, A.J.T., C. Courtney, D.A. Jeffrey, and J.W. Beck, Isotopic evidence for a terrestrial source of organic compounds found in Martian meteorites Allan Hills 84001 and Elephant Moraine 79001, *Science, 279*, 366-369, 1998.

Kerr, R.A., Requiem for life on Mars? Support for microbes fades, *Science, 280*, 412-414, 1998.

Kerridge, J.F., A note on the prebiotic synthesis of organic acids in carbonaceous meteorites, *Evol. Biosphere, 21*, 19-29, 1991.

Klein, H.P., The Viking biological experiments on Mars, *Icarus, 34*, 666-674, 1978.

Klein, H.P., The search for life on Mars: What we learned from Viking, *J. Geophys. Res., 103*, 28,463-28,466, 1998.

Klein, H.P., et al., The Viking biological investigation: Preliminary results, *Science, 194*, 99-105, 1976.

Kong, P., M. Ebihara, and H. Palme, Siderophile elements in Martian meteorites and implications for core formation in Mars, *Geochim. Cosmochim. Acta, 63*, 1865-1875, 1999.

Kotra, R.K., E.K. Gibson, and M.A. Urbancic, Release of volatiles from possible Martian analogs, *Icarus, 51*, 593-605, 1982.

Kring, D.A., and J.D. Gleason, Siliceous igneous rocks on Mars, *Lunar Planet. Sci.* [CD ROM], *XXX*, abstract 1611, 1999.

Kvenvolden, K.A., J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I.R. Kaplan, and C. Moore, Evidence for extra-terrestrial amino acids and hydrocarbons in the Murchison meteorite, *Nature, 228*, 923-926, 1970.

Kvenvolden, K.A., J. Lawless, and C. Ponnamperuma, Nonprotein amino acids in the Murchison meteorite, *Proc. Natl. Acad. Sci. U.S.A., 68*, 486-490, 1971.

Kyser, T.K., Equilibrium fractionation factors for stable isotopes, in *Stable Isotope Geochemistry of Low-Temperature Processes*, *Short Course Handb.,* vol. 13, edited by T.K. Kyser, pp. 1-84, Mineral. Assoc. of Can., Ottawa, 1987.

Lee, D.-C., and A.N. Halliday, Hf-W isotopic evidence for rapid accretion and differentiation in the early Solar System, *Science, 274*, 1876-1879, 1996.

Lee, D.-C., and A.N. Halliday, Hf-W evidence for early differentiation of Mars and the eucrite parent body (abstract), *Lunar Planet. Sci*., *XXVIII*, 795, 1997a.

Lee, D.-C., and A.N. Halliday, Core formation on Mars and differentiated asteroids, *Nature, 388*, 854-857, 1997b.

Leshin L.A., K.D. McKeegan, and R.P. Harvey, Oxygen isotopic constraints on the genesis of carbonates from Martian meteorite ALH84001 (abstract), *Lunar Planet.Sci., XXVIII*, 805-806, 1997.

Leshin, L.A., K.D. McKeegan, P.K. Carpenter, and R.P. Harvey, Oxygen isotopic constraints on the genesis of carbonates from Martian meteorite ALH84001, *Geochim. Cosmochim. Acta, 62*, 3-13, 1998.

Levin, G.V., The life on Mars dilemma and the sample return mission, in *Workshop on Mars Sample Return Science, LPI Tech. Rep., 88-07*, 109-110, 1988.

Levin, G.V., and P.A. Straat, Viking labeled release biology experiment: interim results, *Science, 194*, 1322-1329, 1976.

Lussier, J.D., T. Skiba, J.I. Ziemlewski, K.M. McNamara, E.K. Stansberry, and C.B. Agee, Curation and handling for a Mars sample return mission, *Lunar Planet. Sci.* [CD ROM], *XXXI*, abstract 1245, 2000.

McKay, D.S., E.K. Gibson, K.L. Thomas-Kerpta, H. Vall, C.S. Romanek, S.J. Clemett, X.D.F. Chiller, C.R. Maechling, and R.N. Zare, Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001, *Science, 273*, 924-930, 1996.

McKay, D.S., S.J. Wentworth, K.L. Thomas-Kerpta, F. Westall, and E.K. Gibson, Possible bacteria in Nakhla, *Lunar Planet. Sci*. [CD ROM], *XXX*, abstract 1816, 1999.

