NASA Technical Memorandum 4184

Scientific Guidelines for Preservation of Samples Collected From Mars

APRIL 1990

(NASA) 260 p CSCL 03B

Unclas
H1/91 0290736

NASA Technical Memorandum 4184

Scientific Guidelines for Preservation of Samples Collected From Mars

Edited by
James L. Gooding
Lyndon B. Johnson Space Center
Houston, Texas

NASA
National Aeronautics and Space Administration
Office of Management
Scientific and Technical Information Division
1990

Table of Contents

Executive Summary iii

Preface iv

List of Tables v

List of Figures v

1. Introduction

1.1. Sample Return As Part of Mars Exploration 1

1.2. The 1974, 1977 and 1979 JSC Reports 1

1.3. Need for Updated Report 2

1.4. Scope and Purpose 2

2. Importance of Martian Samples

2.1. Nature and Value of Information Contained in Samples 4

2.1.1. Planetary composition 4

2.1.2. Planetary formation and geologic time scale 6

2.1.3. Climate history 6

2.1.4. Biological history 7

2.2. Relative Merits of Laboratory and *In Situ* Analyses 8

2.2.1. Lessons from *Viking* Lander Experiments 9

2.2.2. Clues from "Martian" meteorites 9

3. Sample Preservation Issues

3.1. Essential Considerations 10

3.2. Contamination 11

3.3. Temperature 14

3.3.1. Sub-freezing (< 273 K) 15

3.3.2. Cool thawing (273-300 K) 16

3.3.3. Sub-sterilization (300-400 K) 16

3.3.4. Sterilization and decrepitation (> 400 K) 16

3.4. Pressure 19

3.5. Ionizing Radiation 21

3.6. Magnetic Fields 23

3.7. Acceleration and Shock 24

3.8 Biology and Planetary Quarantine 25

3.9. Summary 25

4. Recommendations 27

References 29

-- continued --

Table of Contents (continued)

Appendix A1: "Call for input" letter, 1974	A1-1
Appendix A2: List of respondents to 1974 call	A2-1
Appendix A3: Letters and data from respondents, 1974	A3-1
Appendix B1: "Call for input" letter, 1987	B1-1
Appendix B2: List of respondents to 1987 call	B2-1
Appendix B3: Letters and data from respondents, 1987-88	B3-1
Appendix B4: Estimated concentrations of oxidants in sediment samples at the *Viking* Lander sites	B4-1

EXECUTIVE SUMMARY

Science goals for collecting and returning Martian samples for analysis on Earth, as an integral part of Mars exploration, are traceable to the National Academy of Sciences and have been reiterated by various advisory committees and working groups. The desired sample materials include atmosphere, rocks, sediments, soils, deep regolith, and possibly ices.

The maximum scientific value of the samples is retained when they are preserved in the conditions that applied prior to their collection. Any sample degradation equates to loss of information.

Contamination by extraneous elements or compounds might preclude measurement of native Martian chemical or isotopic compositions.

Excessive warming would mobilize adsorbed water and initiate irreversible chemical or isotope-exchange reactions. Temperatures substantially lower than 273 K are required to arrest interfacial water in fine-grained, porous samples. Heat-sensitive materials, including unidentified oxidants discovered by the *Viking* Landers, would decompose if excessively warmed. Hydrate or carbonate minerals might undergo stable-isotopic re-equilibration, thereby erasing their records of ancient Mars climates. Uncontrolled temperature rise would also produce large head-space pressures, through gas desorption from samples, which would further stimulate undesirable reactions. Deliberate heat sterilization would not affect age-dating of igneous rocks but would profoundly degrade paleoclimate information in sediments and soils.

Uncontrolled doses of ionizing radiation might erase or obscure the depth-dependent natural records of cosmic-ray damage in mineral grains. The Martian atmosphere differentially filters solar and galactic cosmic rays and changes in sample shielding, relative to natural shielding, might alter the climate-dependent records of particle tracks and spallation nuclides. Radiation monitors for the samples are highly desirable.

Extraneous magnetic fields might erase or obscure natural remanent magnetism in the samples, or induce magnetic artifacts, that would complicate or even preclude the search for evidence about Martian magnetic fields.

Acceleration and shock loads expected during a sample-return mission should not threaten the integrity of rocks but might disintegrate soil clods.

Based on detailed review of pertinent scientific literature, and advice from experts in planetary sample analysis, recommended upper limits for key parameters in the environmental control of collected samples are as follows:

- Contamination
  - For each element in a geologic sample, < 1% of the concentration in the Shergotty meteorite.
  - For each element or compound in an atmospheric sample, < 1% of the concentration in the *Viking* Lander atmospheric analysis.
- Temperature
  - < 260 K; unweathered igneous rock
  - < 230 K; soil, sediment, deep regolith, or weathered rock
- Pressure (head-space gas, Mars ambient)
  - < 1 atm; unweathered igneous rock
  - < 0.01 atm; soil, sediment, deep regolith, or weathered rock
- Ionizing Radiation — 5 g/cm^2 shielding (should not be much lower or higher)
- Magnetic Fields — < 5.7×10^{-5} T (1 Earth field)
- Acceleration and Shock — < 7 g (1 g = 9.81 m/sec^2)

Parametric values recommended for the most sensitive geologic samples should also be adequate to preserve any biogenic compounds or exobiological relics.

Additional research would be needed before any of the recommended limits could be relaxed on scientific grounds. Especially important is the temperature and pressure dependence of stable isotope exchange reactions for low-temperature minerals containing H_2O or CO_2.

PREFACE

This report represents an updated and revised version of work led by Dr. Larry A. Haskin at the Johnson Space Center in 1974 and that represented one of the earliest attempts to scientifically document the case for collecting and studying well-preserved samples from the planet Mars. Those valuable and insightful contributions have been included in the present version as copies of letters from the specialists who contributed to the original document. New input from other specialists is recorded here as additional letters that I received in 1987-88, in response to my appeal to the scientific community for help in revising the 1974 report. I bear sole responsibility, however, for decisions and interpretations made during integration of the information base.

Many people both inside and outside of NASA contributed to successful completion of this report. The most essential help was provided by Dr. Douglas P. Blanchard, Dr. C. W. Lagle, Mrs. Yvette Damien, Dr. Robert N. Clayton, Dr. Stanley M. Cisowski, Dr. David W. Collinson, Dr. Edward S. Gaffney, Dr. Henry J. Moore, Dr. Robert C. Reedy, Dr. Derek W. G. Sears, Dr. Timothy D. Swindle, Dr. Mark J. Cintala, Dr. John H. Jones, and Dr. Christopher P. McKay. Nonetheless, any lingering errors remain my responsibility.

James L. Gooding
NASA Lyndon B. Johnson Space Center
Houston, Texas USA
January 29, 1990

List of Tables

2.1	Desirable types of Martian samples and their respective values in Mars exploration	4
2.2	Roles of laboratory and *in situ* analyses of Martian materials	8
3.1	Preservation hazards for Martian samples	10
3.2.	Elemental compositions of the Shergotty meteorite and surface sediments at Chryse Planitia, Mars	12
3.3.	Near-surface atmospheric compositions on Mars and Earth	13
3.4.	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/sec for 10 days	13
3.5.	Volatile-release temperatures of geologic materials heated 10 K/min under 1-atm dry N_2	17
3.6.	Temperatures for which one-hour heat treatment anneals nuclear particle tracks	18
3.7	Characteristics of solar cosmic ray and galactic cosmic ray components	21
4.1.	Recommended parametric values for preservation of Martian samples	27

List of Figures

1-1	Development of Mars science goals	3
3-1	Maximum surface skin temperatures predicted for Mars as functions of latitude and season	14
3-2	Typical diurnal temperature variations in the near-surface atmosphere at the *Viking* Lander 1 and 2 sites	15
3-3	Sub-surface temperature profiles modelled for *Viking* Lander sites	15
3-4	Potential degradation of Martian samples during warming	15
3-5	Seasonal variation of atmospheric pressure a the *Viking* landing sites	19
3-6	CO_2 gas adsorption on powdered samples of Mars-analogous geologic materials as a function of temperature	19
3-7	Head-space pressures developed by desorption of gases from Mars-analogous materials inside a fixed volume	20
3-8	Production rates of radiation damage effects in Mars surface materials as a function of shielding	21

-- continued --

List of Figures (continued)

3-9	Relative production rates of track damage and spallation ^{78}Kr at the Mars surface and in the deep regolith	22
3-10	Production rates for tracks and spallation nuclides calculated for a lunar basaltic rock directly exposed to SCRs and GCRs	22
3-11	Acceleration-force milestones for Martian samples	24
3-12	Summary of major concerns regarding preservation of collected Martian samples	26

1. INTRODUCTION

1.1. Sample Return As Part of Mars Exploration

Space science organizations in various countries have consistently recommended exploration of Mars as a high-priority goal. The scientific merits of collecting samples on Mars and returning them to Earth for analysis have been reviewed and endorsed by the U. S. National Academy of Sciences (COMPLEX, 1977, 1978; SSB, 1988), the National Aeronautics and Space Administration (NASA) Advisory Council (SSEC, 1986, 1988), the European Science Foundation (ESF, 1986), and the European Space Agency (Chicarro et al., 1989). In fact, after reviewing all candidate missions beyond the observer-class core program (SSEC, 1983), the NASA Advisory Council concluded that

> *"A sample return mission to Mars before 2000 is the highest priority for an Augmentation Mission to the terrestrial planets" (SSEC, 1986, p. 18).*

Planning for a Mars sample-return mission must include a comprehensive review of the scientific requirements for selecting and acquiring samples on Mars and for preserving them from the time they are collected until the time they are delivered for analysis to laboratories on Earth. The purpose of this report is to update previous reviews of sample-preservation goals in a self-contained guide for mission planners. The summary presented here represents an updated and expanded version of a similar report that was prepared in 1974.

1.2. The 1974, 1977 and 1979 JSC Reports

In recognition of the major advances in understanding the Moon that were provided by return of the *Apollo* and *Luna* samples, scientists at the Johnson Space Center (JSC) prepared a report in April 1974 that summarized the comparable goals and strategies for Earth-based analyses of samples returned from Mars. The stated purposes of the report (JSC, 1974) were as follows:

(a) To identify those experiments that could and should be done on returned Martian samples to characterize their inorganic properties,

(b) To evaluate, insofar as can be done, the effects of potential biological sterilization of the sample by heating prior to its return,

(c) To identify particular analytical techniques needing further improvement in order to make optimum use of a returned sample, and

(d) To identify experiments to be done on simulated Martian samples, with and without sterilization, that better define the limits of information available about the planet from analyses of returned samples.

The report was compiled at JSC based on input solicited from selected members of the planetary science community, following a call-for-input letter from L. A. Haskin (Appendix A1). A general outline of the study was prepared by five members of the JSC Solar System Exploration Division (which was named the Planetary and Earth Sciences Division in 1974) who sent letters to the outside science community requesting advice and opinions. Many scientists responded with letters that discussed problems and experimental approaches in their respective areas of expertise. The list of contributors to the final report (JSC, 1974), and their actual recommendations, are included in this report as Appendices A2 and A3, respectively.

In an independent but concurrent effort, Professor Elbert A. King (University of Houston) organized researchers in various laboratories in a broad, reconnaissance study of the effects of heating on a common set of Mars-analogous mineral, rock, and soil samples. Both the letters returned to JSC by interested scientists and the results of the experiments organized by

Professor King were included as appendices to the JSC (1974) report but are not repeated here, except as summary statements in appropriate chapters.

After the deadline for receipt of the letters at JSC had passed, a committee of scientists assembled to write the report. Toward that end, a meeting was held on March 27-28, 1974 at the Lunar and Planetary Institute (named the Lunar Science Institute in 1974) near JSC. Members of the committee (in alphabetical order) and their affiliations were as follows:

S. O. Agrell, Cambridge University, UK
D. D. Bogard, NASA/JSC
R. Brett, NASA/JSC
S. Chang, NASA/Ames Research Center
M. B. Duke, NASA/JSC
H. P. Eugster, Johns Hopkins University
E. K. Gibson, NASA/JSC
L. A. Haskin, NASA/JSC (Committee Chairman)
J. C. Huneke, California Institute of Technology
E. A. King, University of Houston
L. E. Nyquist, NASA/JSC
W. C. Phinney, NASA/JSC
D. W. Strangway, University of Toronto, Canada
H. P. Taylor, California Institute of Technology
S. R. Taylor, Australian National University, Australia
P. Toulmin III, U. S. Geological Survey, Reston, Virginia
J. L. Warner, NASA/JSC.
R. L. Young, NASA Headquarters.

Subcommittees were formed and given responsibilities for writing individual portions of the report. Summaries of major topics were largely based on the written correspondence that was received.

Although JSC (1974) represented an important scientific contribution, it was never widely distributed and carried no formal publication or catalog number that would permit its easy retrieval by later researchers. To at least partially correct the latter deficiency, and to update the 1974 information in light of results from the *Viking* missions to Mars (1976-1977), a revised summary version of JSC (1974) was prepared (JSC, 1977) and published in amended form by Bogard et al. (1979).

1.3. Need for Updated Report

Although much of the rationale presented in JSC (1974) and Bogard et al. (1979) remains valid, considerable progress has since been made in studies of Mars by remote sensing and in laboratory studies of lunar rocks, meteorites, and interplanetary dust particles. In particular, plans to sample Mars must take into account the following developments:

(a) New knowledge of the Martian environment, gained from analysis of *Viking* data (1976-1987).

(b) Possible new knowledge of Martian materials, gained (since 1979) from laboratory studies of shergottite, nakhlite, and chassignite meteorites which might be Martian rocks.

(c) Advances in analytical methodology, instrumentation, and laboratory geochemical studies (since 1979) that would affect mission designs and sampling strategies.

This report was intended to achieve those updates by integrating new information into the excellent frameworks provided by JSC (1974) and Bogard et al. (1979).

1.4. Scope and Purpose

The purpose of the present report is to provide a summary, based on current knowledge, of the scientific requirements for collecting and preserving Martian samples for laboratory analysis on Earth. This report is intended to supplement and support, rather than replace or compete with, contemporaneous reports, commissioned by NASA, on science or engineering studies of Mars sample-return missions. In particular, this report is not meant to replace or compete with reports on high-level goals for Mars exploration that will be issued by science working groups that have been chartered to support mission-design projects. Instead, this report provides summaries and traceabilities of requirements at a level of detail that is beyond the scope of the working-group activities.

To accomplish the necessary updates relative to JSC (1974, 1977) and Bogard et al. (1979), a new poll of the science community was initiated in

February 1987 on the subject of sample-science goals for Mars. A "Dear Colleague" call-for-input letter (Appendix B1) was sent to each of 733 addressees, including planetary scientists with interests in Mars, Earth-oriented geoscientists, biologists, and selected scientific administrators (Appendix B2). Each person polled was asked to respond to four specific questions:

(1) What aspects of Martian history can be uniquely (or best) addressed by direct analysis of samples returned to Earth?

(2) What types and quantities of samples are needed to support the analyses related to (1)?

(3) What degrees of sample degradation can be tolerated without defeating the analysis goals? (Specify, if possible, upper limits for temperature, pressure, radiation, acceleration/ shock, etc.).

(4) What *in situ* measurements should be made on Mars to supplement or replace information that might be lost from degraded samples?

A total of 89 written responses were received, of which 79 contained useful information (Appendix B3), including a few from individuals who had also participated in the JSC (1974) writing project. Ten of the responses (not included here) were from individuals who politely acknowledged the poll but who declined to provide scientific input for various reasons, including lack of time or professed lack of expertise.

Shortly after the 1987 poll was initiated, NASA chartered a Science Working Group, chaired by M. H. Carr, to support a renewed study of the options for a class of unmanned Mars Rover/Sample Return (MRSR) missions. Accordingly, the writing project organized for this report was redirected to support the needs and schedules of the MRSR Science Working Group. Specifically, definition of high-level science goals was de-emphasized in this report and concentration was focussed on identifying detailed requirements for sample preservation. The functional synergism among this report-writing project, the MRSR Science Working Group, and previous studies is summarized in Fig. 1-1. Many of the preliminary parametric values for sample preservation derived for the present report were adopted by MRSR SWG (1989).

In addition, a scientific workshop on the topic of "Mars Sample Return Science" was convened by the Lunar and Planetary Institute in November 1987. As reflected in the workshop report (Drake et al., 1988), emphasis was placed on identifying sample requirements to address specific scientific issues. The workshop results were complementary to, but not identical with, the JSC poll of 1987 and there remained a need for a cogent summary of detailed sample-preservation requirements.

The body of this report represents integration of the text from JSC (1974) with new text that reflects results of the 1987 poll as well as other information compiled from scientific literature published after 1976. Several data figures were added to illustrate points that were either discussed without graphic aids or not addressed in JSC (1974). In general, the material from JSC (1974) was extensively edited and reorganized during merger with the new material.

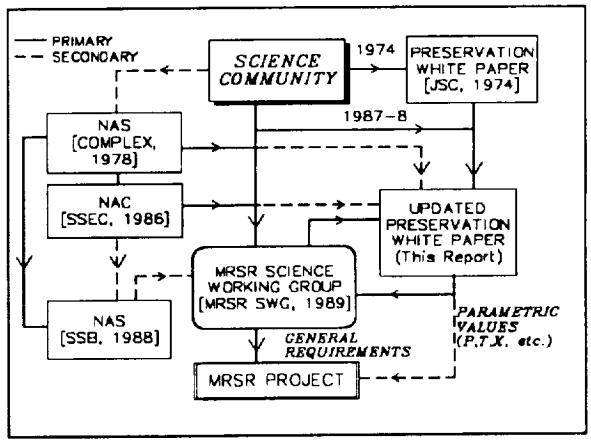


Figure 1-1.

Development of Mars science goals. Post-Viking goals are traceable to the National Academy of Sciences (NAS), through its Committee on Planetary Exploration (COMPLEX) and Space Science Board (SSB) and have been reiterated by the Solar System Exploration Committee (SSEC), of the NASA Advisory Council (NAC), and the Science Working Group of the Mars Rover/Sample Return (MRSR) Project. This report (updated preservation white paper) is focussed on details of sample preservation that have not been addressed by various other committees and working groups. Preliminary results of this work, however, were adopted by the MRSR SWG.

2. IMPORTANCE OF MARTIAN SAMPLES

2.1. Nature and Value of Information Contained in Samples

As recognized by the National Academy of Sciences in the light of *Viking* results, the principal goals of future exploration of Mars must be to establish the chemical, isotopic, and physical state of Martian material, the major surface-forming processes and their time scales and the past and present biological potential of Mars (COMPLEX, 1978; SSB, 1988). Those goals can be best met by direct analysis of carefully selected Martian samples under controlled laboratory conditions. *Mars Observer*, a Mars-orbiting spacecraft which is scheduled for launch in 1992, will provide global geochemical and meteorological maps of Mars but was never intended to serve as a substitute for a sample-return mission (SSEC, 1983, 1986).

The correspondence between sample type and information content is summarized in Table 2.1 and further explained in following sections.

The well-established scientific case for Mars sample return has been elaborately presented elsewhere (COMPLEX, 1978; SSB, 1988; Drake et al., 1988; Gooding et al., 1989). Rather than repeat those detailed arguments, the following sections review information sought in Martian samples as it relates to issues of sample preservation.

2.1.1. Planetary Composition

Major geochemical differences exist among the inner planets, as demonstrated by lunar-sample studies and by observed differences in planetary bulk densities and moments of inertia. Accordingly, the chemical characterization of any returned Martian sample is essential. Refinements in analytical techniques, resulting largely from lunar studies, have enabled experiments on very small samples (often < 50 mg). Thus, comprehensive information can be obtained from minimal material.

Table 2.1. Desirable types of Martian samples and their respective values in Mars exploration

Sample Type	Expected Information Content
Atmosphere	Elemental and isotopic compositions of gases expelled from the Martian mantle by planetary outgassing; tests for hypotheses regarding volatile-element inventory of Mars and possibility of ancient, dense atmospheres; solar wind interactions
Rock	Petrological variety of Martian crust and mantle; chemical processes that differentiated the planet; evidence for core formation; radiometric ages of local bedrock surfaces; absolute calibration of crater-count ages of surfaces; shock-implanted, trapped-gas samples of ancient atmosphere
Sediment	Composition of loose, fine-grained material derived by chemical and physical weathering of crustal rocks. Windblown sediments blanket large portions of the surface and strongly influence geochemical mapping from Mars orbit. Water-laid sediments might contain chemical and isotopic information about pre-biotic evolution.
Soil	Mineralogical, chemical, and isotopic records of local climate during soil development; records of climate change through time as depth-dependent cosmic radiation damage
Deep regolith	Chemical, stable-isotopic, and radiation environment of ancient Mars; sub-surface inventory of water and other volatile compounds; test for contemporaneous biogenic compounds or processes
Ice	Chemical and stable-isotopic records of water cycles through Mars history

Major elements comprising the bulk constituents of the terrestrial planets and meteorites include Si, Al, Ti, Fe, Mg, Ca, Na, K, and P. Important minor and trace elements include H, C, N, S, Cl, transition-group metals (Sc through Zn), lanthanide or rare-earth elements (La through Lu), Th, and U. Elemental analyses furnish the basic set of bulk compositional data that is essential to the performance and interpretation of nearly all other experiments done on Martian material. Elemental data also furnish an index of the extent of differentiation (fractional melting, crystallization and liquid immiscibility) of the Martian materials relative to primordial solar system matter. In addition, concentrations and distributions of the biogenic elements (H, C, N, O, P, S) are essential data in assessing the biological history or potential of Mars.

Geochemical studies would focus not only on elemental concentrations but also on speciation of elements as compounds. Without question, water would be the compound most highly sought among the samples. Information derived from water contents of samples is needed to test models for outgassing of the Martian interior and the extent and time of volcanic activity. It is also related to the processes and extent of weathering of primary Martian surface materials to their present conditions. The relationship between the water in a sample and the water content of the Martian atmosphere contains information on secular variations and Martian atmospheric composition. Measured water abundances will also play strongly in models for past or present Martian biology.

The most fundamental data needed for interpreting the gross composition of Mars are identities of minerals and rocks and their geochemical properties. Features that must be described and documented include sizes, shapes, and surface features of mineral particles and the nature of fluid inclusions that might have been trapped during growth of mineral grains. Mineralogical and petrological examination of Martian samples will be exhaustive studies involving every returned grain and fragment.

Primary igneous minerals (those formed by crystallization of magmas or lavas) have obvious relevance to such fundamental problems as the degree of planetary differentiation and the geologic history of the Martian surface and interior. Major problems to be addressed include volcanic activity and its depth of origin, sedimentary deposits and their transport mechanisms, and metamorphic products and the thermal and tectonic settings of their formation.

Secondary minerals (those formed by processes other than igneous crystallization) may result from surface-related mineral growth and phase changes during the chemical alteration processes that have undoubtedly occurred on the Martian surface through time. Another important aspect of the planet's history, the record of any living matter, might be preserved in fossil assemblages which could be encountered during studies of secondary-mineral associations. In interpreting petrologic data, care would be needed to identify mineralogical changes resulting from sample collection or storage during Earth return.

Mars should provide two sources of rock material: endogenous rocks ranging from igneous to sedimentary, and a small proportion of impact-produced rocks associated with minor amounts of exogenous material of meteoritic origin. The igneous rocks may have a wide range of compositions and may occur in states ranging from slowly cooled to quenched. The igneous rocks should consist predominantly of primary minerals of high temperature origin, namely, olivines, pyroxenes, feldspars, silica minerals, and possibly amphiboles and micas. Some of the rocks may have been locally subjected to fumarolic or hydrothermal alteration where secondary minerals such as oxides, sulfides, sulfates, halides, hydroxides, clay minerals, and zeolites may have developed.

Because Mars has an atmosphere containing both H_2O and CO_2, it is likely that hydrates and carbonates occur among the weathering products at the Martian surface. Weathering processes on Mars are likely to be both chemical and mechanical, including redistribution of original secondary minerals and generation of new secondary minerals.

In addition to single mineral (or phase) particles, four types of polyphase particles are expected: igneous rock fragments, sedimentary rock fragments, particles with coatings, and indurated soil clods of many particles. The mineral-mineral relations, both of an equilibrium and a reaction nature, that are preserved in these types of particles are the most important types of data for deducing Martian rock-forming processes.

2.1.2. Planetary Formation and Geologic Time Scale

Planetary gases, originally trapped in the solid materials that accreted to form Mars, may have been degassed from the Martian interior through volcanism and now reside in the Martian atmosphere. The Earth, Moon, Sun and various classes of meteorites all possess characteristic elemental and isotopic abundance patterns of the trapped noble gases which reflect differences in the volatile components of materials that formed these objects. Measurements of such gases in Martian atmosphere samples will give an indication of the general type of volatile material incorporated by Mars and will aid in the characterization of volatile species present in the early solar-planetary nebula.

Three-isotope oxygen compositions of individual samples will define the material pool from which Mars was formed. Studies of terrestrial samples, lunar samples, and meteorites have shown that differences in planetary source materials can be mapped on diagrams of $^{17}O/^{16}O$ vs. $^{18}O/^{16}O$. Although $^{18}O/^{16}O$ ratios can change as a function of temperature in chemical reactions (Section 2.1.3), the three-isotope signature is immutable with respect to geochemical processes and remains a fingerprint of the planet.

Information about the timing and duration of volcanic and metamorphic activity on Mars must come from the applications to samples of one, or preferably all, of the radioactive dating techniques involving the decay of a long-lived radioactive parent isotope (P) to a stable daughter product (D). The P/D pairs of isotopes which can be used for radiometric age dating are $^{235}U/^{207}Pb$, $^{238}U/^{206}Pb$, $^{232}Th/^{208}Pb$, $^{87}Rb/^{87}Sr$, $^{147}Sm/^{143}Nd$, $^{138}La/^{138}Ce$ and $^{40}K/^{40}Ar$. Radiometric ages would provide constraints on the thermal history of Mars, including formation, crustal differentiation, and the cataclysmic bombardment evidenced by the heavily cratered surface, as well as the history of volatiles and of the hydrologic cycle.

Absolute ages of lava flows are needed to calibrate geologic ages derived by interpretation of impact-crater densities on various Martian surface units. Impact-metamorphic ages of rocks ejected from major craters are needed to establish the timing of important surface-modifying events. Such age-dating of craters might be especially important for craters that appear to have formed in water- or ice-laden ground or that appear to closely pre-date or post-date formation of water-cut channels.

Additional information on the bulk structure and evolution of Mars could be obtained by analyzing fresh igneous rock samples for evidence of natural magnetization. Natural remanent magnetization would imply core formation on Mars in a manner analogous to that on Earth. Radiometric ages of different magnetic samples could help define the history of Mars' magnetic field.

2.1.3. Climate History

Evidence for atmospheric evolution and climate changes on Mars should be preserved as stable-isotopic signatures of volatile elements in a variety of weathered Martian materials.

Oxygen isotope analyses of coexisting minerals from a returned Mars sample should prove very useful in the following ways:

(a) estimating the temperatures of formation of the mineral assemblages, and

(b) determining whether or not the minerals in such rocks or in the bulk soil were formed in equilibrium, or whether they represent different stages of mineral formation.

Certain minerals are inherently much more susceptible to $^{18}O/^{16}O$ exchange that are others, and analyses of these may allow us to monitor secondary alteration processes that have affected the rocks or soil, such as exchange with H_2O or CO_2. This type of isotopic study is essential in interpreting the origin and history of H_2O and CO_2 in the rocks and the atmosphere of Mars.

Hydrogen isotope analyses ($^2H/^1H$ or D/H) of water vapor and hydrous minerals from Mars, in conjunction with $^{18}O/^{16}O$ analyses, should be very useful for the following reasons:

(a) they may enable us to evaluate the contribution of deep-seated igneous (juvenile?) H_2O to the surface rocks and to the atmosphere. If high-temperature igneous or metamorphic minerals such as micas or amphiboles are indeed found, comparison with the D/H ratios obtained on analogous samples from Earth will be valuable.

(b) D/H data can aid in defining the total amounts of H_2O and hydrogen loss from Mars, as well as the degree of isotopic fractionation that has accompanied such escape.

(c) D/H analyses are probably the only way to determine the overall contribution (if any) of deuterium-free solar wind hydrogen to the Martian atmosphere or surface.

(d) They may help define the extent of formation of cosmic-ray spallation deuterium in Martian surface minerals.

(e) They will be very useful in tracing the hydrologic cycle on Mars and in interpreting the temperatures and the mechanisms involved in hydration of Martian minerals and glasses.

Given knowledge of the isotopic compositions of both water and minerals, D/H and $^{18}O/^{16}O$ ratios can be used to deduce temperatures at which secondary minerals formed through water-mineral reactions. Accordingly, stable-isotopic analyses of soils or weathering rinds on rocks are the most promising pathways to deriving average temperatures of ancient climatic regimes.

Variations in atmospheric density through time, another parameter expected to serve as an index of climate change, could be sought as variations in cosmic-ray-produced nuclides in surface samples. Galactic cosmic rays penetrate the Martian atmosphere and, through high-energy nuclear reactions, produce radioactive species in the atmosphere and in the surface minerals. Among the more scientifically valuable, long-lived radionuclides are ^{14}C, ^{3}H, ^{10}Be, ^{22}Na, ^{26}Al, ^{39}Ar, ^{53}Mn, and ^{81}Kr. Measurement of specific activities of those radionuclides in surface samples can characterize the spatial and general nature of the cosmic-ray flux at the Martian surface. By comparing the activities of very long-lived nuclides (of the order of a million years) with those with mean lives of only a few years, major changes in the density of the Martian atmosphere might be detected.

2.1.4. Biological History

Studies of possible Martian biology are expected to emphasize identification and geochemical characterization of carbon-bearing materials. The first-order task will be to establish that the carbon compounds are native to Martian samples and not contaminants added by sampling activity. Next, work will focus on whether the carbon compounds appear to be residues of living organisms or abiotic molecular precursors of life forms.

Carbon isotope measurements ($^{13}C/^{12}C$ ratios) and sulfur isotope measurements ($^{34}S/^{32}S$ ratios) have the potential for helping decide whether organic compounds are of biological or abiotic origins. Appreciable $^{13}C/^{12}C$ and $^{34}S/^{32}S$ fractionations are produced by animal and plant metabolism on Earth and similar fractionations would be expected of extraterrestrial organisms. Such fractionations can be larger than fractionations produced by inorganic mineral reactions if the biological reactions are more effective at low temperatures. Nonetheless, use of stable-isotope ratios as fingerprints of biological processes would require detailed understanding of competing inorganic reaction pathways.

There is a strong possibility that carbonate minerals will be found on Mars. Measurement of $^{13}C/^{12}C$ ratios in such carbonates will aid markedly in deciphering their origins. Comparison with similar data for terrestrial and meteoritic materials will help in interpreting the entire carbon geochemical cycle on Mars. Isotopic comparison of Martian carbonates with terrestrial sedimentary carbonates, which are strongly influenced by biological processes, should be important in the search for isotopic signatures of possible Martian biological processes.

Because there is no evidence for life on Mars under current conditions (Section 2.2.1), it seems most appropriate to focus attention on the environmental conditions that either fostered or pre-empted evolution of life during the earliest period of Martian history. Accordingly, it is essential to study samples from localities where water was present during the first 10^9 years of Martian history and to compare them with samples where water might be available on present-day Mars.

Electron microscopy would be a major tool in life-science studies as a means for finding microfossils. In addition, direct cultures and biological assays would involve wet-chemical procedures. A major effort would probably involve characterization of the trace quantities of highly reactive compounds that produced false positive results in the *Viking* biology experiments (Section 2.2.1). Principal tools would include gas and ion chromatography, mass spectrometry, and nuclear magnetic resonance and electron-spin resonance spectrometry.

In all cases, searches for biogenic compounds or biological relics would be predicated upon access to samples free of degradation or contamination.

2.2. Relative Merits of Laboratory and *In Situ* Analyses

The mineral separations, chemical treatments, and instrumental sensitivities required for key geochronological, chemical and biological measurements make remotely-operated instruments impractical and point to Earth-based analyses on returned Martian samples as the best means for meeting the stated objectives (Table 2.2). Measurements made *in situ* should be used to supplement rather than replace analyses performed in laboratories on Earth.

In contrast with data collected by remotely operated instruments of limited capabilities, samples of Mars would never become obsolete. It has been abundantly demonstrated with meteorites and lunar rocks that planetary samples remain fertile sources of new information that are limited only by the sensitivity and power of the analytical tools that are applied to them. As analytical methods advance with time, new information can be harvested repeatedly from a single suite of samples. By modern standards, a kilogram of sample can literally support hundreds of man-years of meaningful research. Lunar rocks and soils, for example, are now being productively studied by a second generation of scientists using analytical methods and interpretational models that were unavailable and, in some cases, unanticipated in 1969 when the first lunar samples were collected (LAPST, 1985). Prospects for study of Martian samples are even greater because it is already clear that Mars is much more complex than either the Moon or the (presumed) asteroid parent bodies of most meteorites.

In addition, laboratory analyses of samples permit the greatest possible flexibility in responding to unanticipated properties. Unlike automated instruments of fixed design, laboratory analyses can use preliminary results to guide the re-design of experiments in order to achieve analyses of the highest possible precision and accuracy.

Automated experiments performed *in situ* serve best to analyze those properties that either exceed the scale of a returnable sample or that are unlikely to survive during return of the sample to Earth. Because of the latter consideration, sample preservation and *in situ* experimentation should be orchestrated in roles of mutual support. Practical limitations of sample preservation should exert a strong influence on selection and design of experiments to be performed on Mars.

Table 2.2. Roles of laboratory and in situ analyses of Martian materials

Measurement Objective	Preferred Approach: Laboratory (Earth)	Preferred Approach: In Situ (Mars)
Particle-size distribution (requires sieving or other physical separations)	X	
Particle morphology (requires evaporative coating and electron microscopy)	X	
Rock identification (requires thin sections)	X	
Mineral Identification (may require serial analyses by multiple techniques)	X	
Trace-element chemistry (requires neutron irradiation, gamma-ray counting and possibly wet chemistry)	X	
Radiometric age dating (requires mineral separations, wet-chemical processing and ultrasensitive mass spectrometry)	X	
Stable-isotopic analysis (requires extensive sample pre-treatment and ultrasensitive mass spectrometry)	X	
Abundance and composition of adsorbed gas (gases may desorb before Earth return)		X
Water content of regolith (metastable ice may evaporate; level of heterogeneity may exceed sample size)		X

2.2.1. Lessons from *Viking* Lander Experiments

Material properties of the Martian surface at the two *Viking* landing sites were summarized by Arvidson et al. (1989). Results from Lander 1 (Chryse Planitia, 22.482° N, 47.968° W) were generally consistent with those from Lander 2 (Utopia Planitia, 47.996° N, 225.736° W) . The Landers made no mineralogical analyses but performed several experiments that revealed some of the chemical properties of sediments and soils within about 25 cm of the surface at Lander 1 and within about 6 cm of the surface at Lander 2. No rocks were analyzed at either site.

All three biology experiments produced positive results for active surface chemistry among fine-grained materials at both landing sites but absence of detectable organic compounds (apparently less than a few parts per billion) argued strongly against life-based processes as the correct explanation (Klein, 1978). It is now clear that designing remotely operated experiments that will give unambiguous answers to critical life-science questions is exceedingly difficult, if not impossible. Consequently, the prevailing body of scientific thought now endorses detailed Earth-based studies of returned samples as the only effective means of assessing the biological prospects for Mars (COMPLEX, 1977).

The *Viking* results did reveal the presence in the near-surface sediments of chemical species that can fix carbon from gaseous CO_2 and that oxidize organic compounds such as Na-formate (Klein, 1978). In addition, at least one of the unidentified species evolves gaseous O_2 by reaction with water. The reactive species occur at the parts-per-million level of concentration (Appendix B4) and can be deactivated (presumably decomposed) by heat treatment. In addition, the fine-grained sediments contain significant quantities of adsorbed atmospheric gases (Oyama and Berdahl, 1977) and approximately 1-3% water by weight (Biemann et al., 1977; Anderson and Tice, 1979).

The bulk elemental compositions of surface sediments, which are probably highly oxidized, are rich in Fe, S, and Cl (Clark et al., 1982) and contain approximately 1-7% of a strongly magnetic mineral (Hargraves et al., 1977). The bulk-elemental compositions and biology results have been used to argue for a sediment composition dominated by smectite clay minerals (Banin and Margulies, 1983) -- materials that would require special handling during collection and Earth return.

2.2.2. Clues from "Martian" Meteorites

If shergottite, nakhlite, and chassignite (SNC) meteorites are rocks delivered to Earth by meteoroid impacts on Mars (e.g., Wood and Ashwal, 1981), why then do we need additional samples? The answers fall into two major categories. First, in the absence of independently documented samples from Mars, it is logically impossible to establish with certainty that the SNC meteorites are Martian rocks. Only one of the eight meteorites in question, namely the Elephant Moraine, Antarctica, A79001 shergottite (EETA79001), contains physical evidence that links it directly with Mars. Glassy inclusions in EETA79001 contain trapped gases that resemble the Martian atmosphere (as analyzed by *Viking* Landers) both in elemental and isotopic composition (Bogard and Johnson, 1983; Becker and Pepin, 1984) as well as relict grains rich in sulfur and chlorine that compositionally resemble the sediments at the *Viking* landing sites (Gooding and Muenow, 1986).

Second, even if SNC meteorites are genuine Martian rocks, they were randomly selected and by no means represent the suite of samples that is needed to answer first-order questions about Mars. For example, the SNC meteorites are all igneous rocks from unknown geologic terranes so that their radiometric ages provide few constraints on ages of surface-forming units on Mars. Furthermore, they carry little, if any, information about the mineralogy and volatile-element inventory of Martian soils and sediments or evidence about climate changes. Nonetheless, discovery of carbonate minerals (Gooding et al., 1988) and associated traces of possible organic matter (Wright et al., 1989) in shergottite EETA79001 argues strongly for existence of materials that would require careful preservation.

The strategies and methodologies appropriate for analyzing returned Martian samples can be illustrated by reference to work performed on SNC meteorites. For example, an intensive consortium study of the Shergotty, India meteorite, the type specimen for shergottites, was performed on less than 25 g of material but produced data on trace-element compositions, radiometric ages, cosmogenic nuclide abundances, noble-gas abundances, stable-isotopic compositions, and general petrology (Laul, 1986 and papers in same issue).

3. SAMPLE PRESERVATION ISSUES

3.1. Essential Considerations

The value of analyses to be made on returned Martian samples could be seriously weakened if the samples are not properly preserved from the time they are collected until the time they are received in laboratories on Earth. In essence, sample degradation equates to loss of information. Although susceptibility to degradation can be expected to vary as a function of sample type and measurement category, the parameters that are at the heart of the sample-preservation issue are defined in Table 3.1.

The information equation pertaining to material analyses of Martian samples is

$$I_S = I_R + I_M \qquad [3\text{-}1]$$

where the I_S denotes information contained in pristine (unaltered) samples on Mars, I_R represents information retained in samples returned to Earth, and I_M is the difference in information content between pristine and returned samples that must be recovered through *in situ* analyses on Mars.

Ideally, each sample collected on Mars would be returned to Earth under conditions that were identical to those of the environment from which it was collected so that $I_R/I_S = 1$. Complete fidelity of preservation would assure that sample properties measured on Earth were truly representative of the natural environments on Mars. No single set of preservation conditions can be specified, though, because no single set of environmental conditions applies to all places on Mars. Mars is a dynamic planet with temperatures and atmospheric pressures that vary with latitude, longitude, and elevation, as well as with season. In addition, at any one landing site, samples collected from depth will have experienced different temperatures, pressures, and radiation environments than those at the immediate surface.

Table 3.1. Preservation hazards for Martian samples

Hazard	Definition
Contamination	Addition of extraneous solid, liquid, or gaseous matter that would complicate, compromise, or preclude measurement of natural chemical or isotopic compositions of a sample
Temperature	Increase of temperature that would foster decrepitation of solids, evaporation or desorption of volatile elements or compounds, or chemical or isotope-exchange reactions among components in a sample
Pressure	Increase or decrease in confining (head space) gas pressure that would lead to desorption or surface displacement of volatile elements or compounds, or solid-gas reactions
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 natural radiation on Mars
Magnetic Fields	Exposure to magnetic lines of force that would obscure natural remanent magnetism in a sample or introduce remanent artifacts
Acceleration and Shock	Mechanical disturbances that would alter or obscure natural physical attributes of a sample, including porosity, grain shapes, particle-size distributions, degree of induration, or layered sequences

Exact duplication of Martian conditions after sample collection may be either impossible or impractical for various reasons. Accordingly, the problem of sample preservation is best approached by identifying the probable scale of information loss from samples as a function of the deviations of preservation conditions from natural Martian conditions. In essence, the objective is to understand how the I_R/I_S ratio changes with collection and preservation conditions. Preferred conditions for preservation will be those that yield I_R/I_S ratios close to unity.

Threats to the pristine conditions of samples fall into two categories:

- Incidental degradation during collection and return
- Deliberate degradation by sterilization.

Incidental degradation covers all types of alteration caused by sampling or mission operations whereas deliberate alteration would be attributable to pre-planned, precautionary biological sterilization of samples.

Acquisition of samples on Mars would pose risks principally in the areas of material contamination and thermal degradation. Debris abraded or shed from sampling tools, containers, or other items of hardware must be minimized and restricted to innocuous materials. Likewise, mechanical energy transferred from tools to samples during collection operations must be regulated to prevent excessive heating of the samples.