McKirdy, D.M., Biochemical markers in stromatolites, in *Stromatolites*, edited by M.R. Walter, pp. 163-191, Elsevier Sci., New York, 1976.

McKirdy, D.M., and J.D. Hahn, The composition of kerogens and hydrocarbons in Precambrian rocks, in *Mineral Deposits and the Evolution of the Biosphere*, edited by H.D. Holland and M. Schidlowski, pp. 123-154, Springer-Verlag, New York, 1982.

McKirdy, D.M., D.J. McHugh, and J.W. Tardif, Comparative analysis of stromatolitic and other microbial kerogens by pyrolysis-hydrogenation-gas chromatography (PH-GC), in: *Biogeochemistry of Ancient and Modern Environments*, edited by P.A. Trudinger, M.R. Walter, and B.J. Ralph, pp. 187-200, Springer-Verlag, New York, 1980.

McKirdy, D.M., A.J. Kantsler, J.K. Emmett, and A.K. Aldridge, Hydrocarbon genesis and organic facies in Cambrian carbonates of the eastern Officer Basin, South Australia, in *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*, edited by J.G. Palacas, *AAPG Stud. Geol., 18*, 13-31, 1984.

McSween, H.Y., Jr., What we have learned about Mars from SNC meteorites, *Meteoritics, 29*, 757-779, 1994.

McSween, H.Y., Jr., et al., Chemical, multispectral and textural constraints on the composition and origin of rocks at the Mars Pathfinder landing site, *J. Geophys. Res*., *104*, 8679-8716, 1999.

Mitchell, F.J., and W.L. Ellis, Surveyor 3. Bacterium isolated from lunar-retrieved television camera, in *Analysis of Surveyor 3 Material and Photographs Returned by Apollo 12*, p. 34, Sci. Tech. Inf. Cent., NASA Johnson Space Cent., Houston, Tex., 1972.

Moore, H.J., Physical properties of the surface materials at the Viking landing sites on Mars, *U.S. Geol. Surv. Prof. Pap., 1389*, 222 pp., 1987.

Morgan, J.W., and E. Anders, Chemical composition of Mars, *Geochim. Cosmochim. Acta, 43*, 1601-1610, 1979.

Myrick, T.M., et al., The Athena miniature rock coring and rock core acquisition and transfer system (mini-corer), in *Concepts and Approaches for Mars Exploration, Lunar and Planet. Inst. Contrib. No. 1062*, pp. 234-235, Houston, Tex., 2000.

National Research Council, Mars sample return: Issues and recommendations, 47 pp., Natl. Acad. Press, Washington, D.C., 1997.

Neal, C.R., J.C. Ely, J.C. Jain, and A. Sedlar, Differentiation of Mars investigated using high field strength (HFS) and platinum group elements (PGEs), *Lunar Planet. Sci*. [CD ROM], *XXX*, abstract 1002, 1999a.

Neal, C.R., J.C. Ely, and J.C. Jain, Probing the interiors of the terrestrial planets: Data from the Moon and Mars, in *Ninth Annual V.M. Goldschmidt Conference, LPI Contrib. 971,* pp. 207-208, Lunar and Planet. Inst., Houston, Tex., 1999b.

Neal, C.R., J.C.Ely, and J.C. Jain, PGE abundances in Martian meteor-

ites: No need for a "late veneer", *Lunar Planet. Sci.* [CD ROM], *XXXI*, abstract 1975, 2000.

Nealson, K.H., The limits of life on Earth and searching for life on Mars, *J. Geophys. Res*., *102*, 23,675-23,686, 1997a.

Nealson, K.H., Sediment bacteria: Who's there, what are they doing, what's new, *Annu. Rev. Earth Planet. Sci., 25*, 403-434, 1997b.

Nyquist, L.E., J. Wooden, B.M. Bansal, H. Wiesmann, G. McKay, and D.D. Bogard, Rb-Sr age of Shergotty achondrite and implications for metamorphic resetting of isochron ages, *Geochim. Cosmochim. Acta, 43*, 1057-1074, 1979.

Nyquist, L.E., B.M. Bansal, H. Wiesmann, and C.-Y. Shih, "Martians" young and old: Zagami and ALH84001, *Lunar Planet. Sci.* [CD ROM], *XXVI*, abstract 1065, 1995.

Nyquist, L.E., L.E. Borg, and C.-Y. Shih, The Shergottite age paradox and the relative probabilities for Martian meteorites of differing ages, *J. Geophys. Res., 103*, 31,445-31,455, 1998.