The conscious decision to biologically sterilize returned Martian samples to preclude contamination of Earth by alien life forms would profoundly affect the design of the sample-return mission. Biological sterilization of materials is normally accomplished by heat treatment, chemical treatment, or application of lethal doses of ionizing radiation. All three methods would be offensive in different ways to one or more categories of analyses that would be planned for returned Martian samples.

The following sections discuss in detail each of the issues called out in Table 3.1. For documentation, reference is made to published literature as well as to letters received from individual scientists and provided in Appendices A3 and B3. Summaries and recommendations are provided in Chapter 4.

3.2. Contamination

The chemical, mineralogical, isotopic, and biological properties of Martian samples are sought as keys to the similarities and differences between Mars and Earth. Accordingly, Earth materials must not be allowed to contaminate the Martian samples in ways that would confuse or mislead research efforts. In addition, steps should be taken to minimize cross contamination among different Martian samples so that natural variations will not be obscured.

The ultrasensitive analytical methods to be applied to Martian samples will seek precise determination of elemental concentrations and variations among elemental and isotopic ratios. Samples will be sub-divided into their component parts and analyzed as the smallest practical aliquots. Consequently, even minute quantities of extraneous contaminants could have profound effects on the measured properties.

Table 3.2 gives the minimum set of elements that will be analyzed in Martian samples. Regardless of whether shergottite meteorites are Martian rocks (Chapter 2), the data in Table 3.2 illustrate the order-of-magnitude concentrations expected for various elements in Martian geologic samples. Contamination would occur if extraneous matter introduced an element into a sample at a concentration that approached or exceeded the natural concentration of that element in the pristine sample. Clearly, Martian samples will be extremely sensitive to contamination for elements that occur naturally at the parts-per-million or parts-per-billion levels. In contrast, a few ppm contamination by iron or aluminum would be more tolerable because Fe and Al occur naturally at concentrations of several weight percent.

For example, indium-silver metal alloy was employed as a seal material in boxes used to containerize lunar samples on the Moon (Allton, 1989). Unfortunately, later attempts to measure the intrinsic concentrations of volatile siderophile elements (at ppb concentrations) in some of the lunar samples fell into question because of possible In contamination.

Curation of Martian samples on Earth will probably utilize procedures for non-contamination that were developed for lunar samples and meteorites. However, those efforts can never reverse contamination introduced during sample collection and packaging on Mars. Therefore, procedures used on Mars should be designed for minimal contamination of the samples.

Table 3.2. Elemental compositions of the Shergotty meteorite and surface sediments at Chryse Planitia, Mars (Viking Lander 1) in percent (%), parts per million (ppm), and parts per billion (ppb) by weight

Atomic No.		Shergotty[a]	Mars[b]
2	He	0.19-0.21 ppb[c]	
3	Li	3.3-5.6 ppm	
6	C	430-620 ppm; 44-210 ppm[d]	
7	N	132-794 ppb[e]	
8	O	(40.7-43.6%)[h]	
9	F	41-42 ppm	
10	Ne	0.015-0.017 ppb[c]	
11	Na	0.95-1.09 %	
12	Mg	5.40-5.7 %	3.6 %
13	Al	3.60-4.02 %	3.9 %
14	Si	23.1-24.0 %	21 %
15	P	0.24-0.35 %	
16	S	0.13-0.16 %	2.7 %
17	Cl	108 ppm	0.8 %
18	Ar	3.3-9.9 ppb[c]	
19	K	0.12-0.16 %	< 0.4 %
20	Ca	6.80-7.15 %	4.1 %
21	Sc	52-59 ppm	
22	Ti	0.4-0.5 %	0.37 %
23	V	260-265 ppm	
24	Cr	0.12-0.16 %	
25	Mn	0.40-0.42 %	
26	Fe	15.1-15.6 %	12.2 %
27	Co	37.2-45 ppm	
28	Ni	56-88 ppm	
29	Cu	26-54 ppm	
30	Zn	62-83 ppm	
31	Ga	15-17.6 ppm	
33	As	0.025 ppm	
34	Se	0.29-0.47 ppm	
35	Br	0.60-0.89 ppm	
37	Rb	4.5-7.27 ppm	< 30 ppm[g]
38	Sr	45-51 ppm	60 ppm[g]
39	Y	–	70 ppm[g]
40	Zr	50-67 ppm	< 30 ppm[g]
42	Mo	0.37 ppm	
47	Ag	6.8-110 ppb	
48	Cd	0.014-0.34 ppm	
49	In	0.023-0.026 ppm	
51	Sb	<5 to 20 ppb	
52	Te	3.2-19 ppb	
53	I	0.036-0.050 ppm	
55	Cs	0.36-0.48 ppm	

– continued –

Table 3.2. (continued)

Atomic No.		Shergotty[a]	Mars[b]
56	Ba	27-40 ppm	
57	La	1.50-2.44 ppm	
58	Ce	3.51-6.4 ppm	
59	Pr	0.70-0.88 ppm	
60	Nd	2.60-4.7 ppm	
62	Sm	1.01-1.89 ppm	
63	Eu	0.43-0.65 ppm	
64	Gd	1.64-2.8 ppm	
65	Tb	0.41-0.52 ppm	
66	Dy	2.16-4.8 ppm	
67	Ho	0.56-0.86 ppm	
69	Tm	0.30-0.38 ppm	
70	Yb	1.19-1.80 ppm	
71	Lu	0.18-0.26 ppm	
72	Hf	1.50-2.23 ppm	
73	Ta	0.18-0.29 ppm	
74	W	0.4-0.5 ppm	
77	Ir	< 5 ppb	
79	Au	0.81-16 ppb	
81	Tl	0.15-14.0 ppb	
82	Pb	94 ppb[f]	
83	Bi	0.47-2.4 ppb	
90	Th	0.25-0.39 ppm	
92	U	0.055-0.17 ppm	

[a] Laul et al. (1986), except where noted

[b] average "deep" sample; Clark et al. (1982)

[c] all isotopes; Becker and Pepin (1986)

[d] excluding C extracted at < 600 C; Wright et al. (1986)

[e] excluding gas extracted at < 600 C; Becker and Pepin (1986)

[f] sample 3A; Chen and Wasserburg (1986)

[g] Clark et al. (1976)

[h] by difference from sum of major elements

Apollo designs were required to avoid Pb, U, Th, Li, Be, B, K, Rb, Sr, noble gases (He, Ne, Ar, Kr, Xe), rare earths (La-Lu), microorganisms, and organic compounds; those same contaminants (including In and other trace siderophile elements) should be avoided among Mars sample tools and containers. Acceptable *Apollo* materials included Teflon, aluminum, and certain stainless steel alloys (Allton, 1989). Mars tools and containers should be fabricated of materials that are chemically nonreactive and that can be readily recognized as artificial if unavoidably introduced into a sample. Ideally, each tool/container material should be homogeneous and possess distinctive chemical and isotopic signatures that would permit its reliable "subtraction" from an analytical data set.

For geologic samples, contamination by a given chemical element should be tolerable if it does not exceed a small fraction of the concentration of the element as listed in Table 3.2. For example, the *Viking* Landers found no fixed carbon in near-surface Martian sediments at the detection limits of a few ppm. Except for traces of carbonate minerals, the total carbon contents of shergottite meteorites are only a few hundred ppm, most of which might represent terrestrial contamination. In fact, if the carbon extracted from the samples at < 873 K is dismissed as contamination, the concentrations of indigenous, non-carbonate carbon in shergottites might be as low as 44 ppm (Wright et al., 1986). Accordingly, any carbon contamination of Martian samples should be assiduously avoided and limited to << 44 ppm.

Given the apparently high oxidizing potential of Martian soils (Section 2.2.1; Appendix B4), a property not displayed by lunar soils, the materials-compatibility problem will require further study. Materials that might be stable with respect to reaction under lunar conditions might exhibit corrosion under Martian conditions.

Because the Martian atmosphere is only about 1% as dense as Earth's atmosphere and very different in elemental composition (Table 3.3), atmospheric samples collected at Martian ambient pressure could be highly susceptible to contamination. Any off-gassing by spacecraft systems or any subsequent leakage of Earth atmosphere into the sample containers would seriously degrade the samples. Container leak rates estimated by Bogard et al. (1979) are summarized in Table 3.4. For the conditions postulated, it was found that a Mars atmospheric sample at Mars-ambient pressure could become contaminated with Earth atmosphere at the level of 0.1% within 10 days for most gases except CO_2. Because CO_2 occurs at such a low concentration in Earth's atmosphere, the partial pressure of CO_2 would be greater inside the Mars sample container than outside it. Consequently, there would be only minor contamination by inward diffusion of CO_2. For all other gases, however, partial pressures inside would be less than those outside and the net tendency for inward leakage of gas would represent a significant contamination threat.

Cross-contamination between samples should also be minimized. Although the compositional variations across the Martian surface remain to be determined, at least two fundamentally different types of samples can be postulated. High sulfur and chlorine concentrations in the soils/sediments (Table 3.2) suggest salt minerals that might be rare or absent in the rocks. The oxidation states and mineralogical compositions of rocks and soils/sediments are also expected to differ significantly. Furthermore, if SNC meteorites are Martian rocks (Chapter 2), then at least three different rock types exist on Mars. In any case, neglect of cross-contamination issues could unnecessarily complicate laboratory analyses of the samples and, in the worst case, prevent recognition of subtle differences among samples.

Little or nothing can be done about contamination of rocks by fine-grained soils or sediments with which they are naturally associated. It is more important that care be taken not to mix different types of rocks or different types of soils/sediments.

Table 3.3. Near-surface atmospheric compositions (volume basis) on Mars (Owen et al., 1977) and Earth.

	Mars	Earth
CO_2	95.3 %	0.03 %
N_2	2.7 %	78.1 %
Ar	1.6 %	0.93 %
O_2	0.13 %	21.0 %
CO	0.07 %	< 1 ppm
H_2O	0.03[a] %	0.8[b] %
O_3	0.03 ppm	< 0.1 ppm
Ne	2.5 ppm	1800 ppm
Kr	0.3 ppm	100 ppm
Xe	0.08 ppm	8 ppm

[a] Typical value; known to vary
[b] 50% relative humidity at 298 K

Table 3.4. 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/sec for 10 days (Bogard et al., 1979).

CO_2	Negligible
N_2	7×10^{-4} cm^3 STP
Ar	9×10^{-6}
O_2	2×10^{-4}
Ne	2×10^{-8}
Xe	8×10^{-11}

3.3. Temperature

Possible effects of temperature rise on Martian material can be separated into two categories: *decrepitation* and *reaction*. *Decrepitation* occurs when solid phases containing volatile elements decompose with evolution of gas. In the broad sense, decrepitation can also include irreversible desorption of gases from solid surfaces. *Chemical reactions* involve destruction of original phases and possible creation of new phases whereas *isotope-exchange reactions* involve redistribution of isotopes of a given element among various chemical phases.

Temperatures at the upper skin of the Martian surface vary greatly with both latitude and season (Fig. 3-1) and with time of day (Fig. 3-2). Below the surface, however, temperature variations are increasingly moderated with depth so that, even during daytime in summer, samples taken from depths greater than 25 cm will be 30-50 K colder than at the upper surface (Fig. 3-3). Therefore, at a given sampling locality on Mars, the appropriate preservation temperature for a sample taken from depth will generally be tens of degrees lower than for a sample taken from the free surface.

Samples from areas poleward of 80° latitude would be accustomed to < 200 K at all depths (Fig. 3-1). Accordingly, it is samples taken from polar areas or from depth at any latitude that could be most sensitive to uncontrolled temperature rise.

Many different changes in Martian samples can be expected as temperatures rise from Mars ambient values (Fig. 3-4). Although the melting point for water ice (273 K) is a well-known milestone, processes unfavorable to sample preservation can also occur at sub-freezing temperatures. Above the melting point, major changes are expected and, above the biological sterilization interval (about 420-430 K), changes would be profound. Detailed accounts of the possible temperature-related sample degradations are given in the following sections.

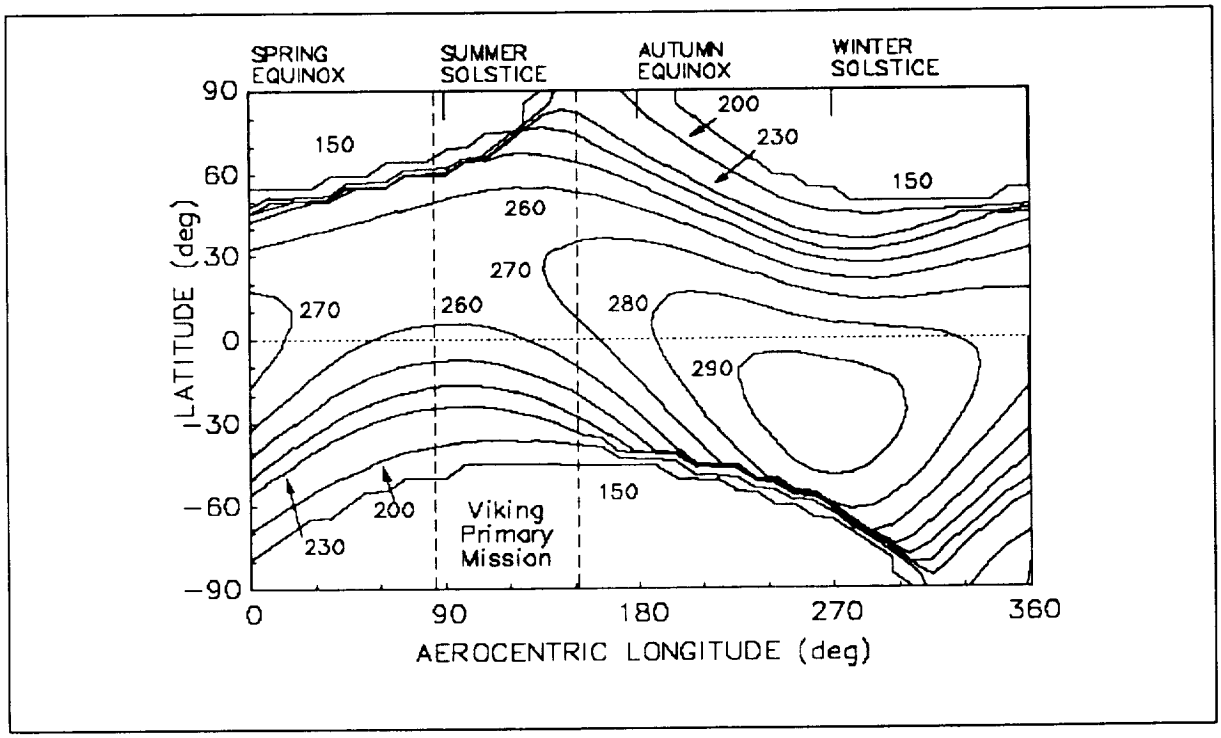


Figure 3-1.

Maximum surface skin temperatures (degrees Kelvin) predicted for Mars as functions of latitude and season (modified from Kieffer et al., 1977). All seasonal milestones refer to the northern hemisphere. Relative to the surface temperatures shown here, sub-surface temperatures should be colder at all locations (see Fig. 3-3). Also, because of differential heating effects, the surface skin temperature will tend to be warmer than that of the near-surface atmosphere at the same location (compare with Fig. 3-2). Viking Landers 1 and 2 sampled latitudes 22° N and 48° N, respectively, with the primary missions occurring during northern summer.

3.3.1. Sub-Freezing (< 273 K)

Samples heated to 200 K should see any cubic water ice converted to ordinary (hexagonal) water ice, sublimation of any CO_2 ice, and incipient desorption of permanent gases such as N_2, O_2, and Ar. Heating to 230 K would substantially desorb gaseous CO_2 (see Section 3.4) and begin liquifaction of any Ca,Mg-chloride brines (Brass, 1980).

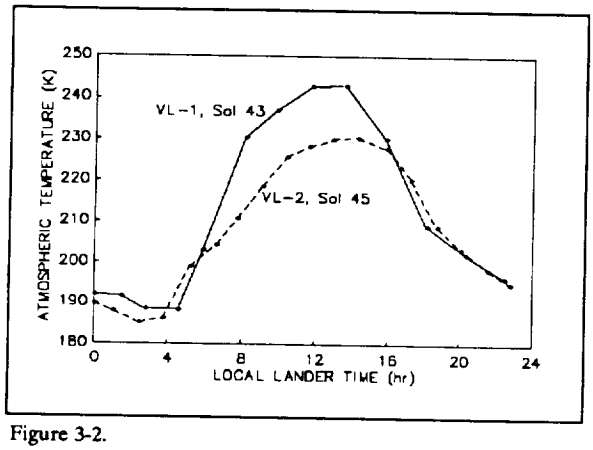


Figure 3-2.

Typical diurnal temperature variations in the near-surface atmosphere at the Viking Lander 1 and 2 sites (modified from Hess et al., 1977). Local noon is at 12 hr and midnight is at 0 and 24 hr.

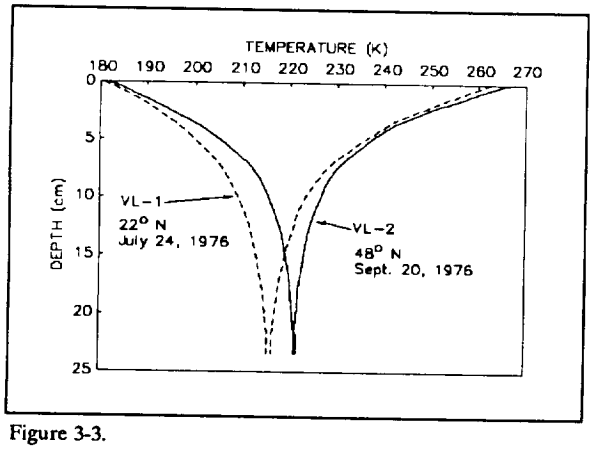


Figure 3-3.

Sub-surface temperature profiles modelled for Viking Lander sites (after Kieffer, 1976). For each landing site, the two-limbed envelope shows the temperature limits expected during one day-night cycle. At depths > 25 cm, though, samples would have probably experienced temperatures no higher than about 220 K.

Heating to 235 K could foster development of liquid-like capillary water on clay-mineral substrates. Survival of unfrozen water to such low temperatures has been documented for montmorillonite-water systems by numerous laboratory experiments (e.g., Anderson and Morgenstern, 1973). Even though the capillary water might not be truly liquid in the strict, thermodynamic sense, its mobility might be sufficient to foster ionic migration and, therefore, aqueous geochemical processes in the ostensibly frozen sample. Both chemical and isotope-exchange reactions might ensue.

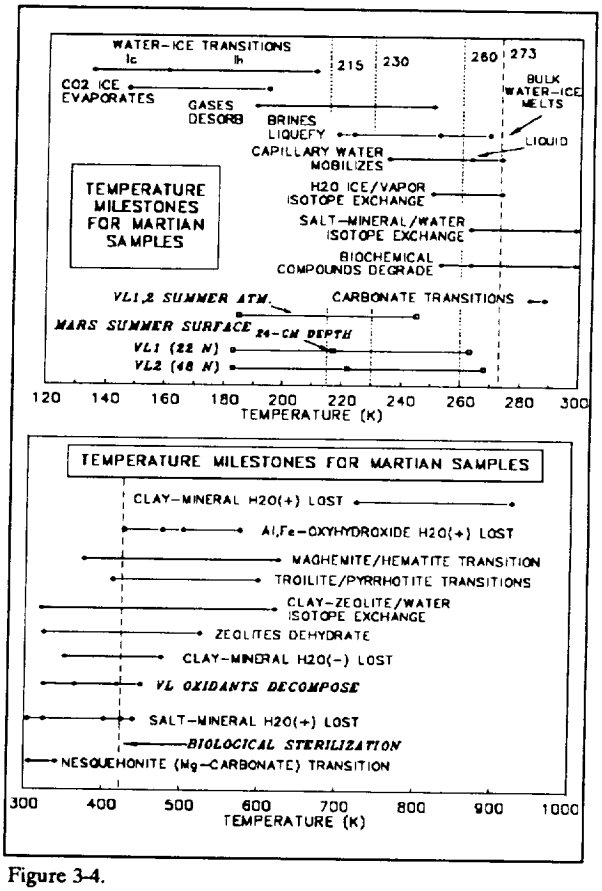


Figure 3-4.

Potential degradation of Martian samples during warming. "VL" temperature ranges are those measured at the Viking Lander sites during northern summer. The 24-cm temperature corresponds to Fig. 3-3. Note that liquid-like capillary water can form at temperatures as low as 235 K and that thermodynamically liquid water can form at $\geq$ 263 K. The 423 K "sterilization" milestone is only a typical temperature within the dry-gas sterilization range of 390-590 K.