O'Neil, J.R., Preservation of H, C, and O isotopic ratios in the low temperature environment, in *Stable Isotope Geochemistry of Low-Temperature Processes*, *Short Course Handb.,* vol. 13, edited by T.K. Kyser, pp. 85-128, Mineral. Assoc. of Can., Ottawa, 1987.

O'Neil, J.R., and H.P. Taylor Jr., The oxygen isotope and cation exchange chemistry of feldspars, *Am. Mineral., 52*, 1414-1437, 1967.

Owen, T., K. Biemann, D.R. Rushneck, J.E. Biller, D.W. Howarth, and A.L. LaFleur, The composition of the atmosphere at the surface of Mars, *J. Geophys. Res*., *82*, 4635-4639, 1977.

Oyama, V.I., and B.J. Berdahl, The Viking gas exchange experiment results from Chryse and Utopia surface samples, *J. Geophys. Res., 82*, 4669-4676, 1977.

Papanastassiou, D.A., and G.J. Wasserburg, Evidence for late formation age and young metamorphism in the achondrite Nakhla, *Geophys. Res. Lett*., *1*, 23-26, 1974.

Pepin, R.O., Evidence of Martian origins, *Nature, 317*, 473-475, 1985.

Ponnanperuma, C., *The Origins of Life*, 211 pp. Thames and Hudson, London, 1972.

Reedy, R.C., J.R. Arnold, and D. Lal, Cosmic-ray record in solar system matter, *Science, 219*, 127-135, 1983.

Rieder, R., T. Economou, H. Wänke, A. Turkevich, J. Crisp, J. Brückner, G. Dreibus, and H.Y. McSween Jr., The chemical composition of the Martian soil and rocks returned by the mobile alpha proton X-ray spectrometer: Preliminary results from the X-ray mode, *Science, 278*, 1771-1774, 1997.

Robert, F., and S. Epstein, The concentration and isotopic composition of hydrogen, carbon, and nitrogen in carbonaceous meteorites, *Geochim. Cosmochim. Acta, 46*, 81-95, 1982.

Sears, D.W.G., and T.A. Kral, Martian "microfossils" in lunar meteorites?, *Meteorit. Planet. Sci*., *33*, 791-794, 1998.

Shearer, C.K., and J.J. Papike, Technical comment, *Science, 274*, 2121, 1996.

Shearer, C.K., G.D. Layne, J.J. Papike, and M.N. Spilde, Sulfur isotopic systematics in alteration assemblages in Martian meteorite Alan Hills 84001, *Geochim. Cosmochim. Acta, 60*, 2921-2926, 1996.

Shih, C.-T., L.E. Nyquist, D.D. Bogard, G.A. McKay, J.L. Wooden, B.M. Bansal, and H. Wiesmann, Chronology and petrogenesis of young achondrites, Shergotty, Zagami, and ALH77005: Late magmatism on a geologically active planet, *Geochim. Cosmochim. Acta, 46*, 2323-2344, 1982.

Shih, C.-T., L.E. Nyquist, and H. Wiesmann, Sm-Nd systematics of nakhlite Governador Valadares (abstract), *Lunar Planet. Sci., XXVII*, 1197-1198, 1996.

Shih, C.-T., L.E. Nyquist, Y. Reese, and H. Wiesmann, The chronology of the nakhlite, Lafayette, *Lunar Planet. Sci.* [CD ROM], *XXIX,* abstract 1145, 1998.

Shock, E.L. and M.D. Schulte, Summary and implications of reported amino acid concentrations in the Murchison meteorite, *Geochim. Cosmochim. Acta 54*, 3159-3173, 1990.

Solar System Exploration Committee (SSEC), Planetary exploration through the year 2000–An augmented program, report, 239 pp., NASA Advisory Counc., U.S. Gov. Print. Off., Washington, D.C., 1986.

Solar System Exploration Committee (SSEC), Planetary exploration through the year 2000–Scientific rationale, report, 88 pp., NASA Advisory Counc., U.S. Gov. Print. Off., Washington, D.C., 1988.

Space Studies Board (SSB), Space science in the twenty-first century: Imperatives for the decades 1995 to 2015 (planetary and lunar exploration), report, 167 pp., Natl. Acad. Press, Washington, D.C., 1988.

Space Studies Board (SSB), Evaluating the biological potential in samples returned from planetary satellites and small solar system bodies: Framework for decision making, report, 100 pp., Natl. Res. Counc., Washington, D.C., 1998.