Heating to 263 K could form true liquid water despite the fact that pure bulk ice exhibits equilibrium melting at 273 K. Extensive studies of the physics of soil mixed with geologic materials have shown that incipient melting of ice disseminated in a fine-grained, porous medium can occur at tens of degrees Kelvin below the 273 K milestone. Above 263 K, this unfrozen water occurs as films that are many molecular layers thick (McGaw and Tice, 1976). Therefore, it appears that water-based chemistry could proceed in any ostensibly frozen soil at temperatures $\geq$ 263 K.

Professor John Oro (personal communication, 1987) suggested that degradation of certain highly sensitive biochemical compounds begins at temperatures of 253-263 K. Franks (1982) reviewed evidence for measurable reaction rates of enzymes at temperatures as low as 250 K. Therefore, concerns for biological materials would seem to require preservation at sub-freezing temperatures.

Stable-isotope exchange reactions can also proceed at sub-freezing temperatures. Notable examples include oxygen exchange between calcite and water and deuterium exchange between liquid water and water vapor (Friedman and O'Neil, 1977). For salt minerals at sub-freezing temperatures, oxygen exchange might be sluggish but hydrogen exchange might be significant over periods of months (Kyser, 1987).

Because water-based chemical or isotopic changes would comprise some of the most rapid and serious sample degradations, preservation temperatures must address the issue of unfrozen water. For deep Martian samples that might never have experienced temperatures > 230 K, relaxation of preservation temperature to 273 K might invite a host of undesirable and irreversible chemical and isotopic changes.

3.3.2. Cool Thawing (273-300 K)

Above 273 K, any ice would be converted to liquid water and both chemical and isotope-exchange reactions would greatly accelerate. Both hydrogen and oxygen exchange reactions would be significant on the time scale of months for CO_2-H_2O gas systems and for some hydrated salt minerals; carbon isotope exchange reactions would be significant for CO_2-CO_3^{2-} in aqueous solutions (Kyser, 1987).

The trace oxygen-rich compound(s) discovered by the *Viking* Lander Gas Exchange (GEX) experiments (Oyama and Berdahl, 1977) would irreversibly decompose by reaction with available water to liberate oxygen gas.

At 280-290 K, any vaterite (a low-temperature polymorph of $CaCO_3$) would irreversibly invert to calcite. Accordingly, possibly important details about carbonate formation on Mars would be irretrievably lost.

3.3.3. Sub-Sterilization (300-400 K)

Several different processes of irreversible change would begin above 300 K. First, any hydromagnesite (a hydrous Mg-carbonate) would irreversibly invert to nesquehonite, thereby destroying important details about carbonate formation on Mars. Next, various hydrated minerals, including sulfates, clay minerals, and zeolites, would begin to lose water. Some of the water loss would be reversible because later humidification could partly or wholly restore the lost water. The stable-isotopic composition of the original water, however, would be information that could not be reconstructed.

As shown by the *Viking* Lander biology experiments (Klein, 1978), the trace quantities of oxidants in Martian sediments decline in reactivity upon heating over the 320-400 K range. Available evidence suggests that more than one oxidant exists and that the loss of reactivity is irreversible and results from decomposition of the oxidants (Appendix B4). Consequently, any hope of identifying the oxidants in returned Martian samples would be lost if the samples were heated above about 320 K.

In this temperature interval, hydrogen and oxygen isotope exchange reactions, between solids and water vapor or liquid water, would occur readily for most non-silicate minerals and carbon isotope exchange reactions involving carbonates would become more rapid (Kyser, 1987).

3.3.4. Sterilization and Decrepitation (> 400 K)

Above the temperature generally recognized as adequate for biological sterilization (423 K), many profound chemical and mineralogical changes would occur in samples. The treatment given below will not address biological concerns which, by definition, are abdicated by electing sterilization. Instead, geochemical consequences of sterilization will be emphasized. The most important mineralogical effects of decrepitation would be loss of H_2O from hydrous silicates, oxides, and salts

and loss of CO_2 from carbonates. Devolatilization is most pronounced for heating under vacuum, where volatiles are removed continuously. Hydrated silicates most susceptible to this type of degradation are clay minerals and zeolites; those least susceptible are amphiboles and micas.

Critical temperatures and products of sterilization-induced mineral reactions can be expected to vary with the total pressure and gas composition (especially partial pressure of water vapor, P_{H2O}) in contact with the sample. Dry sterilization (i.e., performed without steam) is normally accomplished by heat soaking at 390-590 K for a few hours (time varies inversely with temperature); two hours at 423 K would be typical. Transition temperatures expected under low-pressure, dry conditions are those depicted over the 300-1000 K range in Fig. 3-4. Other details can be found in letters by Hower, Fournier, Anderson, Papike, and by Bence, Smith, Baily, Skinner, and Sato (Appendix A3).

For many different Mars-analogous minerals, Kotra et al. (1982) experimentally verified the expected devolatilization reactions (Table 3.5). Threshold temperatures for devolatilization vary with heating rate, atmospheric pressure, and gas composition. For a given heating rate, devolatilization began at lower temperatures under vacuum, relative to one-atmosphere experiments. For a constant heating rate and pressure, decarbonation began at substantially lower temperatures under N_2 than under CO_2. Accordingly, decrepitation of carbonates during sterilization could be retarded by high pressures of CO_2 but carbon and oxygen stable-isotopic exchange reactions between the carbonates and the CO_2 might be extensive.

The effects of internal reaction are more difficult to access and depend initially on the levels of P_{H2O} reached during sterilization. These levels will be highest if heating occurs in a sealed container and either water is added or a large amount of hydrous material is originally present in the sample. In general, sterilization under high P_{H2O} should skew the onset of potential reactions to lower temperatures and increase their rates. Feldspars would probably suffer surface alteration to mica-like phases whereas olivines, pyroxenes, and amphiboles would probably develop surface layers of chlorite-like phases. At temperatures > 373 K, oxygen isotope exchange reactions would occur at significant rates for clay minerals and related silicates (O'Neil, 1987).

Table 3.5. Volatile-release temperatures of geologic materials heated 10 K/min under 1-atm dry N_2 (adapted from Kotra et al., 1982)

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

Perhaps the most delicate property to be affected by sterilization is the extent of oxidation. Determination of the intrinsic oxygen fugacity of igneous minerals would be extremely important to define the role of oxygen in Martian volcanic processes and the origin of the Martian atmosphere. However, as Sato and Wones point out in their letters (Appendix A3), the preservation of the oxidation state of the returned sample depends critically on any sterilization. Heating in vacuum entails loss of hydrogen and a change in oxidation state. If graphite or other carbon-bearing material (including carbonate minerals) is present, heating may produce chemical reduction of silicates and oxides. To overcome the loss of hydrogen, the sample could be sealed within a sample chamber lined with ultrahigh-purity gold.

Rates of thermal decrepitation should be controlled by formation of devolatilized surface layers which slow the outward diffusion of additional volatile compounds through the surface. Careful, well-conceived experiments are still needed to quantify the kinetics of such processes.

In addition to the mineral decrepitations depicted in Fig. 3-4 and discussed above, samples subjected to thermal sterilization might also suffer destruction of any fluid inclusions, resetting of mineral geothermometers, and annealing of radiation damage.

Behavior of fluid inclusions (usually water-based) in minerals during heating and refrigeration can yield unique information concerning the physical and chemical conditions under which the minerals formed. Heat treatment at < 550 K will have relatively little effect except for incompetent and cleavable minerals, such as carbonates and nitrates, which are expected to decrepitate at significantly lower temperatures in response to internal pressures developed in the inclusions (Roedder letter, Appendix A3).

Mineralogical geothermometry uses crystallographic states of certain minerals, or elemental distributions between certain mineral pairs, to deduce the temperature at which the minerals formed. Heat sterilization will negate opportunities for thermometry if it modifies crystal structures or changes elemental distributions in the thermometer minerals. Temperatures of formation based on mineral structure or composition will not be compromised if the assemblage does not change below the sterilization temperature, provided that the threshold for change is not markedly affected by the nature of the vapor phase in equilibrium with the assemblage. The thermometer minerals most resistant to heat modification are those with low diffusivity, high hardness, and high melting points. Therefore, mineral assemblages in igneous or metamorphic rocks are likely to survive, provided that the vapor phase is not greatly different from that present during the history of the assemblage on Mars. Those minerals most amenable to geothermometric methods are silicates, transition element oxides, sulfides with high melting points, and anhydrous carbonates. Those that would not provide geothermometric information after sterilization are hydrated minerals, oxysalts, and sulfides with low melting points.

The extent of heat sterilization of a returned sample would markedly affect the amount of information that could be gained from cosmic-ray-induced or fission-induced nuclear particle tracks or from radiation-induced thermoluminescence (TL) (Section 3.5). The ease of annealing of tracks within a mineral is proportional to rates of self-diffusion of elements within the mineral. As a general rule, the harder a mineral and the higher its decomposition temperature, the greater its resistance to track annealing. Heating would also free trapped electrons, thereby erasing natural TL.

A summary of track annealing temperatures is listed in Table 3.6. Large annealing effects should not be noticed in most minerals below 423 K but very noticeable effects should be observable after one day at 623 K (R. Walker and C. Naeser letters, Appendix A3). The latter treatment would degrade the information to be obtained but would not totally erase it, especially in minerals from basaltic and high-grade metamorphic rocks.

Lower temperatures maintained for longer times would be equivalent to higher temperatures maintained for shorter times. For example, apatite held at 498 K for 10^4 min. (6.9 days) would also be partly annealed (Naeser and Faul, 1969). Presence of water vapor would markedly increase the track annealing rates. Further work is required on the kinetics of track annealing, especially in clay minerals or other minerals of low-temperature origin.

In the context of natural TL, the lower maximum surface temperatures on Mars, relative to the Moon, suggests that a much greater portion of trapped electrons should remain stored in Martian samples. TL could be used on a Martian deep-core sample for determining natural radiation-shielding depths in the material and potentially for derivation of planetary heat flow (Arvidson letter, Appendix A3). TL would be adversely affected by any heat treatment > 373 K.

Table 3.6. Temperatures (K) for which one-hour heat treatment anneals nuclear particle tracks

373	Basaltic glass (MacDougall, 1973)
	Lunar impact glass (Fleischer et al., 1971)
473	Feldspar glass (Fleischer et al., 1968)
	Basaltic glass (Fleischer et al., 1969)
573	Apatite (Naeser and Faul, 1969)
	Lunar impact glass (Fleischer and Hart, 1973)
673	Phlogopite (Maurette et al., 1964)
	Muscovite (Fleischer et al., 1964)
773	Pyroxene (pigeonite) (Fleischer et al., 1965a)
	Olivine (Fleischer et al., 1965b)
873	Sphene (Naeser and Faul, 1969)
	Diopside (P.B. Price, Appendix A3)
	Epidote (Naeser et al., 1970)
	Garnet (P.B. Price, Appendix A3)
973	Zircon (Fleischer et al., 1965b)
	Feldspar (Fleischer et al., 1965a)

3.4. Pressure

At a constant temperature, increase in confining pressure associated with Martian samples can cause adsorption of gases whereas a pressure decrease can cause gas desorption. Either process will almost certainly alter the character of the sample relative to its state when collected. Sufficiently high increases in pressure can drive chemical or isotope-exchange reactions that might irreversibly change the natural character of the sample. Accordingly, preservation of Martian samples must address both the total pressure and composition of head-space gases in contact with the samples.

Atmospheric pressure at the Martian surface varies with both elevation and season. At low elevations such as the two *Viking* landing sites, the seasonal range lies between about 6.5 mb and 10 mb (Fig. 3-5). The chemical composition of the near-surface Martian atmosphere is mostly CO_2 with traces of N_2, Ar, O_2, and H_2O (Table 3.3).

The major source of pressure rise would probably be desorption of gases during warming of a Martian sample in a sealed container. Laboratory experiments have shown that, under simulated Martian conditions, large quantities of gaseous CO_2 can be adsorbed on reasonable geologic analogs of Mars surface materials (Fig 3-6). The same materials can also adsorb substantial

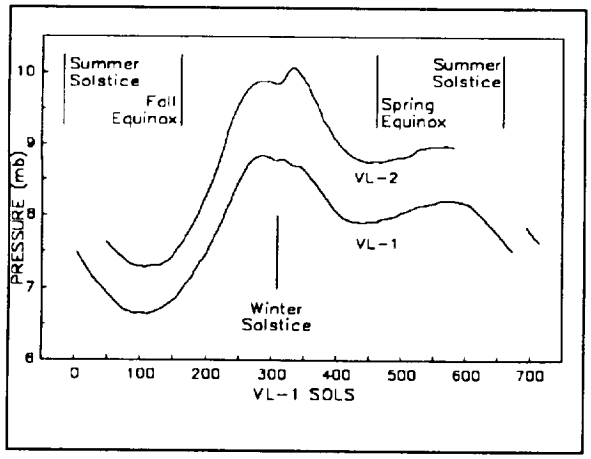


Figure 3-5.

Seasonal variation of atmospheric pressure at the Viking landing sites (modified from Hess et al., 1980). The gap in the VL-2 curve reflects absence of available data from the Lander. Other smaller gaps have been artificially smoothed out in both the VL-1 and VL-2 curves.

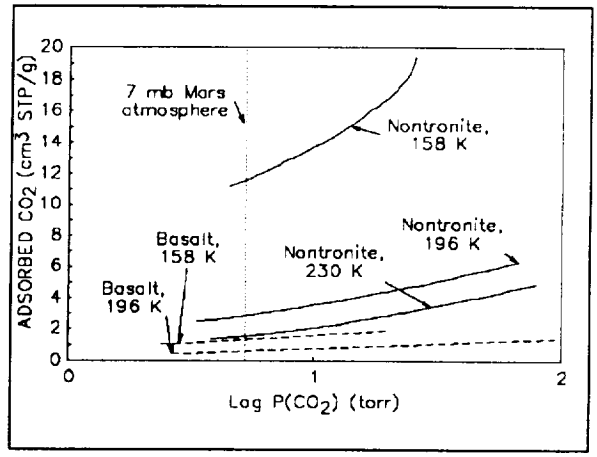


Figure 3-6.

CO_2 gas adsorption on powdered samples of Mars-analogous geologic materials as a function of temperature (modified from Fanale and Cannon, 1979). The vertical dotted line represents a typical partial pressure of CO_2 in the Mars atmosphere.

water vapor (Fanale and Cannon, 1974) as well as noble gases (Fanale and Cannon, 1978). The general trend, as shown in Fig. 3-6, is for increasing adsorbed gas load with decreasing temperature. Accordingly, fine-grained soils and sediments on Mars are expected to contain substantial quantities of adsorbed gases prior to collection.

Two useful end-member materials for gas adsorption/desorption studies are powdered basalt and powdered smectite clays. As reviewed in Chapter 2, mafic igneous rocks akin to basalts are expected to comprise a large proportion of the Martian crust. Chemical alteration and weathering of those mafic rocks is expected to produce various fine-grained, volatile-bearing phases, possibly including smectites or smectite-like mineraloids. Smectites, in particular, are known to have very large specific surface areas and strong gas adsorptivities. Powdered basalts possess only modest specific surface areas and adsorptivities and can be considered a baseline model for a particulate regolith on Mars.

Using knowledge of desorption characteristics, the pressure rise as a function of temperature for a sealed sample can be readily computed. Fig. 3-7 summarizes pressure rises expected for the hypothetical cases of basalt and nontronite (ferroan smectite) regolith samples. Initial CO_2 loads are taken from experimental data (Fig. 3-6) corresponding to a 7-mb Martian atmosphere whereas initial H_2O loads are estimated from basic

mineralogical properties and common experience. Naturally, effective head-space pressures would vary with the volume of the container, the weight of solid sample, and the degassing history of the sample prior to sealing in the container. Nonetheless, results depicted in Fig. 3-7 point out the magnitude of pressure rise to be expected for gas desorption from cold regolith samples.

Fig. 3-7 poses two hypothetical cases: warming of fine-grained samples originally gas-saturated at 158 K and 230 K, respectively. The 158 K case would apply to samples collected from polar areas whereas the 230 K case would apply to samples collected from depths > 25 cm at equatorial and temperate latitudes (Section 3.3).

Beginning at Mars atmospheric pressure (0.01 atm) and using the 7-mb data from Fig. 3-6 to model CO_2 desorption with increasing temperature, it is found that, by 230 K, head-space pressure above basalt and nontronite samples initially gas-saturated with CO_2 at 158 K are 0.56 atm and 6.0 atm, respectively. If all CO_2 desorbs by 300 K, respective pressures become 0.98 atm and 9.1 atm. Above 300 K, pressure increase was modelled according to the ideal gas law.

It is assumed that no H_2O desorption occurs below 230 K so that pressure rise below 230 K is attributable solely to CO_2 desorption. (Additional pressure from desorbed N_2 and Ar is neglected.) Above 230 K, desorption of water is expected to become important. For basalt, an initial water load of 1% was assumed to desorb to 0.1% by 300 K and to 0.01% by 400 K. Consequently, at 300 K, the partial pressures of gas above the initially coldest basalt (158 K) would be 0.98 atm CO_2 and 7.4 atm H_2O. Using an initial water load of 20% for the initially coldest nontronite (158 K), with 18% being retained on the substrate up to 300 K, equivalent results were 9.1 atm CO_2 and 18 atm H_2O at 300 K. For the case of samples gas-saturated at 230 K, corresponding total pressures at 300 K would be 19.5 atm for nontronite and 7.6 atm for basalt. Based on laboratory experience with clay minerals, major desorption of water from nontronite was assumed to occur at 300-400 K.

To minimize pressure rise, gas-rich samples must either be kept extremely cold (i.e., < 230 K) or degassed prior to sealing in containers. Although model desorption profiles for H_2O should be measured precisely, it already seems clear that pressure management should be more difficult for CO_2 + H_2O than for CO_2 alone. Head-space gas pressure should not exceed thresholds for material decomposition or for

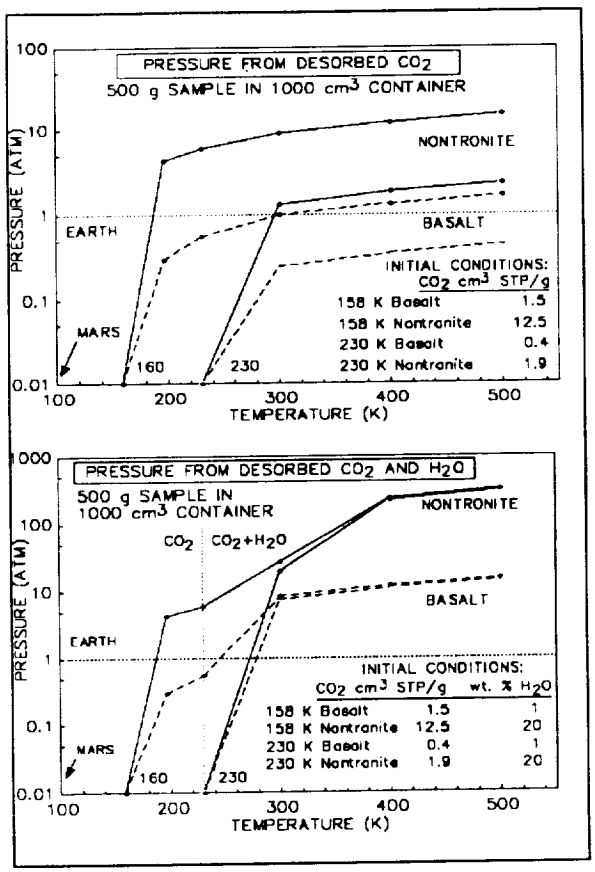


Figure 3-7.

Head-space pressures developed by desorption of gases from Mars-analogous materials inside a fixed volume. (Top) Desorption of CO_2, modelled using data from Fig. 3-6. (Bottom) Total pressure from desorption of CO_2, as above, plus desorption of H_2O estimated from mineralogical properties.

chemical or isotope-exchange reactions.

At least one of the oxidants discovered in Martian sediments by the *Viking* Landers is known to decompose, with voluminous release of O_2, upon humidification (Oyama and Berdahl, 1977). Desorption of water vapor from a sealed sample could humidify the container and decrepitate the subject oxidant.

Stable-isotope exchange reactions under the subject conditions (low T, high P) have not been extensively studied but, from the law of chemical mass action, any increase in P_{CO2} or P_{H2O} should foster increased rates of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ exchange reactions, respectively. Such reactions could irreversibly change the stable-isotopic compositions of any carbonate or hydrated minerals in the sample.

3.5. Ionizing Radiation

The cosmic-ray bombardment records preserved in the surfaces of Martian rocks are expected to provide valuable information about variations in density of the Martian atmosphere through time (Arvidson et al., 1981). Also, radiation damage accumulated in samples through cosmic-ray bombardment and through *in situ* decay of natural radionuclides can be used to age-date the samples through the method of thermoluminescence (TL) (e.g., Wendlandt, 1986). Care must be taken, however, to minimize effects of irradiations experienced by samples outside their natural environments after they are collected. Such extraneous irradiations might obscure the natural records that are sought in the samples. Concerns about preservation of natural irradiation records in Mars samples were expressed in letters by P. Englert and by R. Reedy, W. Feldman, and D. Drake (Appendix B3).