Squyres, S.W., and J.F. Kasting, Early Mars: How warm and how wet?, *Science, 265*, 744-748, 1994.

Squyres, S.W., D.E. Wilhelms, and A.C. Moosman, Large-scale volcano ice interactions on Mars, *Icarus, 70*, 385-408, 1987.

Squyres, S.W., et al., The Athena Mars Rover science payload, *Lunar Planet. Sci.* [CD ROM], *XXIX*, abstract 1101, 1998.

Steele, A,F. Westall, D.T. Goddard, D. Stapleton, J.K.W. Toporski, and D.S. McKay, Imaging of the biological contamination of meteorites: A practical assessment, *Lunar Planet. Sci.* [CD ROM], *XXX*, abstract 1326, 1999.

Taylor, S.R., *Planetary Science: A Lunar Perspective*, 481 pp., Lunar and Planet. Inst., Houston, Tex., 1982.

Taylor, S.R., *Solar System Evolution: A New Perspective*, 292 pp., Cambridge Univ. Press, New York, 1990.

Thomas-Keprta, K.L., C.S. Romanek, S.J.Wentworth, D.S. McKay, D. Fisler, D.C. Golden, and E.K. Gibson, TEM analysis of fine-grained minerals in the carbonate globules of Martian meteorite ALH 84001 (abstract), *Lunar Planet. Sci., XVIII,* 1433-1434, 1997.

Thomas-Keprta, K.L., D.A. Bazylinski, D.C. Golden, S.J. Wentworth, E.K. Gibson, and D.S. McKay, Magnetite from ALH 84001 carbonate globules: Evidence of biogenic signatures?, *Lunar Planet. Sci*. [CD ROM], *XXIX*, abstract 1494, 1998.

Touloukian, Y.S., W.R. Judd, and R.F. Roy, *Physical Properties of Rocks and Minerals,* vol. 2, 548 pp., McGraw-Hill, New York, 1981.

Townsend, J.E., Mars Sample Receiving Facility, *Publ. 24736*, 25 pp., NASA Johnson Space Cent., Houston, Tex., 1990.

Treiman, A.H., A petrographic history of Martian meteorite ALH84001: Two shocks and an ancient age, *Meteoritics, 30*, 294-302, 1995.

Treiman, A.H., and C.S. Romanek, Chemical and stable isotopic disequilibrium in carbonate minerals of Martian meteorite ALH 84001: Inconsistent with high formation temperature, *Meteorit. Planet. Sci*., *33*, 737-742, 1998.

Turner, G., S.F. Knott, R.D. Ash, and J.D. Gilmour, Ar-Ar chronology of the Martian meteorite ALH84001: Evidence for the timing of the early bombardment of Mars, *Geochim. Cosmochim. Acta, 61*, 3835-3850, 1997.

Valley, J.W., J.M. Eiler, C.M. Graham, E.K. Gibson, C.S. Romanek, and E.M. Stolper, Low-temperature carbonate concretions in the Martian meteorite ALH84001: Evidence from stable isotopes and mineralogy, *Science, 275*, 1633-1638, 1997.

Warren, P.H., Petrologic evidence for low-temperature, possible flood evaporitic origin of carbonates in the ALH 84001 meteorite, *J. Geophys. Res*., *103*, 16,759-16,773, 1998.

Warren, P.H., G.W. Kallemeyn, and F.T. Kyte, Origin of planetary cores: evidence from highly siderophile elements in Martian meteorites, *Geochim. Cosmochim. Acta, 63*, 2105-2122, 1999.

Weast, R.C. (Ed.), *CRC Handbook of Chemistry and Physics, 69th ed.*, 2464 pp., CRC Press, Boca Raton, Fla., 1988.

Westall, F., The nature of fossil bacteria: A guide to the search for extraterrestrial life, *J. Geophys. Res., 104*, 16,437-16,451, 1999.

Wood, J.A., and W.V. Boynton, The importance of bringing samples of Mars to Earth, in *Concepts and Approaches for Mars Exploration, Lunar and Planet. Inst. Contrib. No. 1062*, pp. 316-317, Houston, Tex., 2000.

Zent, A.P., and C.P. McKay, The chemical reactivity of the Martian soil and implications for future missions, *Icarus, 108*, 146-157, 1994.

C. R. Neal, Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556. (neal.1@nd.edu).

(Received September 20, 1999; revised May 5, 2000;
accepted May 16, 2000.)