Cosmic radiation is subdivided into solar cosmic rays (SCRs) and galactic cosmic rays (GCRs) (Table 3.7). The Martian surface is mostly shielded from SCRs by the Martian atmosphere (2.6 g/cm^2 shielding for each mbar of pressure), which also provides differential shielding against GCRs. GCRs consist of very heavy (VH) nuclei (Z > 20), which impart damage through ionization of target atoms, and free nucleons (protons and neutrons), which impart damage through nuclear spallation reactions. Products of GCR VH bombardment are microscopic cylindrical traces of crystal-structure damage that become visible as "tracks" in polished grain mounts after suitable chemical etching. Products of spallation include noble-gas nuclides (e.g., ^{39}Ar, ^{78}Kr, ^{83}Kr) that must be extracted from a sample by pyrolysis and measured with an ultrasensitive mass spectrometer.

By-products of GCR (and SCR) bombardment, especially secondary gamma radiation, also produce electron-hole damage that forms the basis of the TL effect. Radiation received by the sample leads to electrons being trapped in energy levels in the "forbidden" band gap of the solid. Ambient temperatures on the planet can cause some of the electrons to be released from these traps. By studying the increase in trapped electrons, in response to radiation intensity and energy release upon systematic heating, information on radiation-filling and thermal drainage should be obtained. From these studies,

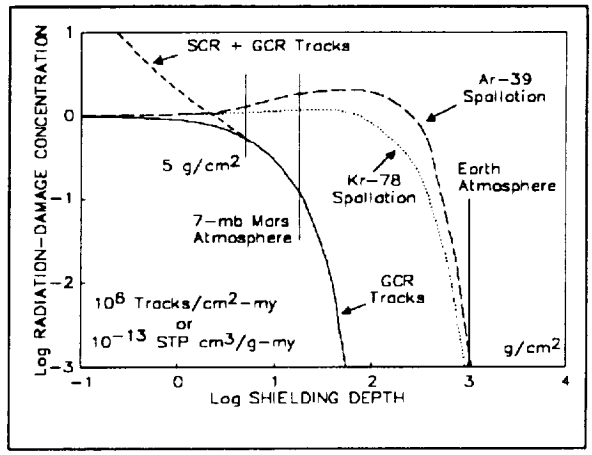


Figure 3-8.

Production rates of radiation damage effects in Mars surface materials as a function of shielding (modified from Arvidson et al., 1981.) Note that SCR effects become important for shielding < 5 g/cm^2, which is equivalent to 2 mb of Mars atmosphere. Under current climatic conditions, with a typical atmospheric pressure of 7 mb, most Mars samples are protected from SCR track damage.

Table 3.7. Characteristics of solar cosmic ray (SCR) and galactic cosmic ray (GCR) components (after Reedy et al., 1983)

Radiation	Energies (MeV/nucleon)	Mean flux at Earth (particles/cm^2/sec)	Penetration Depth in Rocks (cm)
SCR protons and He nuclei	5-100	~ 100	0-2
SCR very heavy (VH) nuclei	1-50	~ 1	0-0.1
GCR protons and He nuclei	100-3000	3	0-100
GCR very heavy (VH) nuclei	~ 100	0.03	0-10

gamma-ray equivalent dose of radiation can be determined and, hence, a radiation history can be obtained for a given sample. The technique has been applied successfully to lunar samples and meteorites. One of the most important kinds of information that can be obtained from TL studies is the depth of burial of a sample below the surface; this can be calculated from the determination of the effective storage temperature for the electron traps. Penetrating radiations seriously affect data that can be obtained. Even exposure to visible light degrades results, and sampling is done ideally in red light (R. E. Arvidson letter, Appendix A3).

The Martian atmosphere effectively shields against VH nuclei but not against nucleons. Therefore, the abundance ratio of tracks to spallation products should be sensitive to variations in density of the Mars atmosphere (Fig. 3-7). In fact, for an atmospheric pressure change from 1 to 100 mbar (i.e., change of 3 to 300 g/cm^2 shielding), the track/spallation-product ratio changes by five orders of magnitude (Fig. 3-9). Because relative production rates for tracks and spallation products are so sensitive to shielding (Figs. 3-8, 3-9), major changes in the shielding history of a sample, during collection and return to Earth, could pose a threat to the recoverable information. Production of tracks and spallation products in bulk meteorite samples irradiated in interplanetary space are ordinarily considered as occurring on time scales of 10^6-10^7 yr. For a planetary surface sample, however, actual measurements may depend on individual mineral grains that could be perturbed by even short-lived fluxes of extraneous radiation. In addition, irradiation effects can vary greatly with depth in a sample. For example, in the outermost 10^{-3} cm of a mineral grain with no atmospheric shielding, the VH-nuclei track production rate could be as high as 10^5 cm^{-2} yr^{-1} (Fig. 3-10) (Reedy et al., 1983). Because the elapsed time between collection and Earth-delivery of a Mars sample might be one year or longer, extraneous track production in improperly shielded samples could accrue into a major fraction of the total measurable track population in a given grain. Similarly, in the absence of atmospheric shielding, production rates of spallogenic ^{10}Be and ^{26}Al within the outermost 1 cm of a rock would be approximately $10^{1\text{-}3}$ decays kg^{-1} min^{-1} (Fig. 3-10). SCRs are especially important in production of ^{26}Al and might become significant once a Mars sample was lifted above the SCR shielding provided by the Mars atmosphere.

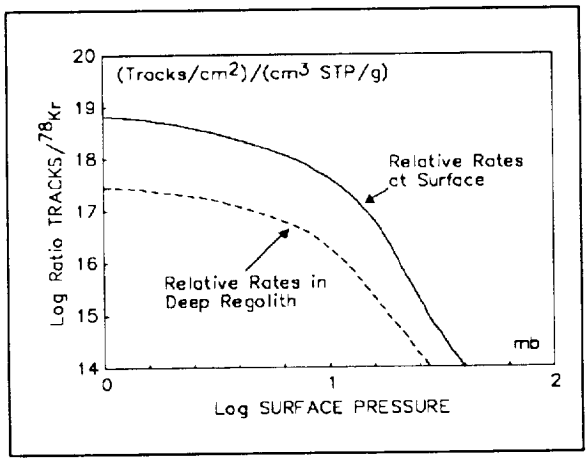


Figure 3-9.

Relative production rates of track damage and spallation ^{78}Kr at the Mars surface (e.g., free surface of a rock) and in the deep regolith (modified after Arvidson et al., 1981). The strong dependence of the track/spallation-gas ratio on atmospheric shielding forms the basis of climatology information in sample irradiation records. The deep-regolith curve represents the same ratio from the bottom of the atmosphere to a depth within the regolith that exceeds the penetration range of GCRs.

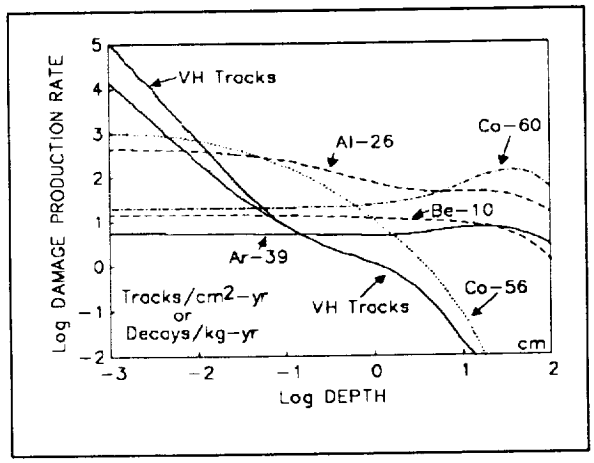


Figure 3-10.

Production rates for tracks and spallation nuclides calculated for a lunar basaltic rock directly exposed to SCRs and GCRs (no shielding) The shaded area reflects uncertainties in fluxes of low-energy SCR VH nuclei (modified after Reedy et al., 1983). Similar rates should apply to Martian rocks. Note that the unshielded outermost surface of a rock would accrue significant damage over the 1-2 years that might typify surface-operation and Earth-return phases of a Mars sample-return mission.

Radiation-shielding requirements for Mars samples are traceable to two major concerns:

- Naturally well-shielded samples taken from depth on Mars (e.g., > 10 cm) will be exposed to high doses of GCRs upon excavation.

- All Mars samples, regardless of depths of origins, will be exposed to high doses of SCRs (or their secondary products) after liftoff from Mars.

GCR nucleons are very highly penetrating and their stoppage requires shielding on the order of 1000 g/cm^2 (Fig. 3-8) -- a value that is extremely impractical in weight-limited spacecraft systems. Furthermore, moderate to large shielding depths levied against ~ 1 GeV nucleons (aside from those needed for complete stoppage) become self-defeating. GCR bombardment of the shield material produces cascades of secondary nucleons that impart additional radiation damage. Indeed, in a mass-limited shielding environment, total radiation damage from GCR nucleons is minimized by minimizing shielding.

Total shielding cannot be "zero", however, because some protection must be provided against the less energetic, but still damaging, primary SCRs. As shown in Fig. 3-8, contributions by SCRs to heavy-nuclei track damage becomes significant only for shielding less than 5 g/cm^2. At higher shielding values, no additional protection against SCRs is gained but additional complications are incurred through rapid changes in the track/spallation production rates and in increasing secondary damage from GCRs. Accordingly, all factors considered, a baseline shielding value of 5 g/cm^2 is recommended for collected Mars samples.

It should be understood that 5 g/cm^2 represents the total shielding, including contributions from containers and spacecraft structures. When container and spacecraft effects are considered, along with effects of adjacent samples, additional dedicated shields may be unnecessary. Indeed, the minimum structures required to containerize and transport samples during Earth return might contribute shielding > 5 g/cm^2. In that case, neutron absorbers (e.g., B, Li, Cd) might be desirable additions to hardware surrounding the samples to reduce secondary radiation from GCRs. In any event, either passive or active monitors of ionizing radiation would be desirable sensor companions to the samples.

3.6. Magnetic Fields

Permanent magnetization of Martian rock samples will be sought as evidence for ancient planetary magnetic fields on Mars. Therefore, any degradation or obscuration of natural magnetization in the samples will be viewed as a significant loss of paleomagnetic information. The samples must be protected against events that might either erase natural magnetization or induce artificial magnetization. Concerns held by specialists in rock magnetism are reflected in the letter by D. Collinson and A. Stephenson (Appendix B3).

Both heating and shock are known to be deleterious to remanent magnetism in rocks and should be avoided. The maghemite/hematite solid-state phase transition, which can occur over the 350-650 K range for various samples (Fig. 3-4), can be avoided by keeping the samples cold.

Altered magnetization is a serious concern if the samples are heated at temperatures approaching those for biological sterilization. First, some material may acquire a non-Martian magnetization when heated and cooled in the presence of a magnetic field. For example, goethite magnetizes on cooling from above 393 K and troilite magnetizes on cooling from above 593 K. Second, it may be impossible to heat the samples significantly without changing the magnetic carrier. For example, the reaction goethite → hematite occurs at 473-623 K in air and the alteration of fine-grained or amorphous iron oxides can occur at temperatures significantly less than 623 K. In addition, any carbon-induced reduction reactions might produce ultrafine-grained metallic iron that might acquire magnetization at temperatures < 423 K. Collinson and Stephenson (Appendix B3) suggest that a temperature of 373 K and an ambient magnetic field strength of < 10^{-4} Tesla could be tolerated without significant change of natural magnetism.

The best strategy for preserving natural magnetization of Martian samples is to keep the samples cold and shielded from artificial magnetic fields. The important issue, requiring carefully planned analog studies, is to understand clearly the magnetic overprinting that might occur by heating a sample significantly above the Martian surface temperature. Care should be taken to insure that the samples are not exposed to magnetic fields, on the spacecraft or on the return to Earth, which are significantly stronger than Earth's magnetic field.

3.7. Acceleration and Shock

Physical properties of interest for Martian regolith samples include particle-size distributions, porosities and permeabilities, zonal structures that vary with depth, and intergranular cementation, as in duricrusts observed at the *Viking* Lander sites. As expressed in the letter from E. Gaffney (Appendix B3), the principal threats to the preservation of such properties are high acceleration (sustained g-force loads) or shock (short-lived, high-intensity pressure) that might break grains, sever grain-to-grain contacts, or cause mixing or compaction. Additional concerns are that shock might degrade natural magnetization of samples (Collinson and Stephenson, Appendix B3).

Stress (directed pressure) experienced by a bulk 1-gram sample, as a force normal to the face of a cube, can be estimated as

$$S = 98.1\ N_g\ d^{2/3} \qquad [3\text{-}2]$$

where S (Pa) is stress, N_g is the "g" number (1, 2, 3, etc.) of the acceleration (N_g = 0.385 at the Martian surface) and d is the specific gravity (normalized bulk density) of the sample Stresses computed as a function of g-load using Eqn. [3-2] are shown in Fig. 3-11.

Fig. 3-11 offers a simplified summary of acceleration-induced stresses on samples but must be qualified by consideration of sample size and geometry. Samples in elongated containers (e.g., regolith core tubes), will experience compression from acceleration of material along the length of the sample column; sample increments at the forward end of the acceleration vector will experience higher stresses than those near the tail of the vector. Accordingly, compression at the bottom (trailing end) of the tube is estimated better as

$$S = 98.1\ N_g\ d\ L \qquad [3\text{-}3]$$

to account for the effect of length, L. (For unit-mass samples modelled by Eqn. [3-2], $L \leq 1$ cm is implicit.) Clearly, stresses will be highest when acceleration is parallel to L. Stress management might be achieved by minimizing L for each sample and by preferentially orienting L transverse to the acceleration vector.

The important consideration is whether computed stresses exceed strengths estimated for Martian regolith materials. The horizontal dotted lines in Fig. 3-11 show the average values of

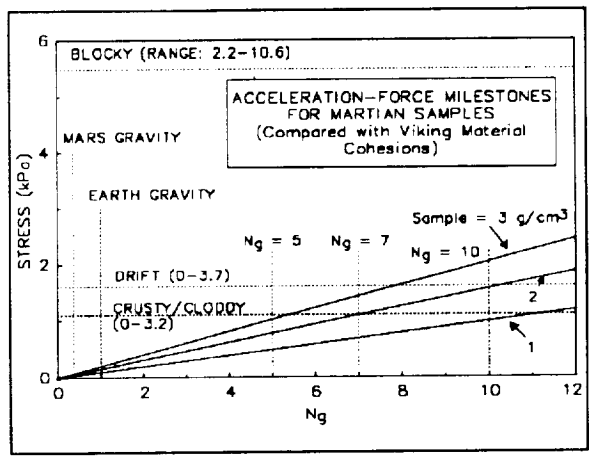


Figure 3-11.

Acceleration-force milestones for Martian samples. Positively sloping straight lines represent stress computed as a function of "g" number (where 1 g = 981 cm/sec^2) for unit-mass (1 gram and approximately 1-cm size) sample materials of various densities. 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).

strength estimated by Moore (1987) for three types of surface materials observed at the *Viking* Lander sites. The two weaker materials ("drift" and "crusty/cloddy") probably also have low densities ($d \leq 2$). From Fig. 3-11, it is apparent that unit-mass (approximately 1-cm-sized) samples of drift or crusty/cloddy materials would fail for stresses greater than about N_g = 7-11. Average blocky material should be resistant to stress-induced failure at all accelerations $N_g < 35$ for d = 2. Of course, S varies with L and there remain large uncertainties in the strengths estimated for all three materials classified by Moore (1987).

Values of N_g required to assure survival of the very weak drift and crusty/cloddy materials are exceedingly low and might be impractical as mission requirements. Given the range of strengths estimated for blocky material, however, it seems that a centimeter-sized blocky material sample could be preserved for all $N_g < 10$. The stress limit of < 1 kPa suggested by Gaffney (Appendix B3) would translate to about N_g = 7 for a unit-mass sample of d = 2. Taking the length effect (Eqn. [3-3]) into account, however, a 7-g acceleration applied to a 10-cm columnar sample of d = 2 would produce a 13.7 kPa load at the bottom of the column, thereby threatening the integrity of even the blocky material.

Assessing the acceleration/shock threat to rocks is simpler than for unconsolidated regolith samples. Crushing strengths of most terrestrial rocks are on the order of 10^7 Pa whereas major mineralogical transformations and melting occur under shock loads of 10^{10} Pa. For d = 3, corresponding accelerations on unit samples (Eqn. [3-2]) would be N_g = 490 (rock crushing) to N_g = 4.9 x 10^5 (rock melting). Clearly, such accelerations would be totally unreasonable for any sample-return spacecraft or mission design.

With respect to shock disturbance of rock magnetism, Cisowski et al. (1976) experimentally determined that demagnetization occurs at shock pressures < 10^9 Pa in basalt targets. It is not clear, however, whether the threshold for such effects is much less than 10^9 Pa. Therefore, protection of rock samples against shock-induced crushing (i.e., 10^7 Pa) should also be adequate for magnetic preservation. Nonetheless, additional work may still be needed to define shock limits for magnetic preservation of soil or sediment samples.

3.8. Biology and Planetary Quarantine

Preservation of the most sensitive geologic materials should also suffice to preserve any non-living Martian biological materials (i.e., organic or biochemical compounds). Accordingly, biological concerns would require few, if any, stipulations in addition to those discussed in sections 3.2-3.7 except in the unlikely event that return of living organisms became an objective. As reviewed previously (Section 2.1.4), however, principal emphasis in Martian exobiology is aimed at returning well-preserved samples of any Martian organic compounds.

Contamination by carbon would be offensive to biological studies but the ~ 40-ppm C background level expected for sterile rock samples (Section 3.2) might represent a practical limit to biological anti-contamination. Sub-freezing temperatures and low head-space gas pressures should favor survival of biochemical compounds by arresting reactions that might otherwise decompose them. Protection of soil clods against acceleration/shock disintegration should also protect any microfossils. Shielding against extraneous magnetic fields, as required for paleomagnetic studies, might be unnecessary for biology but should not be offensive to biology. Only the shielding requirements against ionizing radiation might be expected to differ for geochemistry and biology. If anything, the radiation shielding required for biology would be greater than for geochemistry. Protection from light would not be peculiar to biological samples but would already be required for thermoluminescence samples (Section 3.5).

In addition to threatening the chemical and stable-isotopic integrity of the samples, uncontrolled pressure rise within sample containers might also jeopardize planetary protection. As long as head-space pressures inside Mars sample containers are less than atmospheric pressure on Earth, no leakage of gases into the terrestrial environment should occur. If pressures inside containers exceed 1 atm, however, the pressure difference will cause net diffusion of Mars gases outward through all available leakage pathways. Any putative biohazard posed by the Martian samples would thereby become much more difficult to manage. Therefore, maintenance of minimum, Mars-like head-space gas pressures (Section 3.4) is also highly desirable from the perspective of planetary protection.

3.9. Summary

General concerns about preservation of Mars samples are summarized in Fig. 3-12. Details of various issues were reviewed in Sections 3.2-3.8.

The maximum scientific value of the samples is retained when the samples are preserved in the conditions that applied prior to their collection. Unfortunately, all manipulations of the samples, including collection and containerization, can be expected to degrade the samples to some extent. Design of meaningful sample-preservation precautions must recognize how and why samples become degraded if environmental controls are relaxed.

Avoidance of contamination is an absolute necessity although quantitative limits vary from one chemical element to another. The bulk elemental composition of shergottite meteorites might serve as a guide for setting maximum acceptable limits of elemental contaminants. Prospective tool and container materials rich in trace elements (by the shergottite definition) should be scrupulously avoided.

Temperature is the most important intensive parameter to control. Keeping the samples sufficiently cold will immobilize water (as ice or as adsorbed water vapor) and prevent chemical and isotope-exchange reactions that could otherwise irreversibly change the records of natural history in

the rocks and soils. Strict temperature control would also moderate the desorption of gaseous CO_2 and H_2O from fine-grained soils and sediments that could lead to unacceptably high head-space gas pressures inside sample containers. Uncontrolled pressure rise would decompose pressure-sensitive materials, such as the trace oxidants discovered in surface sediments at the *Viking* landing sites, as well as encourage chemical and isotope-exchange reactions involving any carbonate or hydrated minerals. Deliberate thermal sterilization of samples would irreversibly decompose heat-sensitive minerals, alter stable-isotopic ratios, and possibly erase records of natural radiation doses that would be critical to paleoclimate studies.

Management of ionizing radiation doses, exposure to extraneous magnetic fields, and subjection to high accelerations (including shock) are also important but more difficult to express as quantitative limits that apply uniformly to all samples. Protection against ionizing radiation is most critical for geologic samples (as opposed to atmospheric samples) taken from depth (i.e., a few centimeters or more), whereas magnetic shielding is principally a concern for igneous rock samples. Acceleration/shock limits are of concern only for deep regolith samples and for partially cemented sediments or soil clods.

By observing preservation requirements for the most sensitive geologic materials, preservation of any organic or biochemical materials should also be achieved with no additional effort. Preservation requirements for geologic and organic materials are mutually supportive.

Although many consequences of uncontrolled environment on Mars sample preservation can already be identified, basic research is still needed in several areas prior to specification of firm preservation requirements. In addition, work is needed to establish what scientific measurements can be made on Mars to recover information that is unlikely to be preserved in returned Martian samples. Recommendations both for preliminary preservation requirements and for additional work are given in Chapter 4.

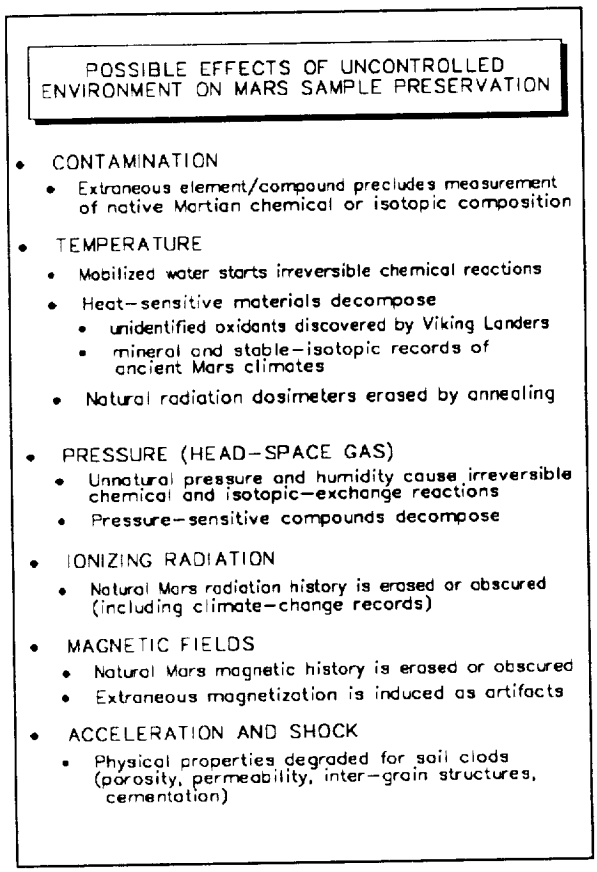


Figure 3-12.

Summary of major concerns regarding preservation of collected Martian samples.

4. RECOMMENDATIONS

Preliminary values for sample-preservation parameters are summarized in Table 4.1. Those values were derived using background information that was explained in detail in Chapter 3 but are subject to modification based on future research. Specific reasoning involved in compiling Table 4.1 is given below.

Contamination. High-purity aluminum and certain stainless steel alloys should be acceptable materials for sample tools and containers. Other materials may be acceptable if they can be certified as non-contaminating with respect to trace elements of geochemical interest. Research is needed to certify prospective materials as non-reactive with oxidants of the type discovered in Martian sediments by the *Viking* Landers.

The Shergotty meteorite, which has been postulated to be a Martian rock, has been extensively analyzed and is a useful guide to acceptable upper limits for contamination of rock, soil, and sediment samples. It is suggested that, for each element, contamination not exceed 1% of the concentration in Shergotty. For example, using data in Table 3.2, derived limits would be < 0.5 ppm C and < 0.9 ppb Pb.

Elemental composition of the Martian atmosphere is known from analyses by the *Viking* Landers. It is suggested that, for each element, contamination of an atmospheric sample not exceed 1% of the concentration in the *Viking* analyses. For example, using data in Table 3.3, derived limits would be < 0.03 % N_2 and < 0.8 ppb Xe. Research is needed to show how contamination of atmospheric samples varies with method of sample collection. Volumes collected and stored at Mars ambient pressure should be representative samples but would be subject to contamination on Earth by inward leakage of the terrestrial atmosphere. Concentrated samples (e.g., collected by compression or sorption on molecular sieves) would be less sensitive to terrestrial contamination but might be either fractionated or contaminated by the concentration process.

Cross-contamination between individual samples should be minimized by separately packaging different samples.

Chemical sterilization would introduce severe chemical and isotopic contamination and should be avoided.

Table 4.1. Recommended parametric values for preservation of Martian samples. (Unless otherwise noted, each stated limit applies equally to every sample). See text for limitations and qualifications.

Contamination	For each element, < 1% of the concentration in Shergotty meteorite (Rock, sediment, or soil sample)
	For each element or compound, < 1% of of the concentration in Viking Lander atmospheric analyses (Atmosphere sample)
Temperature	< 260 K (Igneous rock sample, unweathered)
	< 230 K (Soil, sediment, deep regolith, or weathered rock sample)
Pressure (head-space gas)	< 1 atm (Igneous rock sample, unweathered) < 0.01 atm (Soil, sediment, deep regolith, or weathered rock sample)
Ionizing Radiation	5 g/cm^2 shielding
Magnetic Fields	< 5.7×10^{-5} Tesla (1 Earth field)
Acceleration/Shock	< 7 g (1 g = 9.81 m/sec^2)

Temperature. Temperature is the most important intensive variable to control. Preservation temperatures should be established with the goal of controlling the physical state and reactivity of water. Immobilizing water in the samples as ice, or as unfrozen capillary films that are thinner than the threshold for liquid-like behavior, will minimize chemical and stable-isotope exchange reactions.

The equilibrium freezing point of 273 K is too warm to assure control of the water system. The onset of liquid-like unfrozen water in rocks occurs at 263 K and, in clay-rich soils, at about 235 K. Therefore, it is recommended that fresh igneous rocks be preserved at < 260 K and that samples containing clay-like minerals or mineraloids be preserved at < 230 K.

Supporting research is needed on kinetics of geochemical changes, especially stable-isotope exchange reactions. Also, work is needed to establish the survivability of natural thermoluminescence in Martian samples as a function of preservation temperature.

Thermal sterilization at 400-450 K would decompose sensitive minerals and compounds known or suspected to occur in Martian samples. Studies of igneous minerals and radiometric age-dating should not be affected but records of climate history would be seriously degraded, if not destroyed. In addition, mineral geothermometers and fluid inclusions would be adversely affected.

If thermal sterilization becomes required, it should be done at the lowest possible temperature with complete retention of any liberated gases. Time of sterilization, within reason, has much less effect on mineralogical properties than increased temperature. It is of paramount importance to measure and record the time-temperature-pressure conditions during any sterilization. Much information contained in the pristine sample might thus be recovered. A sealed liner of high-purity gold might be required to manage the loss of hydrogen and its associated effects on the redox conditions of the minerals. Clearly, requirement for a gold lining would need to be carefully balanced against limits for Au contamination.

No water or any other components should be added to the sample for the sterilization process. Although water might help preserve some clay minerals and zeolites, these potential benefits do not begin to offset the disadvantages of acclerated chemical reactions involving other phases.

Pressure. Because of gas desorption from the samples, warming of sealed containers will generate significant head-space gas pressures. The problem will be least for rocks and greatest for fine-grained soils and sediments and, especially, deep regolith samples. The latter samples are also expected to be the most sensitive with respect to pressure-induced chemical or isotope-exchange reactions.

Research is needed on the rates of reactions involving carbonate and hydrated minerals with gases containing high partial pressures of CO_2 and H_2O. Such work might reduce concerns about deleterious effects of pressure and permit higher pressure tolerances to be derived.

In advance of the necessary research, however, a pressure limit of 0.01 atm (effectively Mars ambient) is recommended for most geologic samples. A maximum limit of 1 atm is suggested not on the basis of geochemistry but in anticipation of planetary quarantine requirements. Pressure < 1 atm inside a sealed container will assure that, on Earth, no outward leakage should occur.

Ionizing Radiation. Shielding of 5 g/cm^2 corresponds to the minimum value needed to prevent nuclear particle track damage from solar cosmic rays. (The Martian surface is naturally protected from such effects by atmospheric shielding). This shielding requirement is modest and might be achieved by default in a well-designed sample canister with self-shielding accrued through strategic placement of samples relative to the canister's center. Care must be taken not to inadvertently create greater shielding, however, because, for some radiation effects, shielding > > 5 g/cm^2 stimulates secondary radiation damage from galactic cosmic rays. Radiation monitors should accompany the samples.

Magnetic fields. Magnetic shielding requirements are among those most poorly defined. Research is needed to establish the combinations of applied field strength, temperature, and shock that can be tolerated without disturbance of magnetic records in the samples. Spacecraft design and mission operations must be analyzed to understand the artificial fields to which samples might be subjected. In the meantime, the limit for extraneous applied fields is set equal to that of Earth's field.

Acceleration and Shock. No reasonable accelerations or shocks expected during a Mars sample-return mission should adversely affect igneous rock samples. The 7-g limit corresponds to the stress that would disintegrate Martian materials having the average cohesion of crusty/cloddy material at the *Viking* landing sites.

REFERENCES

Allton J. H. (1989) *Catalog of Apollo Lunar Surface Geological Sampling Tools and Containers,* Rept. No. JSC-23454, NASA Johnson Space Center, Houston, TX, 97 p.

Anderson D. M. and Morgenstern N. R. (1973) Physics, chemistry, and mechanics of frozen ground: a review. In *Permafrost: The North American Contribution to the Second International Conference,* National Academy of Sciences, Washington, DC, 257-288.

Anderson D. M. and Tice A. R. (1979) The analysis of water in the Martian regolith. *J. Mol. Evol., 14,* 33-38.

Arvidson R. E, Gooding J. L., and Moore H. J. (1989) The Martian surface as imaged, sampled, and analyzed by the Viking Landers. *Rev. Geophys., 27,* 39-60.

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

Banin A. and Margulies L. (1983) Simulation of Viking biology experiments suggests smectites not palagonites, as martian soil analogues. *Nature, 305,* 523-525.

Becker R. H. and Pepin R. O. (1984) The case for a martian origin of the shergottites: nitrogen and noble gases in EETA 79001, *Earth Planet. Sci. Lett., 69,* 225-242.

Becker R. H. and Pepin R. O. (1986) Nitrogen and light noble gases in Shergotty. *Geochim. Cosmochim. Acta, 50,* 993-1000.

Biemann K., Oro J., Toulmin P. III, Orgel L. E., Nier A. O., Anderson D. M., Simmonds P. G., Flory D., Diaz A. V., Rushneck D. R., Biller J. E., and LaFleur A. L. (1977) The search for organic substances and inorganic volatile compounds in the surface of Mars. *J. Geophys. Res., 82,* 4641-4658.

Bogard D. D. and Johnson P. (1983) Martian gases in an Antarctic meteorite? *Science, 221,* 651-654.

Bogard D. D., Duke M. B., Gibson, E. K., Minear J. W., Nyquist L. E. and Phinney W. C. (1979) *Consideration of Sample Return and the Exploration Strategy for Mars,* **NASA Tech. Memo. 58213,** NASA Johnson Space Center, Houston, TX, 91 p.

Brass G. W. (1980) Stability of brines on Mars. *Icarus, 42,* 20-28.

Carr, M. H. (1981) *The Surface of Mars,* Yale University Press, New Haven, 232 p.

Chen J. H. and Wasserburg G. J. (1986) Formation ages and evolution of Shergotty and its parent planet from U-Th-Pb systematics. *Geochim. Cosmochim. Acta, 50,* 955-968.

Chicarro A. F., Scoon G. E. N., and Coradini M. (1989) *Mission to Mars: Report of the Mars Exploration Study Team,* ESA SP-1117, European Space Agency, Paris, France, 138 p.

Cisowski S. M., Dunn J. R., Fuller M., Wu Y., Rose M. F., and Wasilewski P. J. (1976) Magnetic effects of shock and their implications for lunar magnetism. *Proc. Lunar Sci. Conf. 7th,* 3299-320.

Clark B. C., Baird A. K., Rose H. J. Jr., Keil K., Castro A. J., Kelliher W. C., Rowe, C. D., and Evans P. H. (1976) Inorganic analyses of Martian surface samples at the Viking Landing sites. *Science, 194,* 1283-1288.

Clark B. C., Baird A. K., Weldon R. J., Tsusaki D. M., Schnabel L., and Candelaria M. P. (1982) Chemical composition of Martian fines. *J. Geophys. Res., 87,* 10059-10067.

COMPLEX (Committee on Planetary and Lunar Exploration) (1977) *Post-Viking Biological Investigations of Mars,* Space Science Board, National Academy of Sciences, Washington, DC, 26 p.

COMPLEX (Committee on Planetary and Lunar Exploration) (1978) *Strategy for Exploration of the Inner Planets: 1977-1987*, Space Science Board, National Academy of Sciences, Washington, DC, 97 p.

Drake M. J., Boynton, W. V. and Blanchard D. P. (1987) The case for planetary sample return missions: 1. Origin of the solar system, *Eos (Trans. Amer. Geophys. Union), 68*, 105, 111-113.

Drake M. J., Greeley R., McKay G. A., Blanchard D. P., Carr M. H., Gooding J., McKay C. P., Spudis P. D., and Squyres S. W. (1988) *Workshop on Mars Sample Return Science*, LPI Tech. Rept. 88-07, Lunar and Planetary Institute, Houston, TX, 196 p.

ESF (1986) Report on the Exploration of Mars, Sub-Group of ESF/NAS Joint Working Group, H. Fechtig (Chairman), European Science Foundation, September 1986, 12 p.

Fanale F. P. and Cannon W. A. (1974) Exchange of adsorbed H_2O and CO_2 between the regolith and atmosphere of Mars caused by changes in surface insolation. *J. Geophys. Res., 79*, 3397-3402.

Fanale F. P. and Cannon W. A. (1978) Mars: Regolith adsorption and the relative concentrations of atmospheric rare gases. *J. Geophys. Res. Lett., 5*, 77-80.

Fanale F. P. and Cannon W. A. (1979) Mars: CO_2 adsorption and capillary condensation on clays -- significance for volatile storage and atmospheric history. *J. Geophys. Res., 784*, 8404-8414.

Fleischer R. L., Price P. B., Symes E. M., and Miller D. S. (1964) Fission track ages and track annealing behavior of some micas. *Science 143*, 349-351.

Fleischer R. L., Price P. B., and Walker R. M. (1965a) Solid state trace detectors: Applications to nuclear science and geophysics. *Ann. Rev. Nuclear Sci. 15*, 1-18.

Fleischer R. L., Price P. B., and Walker R. M. (1965b) Effects of temperature, pressure, and ionization on the formation and stability of fission tracks in minerals and glasses. *J. Geophys. Res. 70*, 1497-1502.

Fleischer R. L., Price P. B., and Walker R. M. (1968) Charged particle tracks: Tools for geochronology and meteorite studies. In E. Hamilton and R. M. Farquhar (eds.), *Radiometric Dating for Geologists*, Interscience, 417-435.

Fleischer R. L., Viertl J. R. M., and Price P. B. (1969) Age of Manicouagan and Clearwater Lake Craters. *Geochim. Cosmochim. Acta Suppl. 33*, 523-537.

Fleischer R. L., Hart H. R. Jr., Comstock G. M., and Evivaraye A. O. (1971) The particle track record of the Ocean of Storms. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, M.I.T. Press, 2559-2568.

Fleischer R. L. and Hart H. R. (1973) Particle track record of Apollo 15 green soil and rock. *Earth Planet. Sci. Lett. 18*, 357-364.

Franks F. (1982) The properties of aqueous solutions at subzero temperatures. In F. Franks (ed.), *Water, A Comprehensive Treatise, Vol. 7*, Plenum, 215-338.

Friedman I. and O'Neil J. R. (1977) Chapter KK. Compilation of stable isotope fractionation factors of geochemical interest. In M. Fleischer (ed.), *Data of Geochemistry* (Sixth Ed.), U. S. Geol. Survey Prof. Paper 440-KK.

Gooding J. L. and Muenow D. W. (1986) Martian volatiles in shergottite EETA79001: New evidence from oxidized sulfur and sulfur-rich aluminosilicates. *Geochim. Cosmochim. Acta, 50*, 1049-1059.

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

Gooding J. L., Carr M. H., and McKay C. P. (1989) The case for planetary sample return missions. 2. History of Mars. *Eos (Trans. Amer. Geophys. Union), 70*, 745 ff..

Hargraves R. B., Collinson D. W., Arvidson R. E., and Spitzer C. R. (1977) The Viking magnetic properties experiment: primary mission results. *J. Geophys. Res., 82,* 4547-4558.

Hess S. L., Henry R. M., Leovy C. B., Ryan J. A., and Tillman J. E. (1977) Meteorological results from the surface of Mars: Viking 1 and 2. *J. Geophys. Res., 82,* 4559-4574.

Hess S. L., Ryan J. A., Tillman J. E., Henry R. M., and Leovy C. B. (1980) The annual cycle of pressure on Mars measured by Viking Landers 1 and 2. *Geophys. Res. Lett., 7,* 197-200.

JSC (1974) *On the Petrological, Geochemical, and Geophysical Characterization of a Returned Mars Surface Sample and the Impact of Biological Sterilization on the Analyses*, NASA Johnson Space Center, Houston, TX, April 1974.

JSC (1977) Consideration of Sample Return and the Exploration Strategy for Mars, Lunar and Planetary Sciences Division, NASA Johnson Space Center, Houston, TX, March 1977, 76 p.

Kieffer H. H. (1976) Soil and surface temperatures at the Viking landing sites. *Science, 194,* 1344-1346.

Kieffer H. H., Martin T. Z., Peterfreund A. R., Jakosky B. M., Miner E. D., and Palluconi F. D. (1977) Thermal and albedo mapping of Mars during the Viking primary mission, *J. Geophys. Res., 82,* 4249-4291.

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

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

Kyser T. K. (1987) Equilibrium fractionation factors for stable isotopes. In T. K. Kyser (Ed.), *Stable Isotope Geochemistry of Low Temperature Processes,* Short Course Handbook, Vol. 13, Mineralogical Association of Canada, 1-84.

LAPST (Lunar and Planetary Sample Team) (1985) *Horizons and Opportunities in Lunar Sample Science,* LPI Tech. Rept. 85-04, Lunar and Planetary Institute, Houston, TX, 32 p.

Laul J. C. (1986) The Shergotty consortium and SNC meteorites: An overview. *Geochim. Cosmochim. Acta., 50,* 875-887.

Laul J. C., Smith M. R., Wänke H., Jagoutz E., Dreibus G., Palme H., Spettel B., Burghele A., Lipschutz M. E., and Verkouteren R. M. (1986) Chemical systematics of the Shergotty meteorite and the composition of its parent body (Mars). *Geochim. Cosmochim. Acta., 50,* 909-926.

MacDougall D. (1973) Fission track dating of oceanic basalts. *Eos (Trans. Amer. Geophys. Union), 54,* 987-988.

Maurette M., Pellas P., and Walker R.M. (1964) Etude des traces de fission fossils dans le mica. *Bull. Soc. Franc. Mineral. Crist., 87,* 6.

McGaw R. W. and Tice A. R. (1976) A simple procedure to calculate the volume of water remaining unfrozen in a freezing soil. *Proc. Second Conf. on Soil-Water Problems in Cold Regions,* Edmonton, Alberta, Canada, 114-122.

Moore H. J. (1987) Physical properties of the surface materials at the Viking landing sites on Mars. *U. S. Geol. Surv. Prof. Paper 1389,* Washington, DC, 222 p.

MRSR SWG (Mars Rover/Sample Return Science Working Group) (1989) *Mars Rover Sample Return Mission Science Objectives Document,* JPL D-6247, Jet Propulsion Laboratory, Pasadena, CA, 34 p.

Naeser C. W. and Faul H. (1969) Fission track annealing in apatite and sphene. *J. Geophys. Res., 74,* 705-710.

Naeser C. W., Engels J. G., and Dodge F. C. W. (1970) Fission track annealing and age determination of epidote minerals. *J. Geophys. Res., 75,* 1579-1584.

O'Neil J. R. (1987) Preservation of H, C, and O isotopic ratios in the low temperature environment. In T. K. Kyser (Ed.), *Stable Isotope Geochemistry of Low Temperature*

Processes, Short Course Handbook, Vol. 13, Mineralogical Association of Canada, 85-128.

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

Oyama V. I. and Berdahl B. J. (1977) The Viking Gas Exchange Experiment results from Chryse and Utopia surface samples. *J. Geophys. Res., 82,* 4669-4676.

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

SSB (Space Science Board) (1988) *Space Science in the Twenty-First Century: Imperatives for the Decades 1995 to 2015 (Planetary and Lunar Exploration),* National Academy Press, Washington, DC, 111 p.

SSEC (1983) *Planetary Exploration Through the Year 2000 - A Core Program*, Solar System Exploration Committee, NASA Advisory Council, U. S. Government Printing Office, Washington, DC, 167 p.

SSEC (1986) *Planetary Exploration Through the Year 2000 - An Augmented Program*, Solar System Exploration Committee, NASA Advisory Council, U. S. Government Printing Office, Washington, DC, 239 p.

SSEC (1988) *Planetary Exploration Through the Year 2000 - Scientific Rationale*, Solar System Exploration Committee, NASA Advisory Council, U. S. Government Printing Office, Washington, DC, 88 p.

Wendlandt W. W. (1986) *Thermal Analysis* (third ed.), John Wiley and Sons, 814 p.

Wood C. A. and Ashwal L. D. (1981) SNC meteorites: Igneous rocks from Mars? *Proc. Lunar Planet. Sci. 12B,* 1359-1375.

Wright I. P., Carr R. H., and Pillinger C. T. (1986) Carbon abundance and isotopic studies of Shergotty and other shergottite meteorites. *Geochim. Cosmochim. Acta., 50,* 983-991.

Wright I. P., Grady M. M., and Pillinger C. T. (1989) Organic materials in a Martian meteorite. *Nature, 340,* 220-222.

APPENDIX A1

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS 77058

REPLY TO ATTN OF TN

MEMORANDUM

TO: Distribution

FROM: TN/Chief, Planetary and Earth Sciences Division

SUBJECT: The Effects of Biological Sterilization on Inorganic Properties of Proposed Returned Martian Sample

NASA is considering the return of material from the Martian surface in the 1980's. Such a sample return is attended with problems of biological quarantine or sterilization. The NASA Administrator has requested some evaluation of the effects of biological sterilization on the inorganic, as opposed to the organic, properties of the Martian material by April 1.

A proper assessment of these effects would require carefully-designed, well-founded experiments and sufficient time in which to do them. The design for these experiments would have to consider a variety of possible simulants based on our best estimates of the compositions of Martian surface materials as well as materials designed to serve as controls for testing other experimental parameters; for example, contamination of the simulant during the sterilization process. The design must carefully establish all protocols for equipment, containers, and handling of the samples under the various conditions of sterilization to be tested.

Some work along these lines has been initiated, with Elbert King serving as the principal representative for inorganic properties (see attached memo). The experiments being done by this group will, no doubt, provide some useful data but because of the time constraint of the April 1 deadline, they are necessarily inadequate in scope and design. We must avoid the danger that those experimental results might be used as a definitive result for a study of the effects of sterilization on inorganic properties. (This problem is well recognized by King and the other participants in the tests.)

We have been asked by NASA's Planetary Programs Office to undertake a somewhat broader evaluation of the problem based principally on existing information. The procedures we will use in order to meet the early deadline are the following: We will discuss the problem of the effects of sterilization with a variety of experts in fields that bear on the problem. We will gather data and their opinions and obtain the right to reference them. We will also gather, through them, a bibliography of supporting information. Finally, we will select a subgroup of the most knowledgeable and interested experts consulted who represent some range in expertise and who have accepted responsibility for gathering the needed information. This subgroup will gather here with several of us at JSC to discuss the information and to prepare a document giving our present evaluation of the problem.

In order to meet the problem as posed, we shall restrict our efforts to the assessment of the effects of biological sterilization on the inorganic properties of returned Martian materials. Biological protocols have not yet been established or tested. The enclosed documentation offers an assessment of the present state of the efforts of biologists to determine the least severe conditions required to assure adequate sterilization. We shall not, in this study, debate the larger issues of whether a Martian sample should be sterilized or whether, in fact, a Martian sample should be returned. Information bearing on those important questions will, no doubt, result from the considerations required to assess the effects of sterilization. Nevertheless, they must be handled as a separate issue.

In order to structure this study, I list below four questions which I believe will serve as a framework for our analysis.

a. What properties should we measure in returned Martian materials?

b. What is the importance of each of those properties toward understanding the original nature of that material, its development while on the Martian surface, and its inferences for the planetary evolution of Mars?

c. What is the potential effect of sterilization on each of these measurements?

d. What further research is needed in order to provide answers to the previous questions?

For purposes of getting the study underway, I have made an outline of a number of areas of concern that should be considered. In that outline, and as a result of discussions with you and others, I have listed experts in the various fields identified. I request that each of you take responsibility for the area of study in the outline below to which you have been assigned. This includes initial contact with the experts listed below, assistance in drawing together all the information, and assistance in organizing the small gathering to write this document and in helping

produce the finished product. Please note that Pete Toulmin of the U.S. Geological Survey in Washington, who has extensive expertise with the Mars Viking program, has agreed to help us in any way he can.

I. Mineralogy and Petrology (W. Phinney)

A. High Temperature Properties

1. General (D. Wones, J. Papike, E. King, E. Roedder, J. V. Smith)

2. Sublimates, Sulfides (B. Skinner)

3. Microscopic Morphology (D. McKay, J. Schopf)

B. Low Temperature Properties

1. Differential Thermal Analysis Studies (D. Anderson)

2. Carbonate Minerals
3. Clays
4. Limonite, Goethite, Etc.

} H. Eugster, J. Hower, B. Jones

II. Chemical Properties (E. Gibson)

A. Lithophile Elements (R. Schmitt, J. Philpotts, L. Haskin, P. Johnson, R. Taylor)

B. Siderophile, Semi-Volatile Elements (E. Anders, G. Reed, L. Silver)

C. Light, Volatile Elements (E. Gibson, K. Kvenvolden, S. Chang)

D. Surface Properties (D. Cadenhead)

E. Redox Effects (M. Sato)

F. Martian Surface, General (P. Toulmin, H. Holland)

III. Isotopes (L. Nyquist)

A. Noble Gases (D. Heymann, P. Eberhardt, D. Bogard)

B. Stable Light Isotopes (R. Clayton)

C. Ages (G. Wasserburg, B. Doe, M. Tatsumoto)

IV. Physical Properties

A. Tracks (B. Price, C. Naeser)

B. Thermal Luminescence (R. Walker)

C. Magnetics (D. Strangway, M. Fuller)

D. General (R. Housley, O. Anderson)

You should feel free to get assistance from other members of P&ESD as needed both to contribute expertise and to assist you in communicating with the outside experts. Every effort should be made to obtain well-documented opinions from the experts with a minimum of impact on their time. Our final document will not be a definitive assessment of the impact of sterilization on the returned Martian sample; it will merely give our best present estimate and identify areas of research that should be pursued before a definitive assessment can be made.

The list of experts given in the outline and topics given in the outline are, of course, not comprehensive. You should add additional people and topics as necessary for us to develop a proper appraisal of the problem.

Please complete your preliminary survey with these investigators as rapidly as possible. In order to meet the desired schedule, we should discuss our progress on February 25 and have the final inputs from all consulted experts by March 11.

Original Signed By
LARRY A [illegible]

Larry A. Haskin

5 Enclosures:
1. Letter from E. A. King, Jr.
   to L. A. Haskin, dtd 2/6/74
2. Report on Mars Surface Sample Return
3. Letter from E. A. King, Jr.
   to S. E. Dwornik, dtd 12/27/73
4. Letter from E. A. King, Jr.
   to D. Young, dtd 2/5/74
5. Summary of the Proceedings of the
   Mars Surface Sample Return Symposium

Distribution:
TN6/Dr. W. C. Phinney
TN7/Dr. P. R. Brett
TN7/Dr. E. K. Gibson
TN7/Dr. L. E. Nyquist

ORIGINAL PAGE IS
OF POOR QUALITY

cc:
TA/Mr. A. J. Calio
TL/Dr. M. B. Duke
NASA Hqs, Mr. S. E. Dwornik, SL
NASA Hqs, Mr. S. I. Rasool, SL
NASA Hqs, Dr. R. S. Young, SL
Dr. B. R. Doe, U.S.G.S.
Dr. J. W. Head, LSI
Dr. E. A. King, Univ. of Houston
Dr. G. J. Wasserburg, Cal Tech

ORIGINAL PAGE IS
OF POOR QUALITY

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS 77058

REPLY TO
ATTN OF TN7

February 19, 1974

Dear

NASA is presently considering the feasibility of returning material from the Martian surface in the 1980's. Such an exercise again raises the spectre of possible biological contamination of the Earth by harmful organisms. One approach to solving this problem is biological sterilization of the sample prior to its return to Earth. We are soliciting your ideas along with supporting data which might pertain to the problem of how a biological sterilization would affect the useful scientific information available from a Martian sample. The NASA Administrator has requested an initial evaluation of this problem by April 1. Quite simply stated, "What useful information is retained in a sample after biological sterilization?" A proper assessment of these effects will require carefully designed, well founded experiments and sufficient time in which to do them. However, the results of our initial survey must go to the NASA Administrator by April 1.

In order to meet our deadline, we are soliciting the advice and opinions of a variety of experts such as yourself. We wish to obtain data, opinions, and the right to reference them in the report. In addition, we will compile a bibliography of supporting information. The report will be put together at JSC the week following the Fifth Lunar Science Conference.

We are fully aware of different views concerning a returned Martian sample. We shall not, in our study, debate the larger issues of whether a Martian sample should be sterilized to meet the requirements of the biological community or whether, in fact, a Martian sample should be returned. The report that we are preparing will be concerned only with the effects of sterilization on a returned Martian sample. The biological protocols have not yet been established or tested. Several sterilization conditions aboard the returning spacecraft are under consideration, however. They are outlined below:

a. Dry heat sterilization in a container open to interplanetary vacuum.

b. Dry heat sterilized in a sealed container.

c. Heat sterilized in a sealed container with water added to produce 80% relative humidity above the sample.

The times and temperatures under consideration include: (a) 150°C (or lower) for 1 month, (b) 200-250°C for 1 week, (c) 300-350°C for 1 day, and (d) heating to incandescence for a very short time!!!

We need your opinions and data in the following areas:

1. What properties should be measured in a returned Martian sample?

2. What is the importance of each of these properties toward understanding the original nature of that material, its development while on the Martian surface, and its inferences for the planetary evolution of Mars?

3. What is the potential effect of sterilization on each of these measurements?

4. What further research is needed in order to provide answers to the previous questions?

Please note that although we are not concerned with design of the sampling device, the sampling method would influence the nature of the sample returned and, therefore, influence the effects of sterilization on that sample.

We wish to have your written opinions and any supporting data which you might have readily available before March 8. We do not wish to impact your already busy schedule, but whatever information you can supply will be most useful in our report. If you have any colleagues who could provide additional help, please contact them.

Enclosed are two documents giving some supportable guesses on the possible composition of Martian materials. We look forward to hearing your opinions and seeing your data.

Sincerely yours,

2 Enclosures

"Nature of the Martian Surface"

In addition to the enclosed summary of physical, chemical and atmospheric properties at the Martian surface, the following additional information has been gleaned from the literature. References are listed at the end. To consider the arguments and data used for the conclusions listed below, please consult the particular paper cited. In case of conflict between the summary (made in 1968) and more recent data, the more recent data probably are preferable.

1. Properties of the planet.

   Mean density = 4 gr/cc (Earth = 5.52 gr/cc) (1).

   Magnetic field is less than 0.03 percent that of Earth; no detectable radiation belt exists (1).

2. Surface temperatures and atmospheric pressure.

   Maximum T = 25°C, average = -62°C, minimum = -100°C (1).

   Total atmospheric pressure 7-20 millibars (1).

   Extensive regions where surface pressure exceeds that of triple point of water (2).

   Near equatorial surface P = 8.9 mbar (max), 4.95 mbar (mean), 2.8 mbar (mean). At Lat. 65° P = 10.3 mbar (max), 8.9 mbar (mean, 7.2 mbar (min) (3).

3. Atmosphere.

   CO_2 >90% (18).

   O_2, O_3, CO trace amounts (18).

   H_2O ≈5-6 millibars pressure (18).

   N_2 upper limit is model dependent (0.5 to 5%) (18).

   Ar model dependent (400 ppm to 10%) (18).

APPENDIX A2

CONTRIBUTORS TO JSC (1974)

According to the copies of correspondence included in JSC (1974, Appendix I), the individuals listed below contributed ideas and information that served as the basis for the 1974 report. For some of the contributors, affiliations in 1987 were different from those in 1974. In each case, the contributor's name is printed as it appeared on the signature line of the letter and the listed affiliation is that last known as of 1987.

Duwayne M. Anderson	Texas A & M University
Raymond E. Arvidson	Washington University, St. Louis
S. W. Bailey	University of Wisconsin
A. E. Bence	Exxon Production Research Co., Houston, Texas
D. A. Cadenhead	University of Buffalo, New York
Michael H. Carr	U. S. Geological Survey, Menlo Park
Raymond Davis, Jr.	Brookhaven National Laboratory, New York
Bruce R. Doe	U. S. Geological Survey, Reston
R. H. Dott	University of Wisconsin, Madison
Samuel Epstein	California Institute of Technology
Fraser Fanale	University of Hawaii
Robert O. Fournier	U. S. Geological Survey, Menlo Park
Clifford Frondel	Harvard University
Michael Fuller	University of California, Santa Barbara
Robert M. Garrels	University of South Florida
Gordon Goles	University of Oregon
Gilbert N. Hanson	State University of New York, Stony Brook
Stanley R. Hart	Massachusetts Institute of Technology
Robert M. Housley	Rockwell International Science Center, California
John Hower (Deceased)	formerly of Case Western Reserve University, Ohio
M. L. Jackson	University of Wisconsin, Madison
Blair F. Jones	U. S. Geological Survey, Reston
Ian Kaplan	University of California, Los Angeles
Keith A Kvenvolden	U. S. Geological Survey, Menlo Park
Michael E. Lipschutz	Purdue University
Kurt Marti	University of California, San Diego
D. McKay	NASA/Johnson Space Center
D. M. Mickelson	University of Wisconsin, Madison
Charles W. Naeser	U. S. Geological Survey, Denver
Tobias Owen	State University of New York, Stony Brook
J. J. Papike	South Dakota School of Mines and Technology
P. Buford Price	University of California, Berkeley
C. C. Patterson (Deceased)	California Institute of Technology
George W. Reed, Jr.	Argonne National Laboratory, Illinois
R. C. Reedy	Los Alamos National Laboratory, New Mexico
John H. Reynolds	University of California, Berkeley
Motoaki Sato	U. S. Geological Survey, Denver

R. A. Schmitt	Oregon State University
J. William Schopf	University of California, Los Angeles
Brian J. Skinner	Yale University
Joseph V. Smith	University of Chicago
D. W. Strangway	University of British Columbia, Canada
M. Tatsumoto	U. S. Geological Survey, Denver
Robert M. Walker	Washington University
H. Wanke	Max-Planck-Institut fur Chemie, Mainz, FRG
S. H. Ward	University of Utah
G. J. Wasserburg	California Institute of Technology
David R. Wones (Deceased)	formerly of U. S. Geological Survey, (Reston)

APPENDIX A3

DEPARTMENT OF THE ARMY
U.S. ARMY COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE 03755

CRREL-RE

11 March 1974

Mr. W. C. Phinney
National Aeronautics &
Space Administration
Lyndon B. Johnson Space Center
Houston, TX 77058

Dear Bill:

In answer to your questions regarding the effects of sterilization on a returned Martian sample, I restrict myself to those aspects bearing on water relationships. A determination of water in the Martian regolith is an important goal of planetary exploration. It is desirable to extract as much information bearing on this question as possible. Ices, frost and other forms of free water likely will be lost or the measurement compromised during sample acquisition and sterilization; combined forms, however, may be preserved if sterilization is skillfully done. Therefore, an analysis of the returned sample for clay minerals and mineral hydrates should be a goal. The clay mineral and mineral hydrate suites revealed in such an analysis would give important clues as to the water regimes experienced earlier by the planet and that now prevail. Too high temperatures during sterilization could cause irreversible water loss, clay lattice collapse and mineral decomposition that would complicate the analysis or render the analysis useless. Temperatures above 200°C are highly undesirable. Chemical sterilization should be considered and the exposure to lethal radiation levels is also an option to be explored. I inclose weight loss (water loss) data illustrative of the problem. It is found on the pages marked and turned down in the inclosed viewgraph package prepared for the planetary soil water analyzer instrument.

Sincerely yours,

for DUWAYNE M. ANDERSON
Chief, Earth Sciences Branch

1 Incl
as stated

ORIGINAL PAGE IS
OF POOR QUALITY

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF EARTH SCIENCES

January 8, 1974

Dr. Stephen Dwornik
Chief, Planetary Programs
Code SL
NASA Headquarters
Washington, D.C. 20546

Dear Steve:

Following is a brief discussion of what we think should be done with Martian samples and what environmental constraints need to be placed on returning, de-contaminating, and handling them. This is written from the point of view of our laboratory only. A more general discussion of other types of measurements that should be made by other laboratories would, of course, add additional constraints. We would be glad to extend any part of the discussion should the need arise.

(1) Delineation of dynamic processes in the Martian environment: This can be examined by cosmic ray particle tracks, rare gas records, and by measurements of thermoluminescence in samples of soil and rock. In addition, observations of rock morphology and surface features (wind abrasion pits and striations, etc.) can help delineate processes modifying the Martian surface.

Cosmic rays easily penetrate the current tenuous atmosphere of Mars producing characteristic effects in surface materials. Both heavy particle tracks and spallation-produced isotopes could be studied to give information about sample surface exposure times and erosion rates. In contrast to lunar samples, solar flare particles would be attenuated by the atmosphere, but there should be no problem with galactic cosmic ray effects.

If a stratified sample of Martian soil could be collected, it would be possible to study the variation in total atmospheric pressure with time. This can be done since additional shielding affects the heavy particles that are responsible for track production much more rapidly than the protons. ~~that~~ would produce a greatly reduced ratio of tracks to spallation products and would also give a characteristic change in the fossil track spectrum.

The amount of thermoluminescence stored in a lunar soil sample depends on its depth below the lunar surface. At the very surface, the TL drains due to surface heating but at greater depths, where the temperature fluctuations are less, the TL first rises and then decreases again. This final decrease is due to an absorption of the cosmic rays originally responsible for the effect. TL studies in lunar samples have proven useful in establishing the depth of certain samples (e.g., half-filled core tubes) and might give important information on Mars concerning the surface motion of materials. We are also attempting to use TL measurements to establish the temperature gradient in the lunar surface, i.e., measure the lunar heat flow. If this is shown to be feasible, it would be an extremely important measurement to make on a Martian core sample.

(2) Evolution of the atmosphere and crust: For samples of any age, rare gas mass spectrometry can be used to determine ages by the ^{39}Ar-^{40}Ar method. This work, which can be done on individual fragments as small as 10 mg, would serve to establish the basic chronology of the planet. Even a simple scoop sample containing numerous small fragments would yield crucial information.

If some of the samples turned out to be extremely old ($\gtrsim 3.9 \times 10^9$ y), the detailed study of extinct isotope effects (^{244}Pu and ^{129}I), which is a speciality of our laboratory, would give a fine scale chronology for the early evolution of the planet.

The study of trapped gases by mass spectrometry might be an extremely fruitful way to investigate the evolution of the planet. Collection and study of an atmospheric sample in concert with gases adsorbed on rock and soil samples would be desireable. Heavy gases such as krypton and xenon may reside primarily on surfaces rather than being free in the atmosphere.

Petrologic and geochemical investigations of rock and soil samples would clearly be an important phase. A formidable amount of information could be obtained from petrologic study of polished thin sections made from Martian rocks. The most obvious observation would be the identification of the major lithologies present in the vicinity of the landing site. Further, since Martian winds may distribute small rock fragments over large areas of the planet's surface, a scoop of soil obtained in one locality might contain samples of rocks that do not outcrop near the landing site. If basaltic rocks are present, as seems likely, inferences may be drawn about the composition of the magmas, their oxygen fugacities, and their pre-and post-eruption crystallization histories from electron microprobe measurements of the compositions of the minerals present. Finally, study of the weathering products of the minerals in Martian rocks would set constraints on the composition of the atmosphere, thereby supplementing direct measurements, and it might also yield data concerning long-term climatic variations.

(3) Sample gathering: Although a simple scoop sample would give much information, it is clear that more information would be obtained from our various measurements with more sophisticated sampling techniques - roving ability, the ability to chip boulders, etc. Perhaps the most important of sampling consideration would be the ability to take a vertical core which might provide a layered structure with a definable chronology.

(4) Handling and sterilization constraints: We now consider the constraints our experimental requirements impose on the sterilization of the samples. These constraints are threefold: exposure to organic materials, exposure to heat, and exposure to light or to penetrating radiations such as x-rays and γ-rays.

ORIGINAL PAGE IS
OF POOR QUALITY

The thermoluminescence work imposes the severest constraints. The samples should not be heated above 100°C or exposed to penetrating radiations. Even exposure to visible light degrades the results and sampling is ideally performed in red light.

Tracks anneal out in different materials at different temperatures. In feldspars and pyroxenes, tracks anneal out in approximately 1 hr at 550°C; however, in glasses they may anneal out in hrs at room temperature or at 500°C depending on the composition of the glass. Extended exposure to temperatures in excess of 300°C would likely wipe out the track work (literally!), but even lower temperatures might severely degrade the information available.

The rare gas work is also constrained by temperature and exposures above room temperature which would degrade the information obtainable. Exposure to organic molecules should be rigorously avoided. Clearly, exposure to the terrestrial atmosphere should be avoided.

The mineralogy and petrology of igneous rocks could be affected by temperatures of a few hundred degrees, depending on the duration of the heating. However, some lunar breccias have textures showing they have never been exposed to temperatures >300°C. Martian analogs of the latter type rocks would therefore be degraded by temperatures >300°C. In contrast to lunar rocks, Martian rocks may have hydrated minerals that could be affected at temperatures as low as 150°C.

(5) Proposed scenario for sample handling: The summary message contained in the last section is simple: Almost any treatment of the samples will result in a degradation of the scientific information contained in them. The problem of sterilization should probably be re-phrased as follows: "What tests can be performed on a portion of any returned sample to ensure that the remainder of the sample can be examined in a pristine condition."

We propose the following scenario for sample handling: (1) gather atmospheric, soil, and rock samples and seal them in light-tight vacuum chambers; (2) return them to an earth-orbiting space station where they can be examined and small portions can be exposed to biological examination; (3) if the results are negative, then the remaining material could be returned to earth. If they are positive, then a portion of the material could be sterilized with an unfortunate, but potentially necessary, sacrifice of information. Some experiments, as for example the track studies and the initial mineralogical and petrographical studies, could be performed directly in an orbiting space station by trained observers using a minimum of equipment.

Both faculty from the Laboratory of Space Physics (C.M. Hohenberg; R.M. Walker) and the Department of Earth Sciences (R.E. Arvidson; G. Crozaz; F.A. Podosek; G.J. Taylor) have contributed to this discussion. Please note that all proposed observations and measurements on a Martian sample could be done at Washington University and all of them have already been applied here to lunar samples.

Cordially,

REA/mb

Raymond E. Arvidson

UNIVERSITY OF WISCONSIN
Department of Geology and Geophysics
Science Hall Madison Wisconsin 53706
Telephone 608 262-2365

February 26, 1974

Dr. W. C. Phinney
N.A.S.A.--Geology
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill,

This letter is in response to your query of February 19 regarding the possible effects of biological sterilization on clay samples returned from Mars.

The following reactions of clay minerals to temperature are relevant.

1. Clays with surface OH groups, such as kaolins, serpentines, and corresponding Fe-compositions start to dehydroxylate around 350°C. The dehydrated phase is X-ray amorphous, and cannot be reconstituted. Temperatures above 350°C, therefore, preclude identification and scientific study of such clays.

2. Clays with 2:1 type layers and H_2O present in the interlayer space will lose their interlayer water as low as 75°-100° C, but do not become amorphous until about 500° to 600°C. For smectite clays (= montmorillonite group) this dehydration is reversible as long as a temperature of 200°-300°C (depending on composition) is not exceeded. Above this temperature the characteristic reversibility of hydration and solvation with organic liquids cannot be studied.

3. Other clay minerals are slightly more tolerant to temperature, but structural changes can be expected in chlorite, sepiolite, and palygorskite above 400°C.

4. Terrestrial smectites sometimes contain organic material in the interlayer space. Indeed, one theory of the origin of life holds that early life forms used the hexagonal clay structure as a template and were shielded in the interlayer space of smectites from an hostile environment. I cannot advise you as to what temperature might change such interlayer material.

Recommendations:

1. 250°C is the maximum permissable temperature, but 150°C would be much safer in view of the unknown types and compositions of Martian clays.

2. A sealed container with 30% relative humidity would appear best for clays, but only if ferrous iron is absent. Distilled water is essential.

Sincerely yours,

S. W. Bailey

CWB:ab

ORIGINAL PAGE IS
OF POOR QUALITY

State University of New York at Buffalo

March 1, 1974

Dr. E. K. Gibson, Jr.
National Aeronautics and
Space Adminstration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Gibson:

Enclosed are my comments on the types of experiments we could complete on possible Martian returns following sterilization procedures. The only thing I seemed to have missed from the list is that we prefer long heating times and low temperatures to short heating times and high temperatures.

Yours sincerely,

D. A. Cadenhead
Associate Professor

DAC:ms

111 ACHESON HALL BUFFALO NEW YORK 14214 TEL (716) 831-2416

Properties to be Measured

1. Gas content and nature on sample outgassing
2. Surface area and (helium) soil specific gravity
3. Soil density and porosity.
4. Gas interactions (physical and chemical) with sample surfaces.

Temperature Conditions

1. Heating to incandescence would mean an almost total loss of all the information which we gather or may be deduced from our studies: nature and amount of gases evolved, surface areas, soil particle specific gravities, soil densities. The outgassing, sintering, changes in the chemical nature of the surface would render our measurements virtually meaningless.
2. As part of our initial preparation of lunar samples for gas interaction studies we have generally outgassed at approximately 150°C assuming this to be a maximum equatorial lunar temperature. In a similar fashion 25°C would certainly be a safe heat treatment temperature for Martian soil, indeed unless Martian materials are substantially different from Lunar materials 150°C would probably have little or no affect on our measurements at least in vacuum. We would expect significant effects to occur as the preheating temperature is raised from 200 to 350°C.

Vacuum Conditions

Obviously exposure to the vacuum of space would result in a substantial loss of information on gas content especially if accompanied by heating. Nevertheless, from the point of the bulk of our measurements we would prefer the use of ultra-high vacuum conditions to high temperatures.

Heat Treatment in a Sealed Container

Simple heat treatment in a sealed container (sample in its own atmosphere) could and would result in sample surface chemical changes accompanyed by a change in both the pressure and nature of the gases present due to catalytic action. Typically, such processes could give rise to a variety of organic molecules or even amino acid precursers depending on the initial gas composition.

We would consider autoclaving with water vapor even more serious since all of our experiments (with lunar materials) indicate that exposure to water vapor at high temperatures can significantly affect surface area and pore structure measurements in addition to possible effects listed above.

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Astrogeologic Studies
345 Middlefield Road
Menlo Park, California
94025

March 5, 1974

Dr. Robin Brett
Code TN-6
NASA Johnson Spacecraft Center
Houston, Texas 77058

Dear Robin:

Enclosed is a very quick write-up on returned Mars samples. I don't like it but it really is all I have time for right now. Sorry I could not put in time and give you something decent.

Yours sincerely,

Michael H. Carr

CC: Masursky

Returned Mars Samples

The analysis of returned lunar samples has completely transformed our concepts of how the Moon formed and what its subsequent history has been. Our present knowledge of the timing of events that led to the Moon's present configuration, the differentiation sequence, the bulk and trace element geochemistry and how it differs from that of the Earth have all been derived from examination of returned samples. The degree to which this understanding could have been achieved soley by remote analysis is a matter of conjecture but here is ample reason to be skeptical. Having lunar samples in hand allowed the complete analytical and intellectual capability of the scientific community to focus on the problem of the Moon's origin. Instead of having a small pre-determined set of analytical techniques applied to the samples, the approach could be both all-encompassing and flexible, the analytical emphasis shifting as the meaning of each set of results become better appreciated. There is no reason to believe that these enormous advantages of returned samples should be any less for Mars. Indeed the apparently more complex geology of Mars enhances the importance of the kind of comprehensive examination that a returned sample allows.

This is not to demean the value of remote analysis. In situ analysis are an essential prelude. Before returning a sample to Earth, selection criteria must be established. We should have some understanding of the degree of crustal differentiation and the extent to which surface materials are fractionated by processes such as aeolian or fluvial action. Only then can we ensure against returning to Earth only fractionated extremes such as a pure quartz sand or an evaporite.

The surface of Mars appears to be markedly heterogeneous, one hemisphere being largely primitive cratered terrain and the other being of later materials. Volcanic and tectonic activity appears to have occurred throughout the planets history, probably up to the present day. Despite the inability of liquid water to exist at the surface, there is abundant evidence of fluvial erosion, seemingly by liquid water, suggesting different past climatic conditions. At the poles, layered deposits may contain a record of past conditions as well as being a repository of volatile compounds. These present concepts, largely established by the Mariner 9 mission, cause the following basic questions to be posed:

1. What is the bulk chemistry of the planet and how does it differ from the Earth, the Moon and meteorites?

2. To what extent is the planet differentiated into separate layers and what is the nature of the layers and the histroy of their formation?

3. Does the hemispheric division of the crust result from a primitive segregation or later erosional and volcanic events?

4. What is the timing and nature of different volcanic and tectonic episodes and how are they correlated with the outgassing history?

5. What is the outgassing history of the planet and the subsequent fate of volatiles on the surface?

An understanding of the fate of volatiles on the surface will immediately result from a returned sample. The efficacy of weathering on Mars is largely unknown. It has been argued that the lack of water to dissolve and remove weathered products results in the formation of a diffusion barrier which prevents further weathering. However, the ability of aeolian processes or adsorbed water to remove weathering products is poorly understood and weathering could be relatively efficient, resulting in large amounts of volatiles being tied up in weathered products. The detailed mineralogy of returned samples will reveal immediately the extent to which weathering has occurred and what the volatiles involved were. Once a weathering model has been established then a meaningful inventory of near surface volatiles can be made. Ages on weathered and unweathered products will allow estimates of rates of accumulation on volatiles in weathered products and place constraints on outgassing models. The chemistry of the volatiles themselves, by comparison with the Earth and the Moon will provide insights into the fractionation histroy of the planet and the primitive solar nebula.

If the large Martian channels are formed by water then evaporite deposits may occur at their mouths. The lack of evaporite would indicate the channels formed by floods of water that have been in contact with the surface for periods of time that are short compared with weathering rates. The presence of carbonates, sulphates and other evaporite minerals would inidcate long periods of run off and evaporation, or residence times for subsurface waters that are long enough to have allowed solution on a large scale.

The interrelation of volcanic activity and outgassing is unclear and of prime importance in understanding the history of present surface. Two general models of outgassing are held. One assumes an early volcanic period with intense outgassing and relatively little subsequent emission of volatiles i.e. later volcanics are relatively volatile poor. The other assumes steady emission of volatiles throughout the planets history. Returned samples would readily resolve the differences.

A wide variety of volcanic features occur on the Mars surface. The extent to which these result from compositional differences is not known but the wide range of morphologic types must surely indicate that chemical differences do exist, both areally and as a function of age. Documentation of the chemical and petrologic characteristics of different types of volcanic rocks and the dating of different volcanic events will lead to an understanding of the variety of Martian volcanic processes and how they differ from those on the Earth and the Moon. More importantly the knowledge will place tight constraints on thermal and compositional models of the interior. Of particular importance here are details of phase relations which would indicate the chemical and physical environment at depths, trace element geochemistry, which would give clues concerning fractionation processes, and the different types of age dates. All these almost certainly require a returned sample. Recent modelling suggests high iron contents in the mantle and peaking of volcanic activity in recent past, but constraints on such models are presently very loose. Returned samples will enable these models to be refined so that they can be used in comparison with the Earth and the Moon to arrive at general models for the evolution of planetary interiors.

The question of whether the crust is differentiated into components analogous to the sial and sima of the Earth is of extreme importance in understanding the early history of Mars and the Earth. The separation of continental masses on the Earth had already been achieved 3.8 b.y. ago, but apparently never occurred on the Moon. The mechanism whereby this was achieved on the Earth, whether it required plate motion, or intensive weathering, is unclear. If Mars represents an intermediate stage, with the two hemispheres being compositionally distinct, then this would provide some insight into how crustal differentiation was accomplished on the Earth. Returned samples will certainly reveal whether the different morphologies of the two hemispheres reflect fundamental compositional differences and whether they are similar to those found on Earth. Detailed chemistry and dates will give clues as to the particuliar mechanism.

One of the most striking results of the lunar sample return program was the unexpected bulk composition of the Moon. The bulk composition of Mars is of even more significance in that it will be the first time we have sampled in another part of the solar system. We will then be in a position to address some fundamental questions concerning the evolution of the solar system such as what was the nature of any chemical inhomogeneities in the solar nebula just prior to accretion, what were the physical conditions which gave rise to the inhomogeneities and did the final accretion give rise to the present array of bodies or an array that was subsequently altered. Unfortunately, bulk composition cannot be directly measured. Its evaluation requires very detailed and subtle knowledge of the chemical balance within the planet. To achieve this, we must have a general understanding of all the processes that have caused chemical change within the planet and the history of their action. Such an understanding can be realized with the kind of comprehensive analytical approach that a returned sample allows.

TYPED COPY OF HANDWRITTEN LETTER

TO: Larry Nyquist

SUBJECT: Sterilization Procedure for Mars Mission and Radioactive Isotopes

The production of radioactive tritium (12.6g) and ^{14}C (5700g) by galactic cosmic radiation in the Mars atmosphere and surface materials could be of great importance in understanding geochemical processes on Mars. An initial determination of the specific activities of tritium in water, and ^{14}C in carbon dioxide, carbonates, and possible organic compounds should be measured on returned materials. These compounds would be in the vapor phase if the sample were in a sealed container. Provisions should be made for removing the gas (via a puncture seal) from the container to measure these activities and make other studies. I can conceive numerous biological and chemical observations that should be made on these gases.

My first thoughts are that the activity determinations would not be severely affected by a mild sterilization if that is deemed necessary. Of the options given in Dr. Clark's letter of February 19, I would strongly favor dry heat sterilization in a sealed container at minimum temperatures, say 150°C for a month.

Sincerely yours,

(Original signed by Raymond Davis, Jr.)

Raymond Davis, Jr.
Brookhaven National Laboratory
Upton, New York 11973

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO:

Branch of Isotope Geology

February 20, 1974

Mr. Larry A. Haskin
Code TN
Planetary and Earth Sciences Division
NASA, Johnson Space Center
Houston, Texas 77058

Dear Larry:

Naturally, I am flattered to receive the various documents regarding a possible sample return from Mars in the 1980's and to have my advice solicited. In the time period available for reply, I fear I cannot give the matter very penetrative thought. My duties the rest of this fiscal year as Vice-Chairman of LSAPT provide me with more action than I can handle in a satisfactory manner, and next fiscal year I will be participating in a minerals program. However, I will furnish you with my best "top of the head" thoughts, which seem to be what is called for at this time.

(1) There are three prime dating techniques that should be pursued:

(a) K-Ar (and $^{40}Ar/^{39}Ar$) method which can also be coupled with rare gas studies (extinct ^{244}Pu, etc.).

(b) Rb-Sr method, which has proven so useful in dating the time of formation of unmetamorphosed rocks or the age of metamorphism on metamorphosed rocks. If Martian rocks returned are "granitic," both rock formation and metamorphic ages might be determined by use of whole-rock and mineral isochrons.

(c) U-Th-Pb method, which also involves two refractory elements (U and Th) as well as one of the best "volatile" metallic elements, Pb. This method offers certain advantages arising from an essentially constant ratio of $^{238}U/^{235}U$ in nature, so far as we know, in permitting a direct solution to two-stage effects. Should

all complicating effects on the ratio of radioactive parent to radiogenic daughter occur only very recently, the U-Pb system is the only one not dependent of the observed value of U/Pb.

(2) The effects of the candidate sterilization procedures on the above techniques will require extensive research work, and I recommend a one-year contract be let on each of the above dating methods to determine the possible effects of the candidate sterilization procedure on the most likely rock types.

(a) If the returned sample is rich in clays, argon may be lost in all heating methods.

(b) We do not know what effects water or CO_2 may introduce to the Rb-Sr and U-Th-Pb systems in the Martian sample case, particularly in destroying internal isochrons, although little effect seems to have occurred to the anhydrous lunar *rocks* (soils are a different matter) under lunar ambient conditions of temperature and vacuum. We do know that about 10 percent of the lead can be volatilized from lunar samples in vacuum heated to 500°C for a few hours.

(3) I am most attracted at this stage to sterilization in a sealed container at the lowest possible temperature, even if for the longest time. However, the Rb-Sr and U-Th-Pb systems on anhydrous *rocks* (not soils) might be least affected, if heated to incandescence for an "instant" at 1 atm of nitrogen. The sealed container would be important to trap released condensibles to judge what actually happened. I hope that other radiative non-thermal sterilization procedures will be investigated (radar waves or some such). I am surprised that cosmic ray exposure for several months during return is not judged sufficient, in fact. Experimentation will be required, and testing effects of sterilization on internal isochrons is a big job.

(4) I would hope that in addition to sterilization protocols, display and political privilege protocols would also be worked out well in advance. I recommend that no more than 10 percent of the returned Martian samples be used for such purposes. In view of the small size of the sample return, three displays would appear to be suitable: a stationary display at the National Museum of Natural History, a traveling display devoted to touring the U. S., and a traveling display to tour UN countries. I feel it is important to prevent the types of dubious practices being applied to lunar samples from recurring on the smaller return of Martian samples.

Sincerely,

Bruce R. Doe

Copies to: Larry Nyquist
Everett Gibson
M. Tatsumoto
G. J. Wasserburg

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA CALIFORNIA 91109

DIVISION OF GEOLOGICAL AND PLANETARY SCIENCES

TELEPHONE 213/ 795-6811

March 11, 1974
RE: TN7

Everett K. Gibson, Jr.
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett,

In response to your letter requesting my opinions regarding the nature of research that could be done on Martian samples in the light of the various degrees of sterilization that they will undergo, I am assuming that you are primarily interested in the sort of work in which I have some expertise, Otherwise if I were to respond to your questions regarding all scientific work that could be done, I am sure that I, like many other of my colleagues, would probably have to write a textbook. On that premise I will make the following comments.

I would consider Mars a stable isotope planet in that like the Earth it should be subject to enormous isotopic fractionation due to a large number of processes of evaporation, low temperature reactions, long term isotopic exchange between the CO_2, H_2O and rocks, and a host of other very important parameters. The isotopic abundances would therefore give very interesting information, making the study of processes of Mars isotopically somewhat similar to the uses of isotopes that can be made on the surface of the Earth's materials. In this sense I believe Mars would be a fascinating planet to investigate isotopically.

(a) Dry heat sterilization in a container open to interplanetary vacuum.

Naturally the less heating and the shorter the time of heating the sample suffers the more desirable would be the sample. Any kind of exposure of the sample to interplanetary vacuum introduces the peril of loss of many volatiles including CO_2, water, CO, H_2, etc., which for my part would be most unfortunate because I believe that the volatiles on Mars could give us an enormous amount of information regarding surface conditions of Mars as well as the history of escape of water and CO_2 from the Martian atmosphere and the nature and perhaps the mechanisms of introduction of these volatiles to the atmosphere of Mars. The isotopic abundances of hydrogen, carbon, and oxygen would be most valuable for these volatile materials. On the other hand as far as the nonvolatile materials like the silicates and other crystallized materials are concerned, low temperature (150°C) sterilization in vacuum would probably not destroy the isotopic equilibrium relationships between the various minerals in which there could be a record of both low and high temperature processes. Under all circumstances there would always be some materials which would be useful for stable isotope analysis irrespective of the degree of loss in interplanetary vacuum provided that the loss is not complete.

(b) Dry heat sterilization in sealed vacuum.

Aside from the choice of bringing back pristine samples from Mars, the driest heat sterilization in a sealed vacuum probably appeals to me most. It would probably preserve much of the gases as well as other volatile materials and, if this sterilization is carried out at reasonably low temperatures, there would be a great deal of samples with their integrity preserved. Again I opt for the low temperature, long period of time rather than heating to incandescence over a very short time. It might be possible, if high temperature is avoided, to measure equilibrium partition between various phases and many of the rare gases that there would be in these samples. This information would be most valuable for understanding the history of Martian rocks.

(c) Heating sterilization in a sealed container with water added to produce 80% relative humidity.

This method of sterilization is almost on a par with heating it in vacuum. Water is an excellent catalyst facilitating oxygen and hydrogen re-equilibration with minerals. There would be a good chance that some hydrous minerals might form in the sample container and so on. Such conditions as (c) might well be tolerable if the water was from Mars but the addition of terrestrial water is again very bad. I would consider this alternative not as good as alternative (b) but better than alternative (a), heating in an interplanetary vacuum. I should like to stress that temperature accelerates processes usually in an exponential way whereas time is much more gentle on rates. The lower the temperature of sterilization, the better I would like it.

Generally speaking then samples from Mars would be extremely valuable almost irrespective of what is done to them in terms of temperature. On the other hand as a general principle the less is added and taken away from them on their way to Earth the better. It appears to me that this is mainly a choice as to which one prefers, high temperature and short sterilization time or relatively low temperature and long sterilization time. I definitely prefer the latter.

As to what research is needed to provide knowledge of the conditions of the preservation of the samples with the type of sterilization, it seems to me rather obvious that one can simply mix all the various things that are listed in the report and subject them to these different sterilization processes.

It is almost impossible for me to sit down and consider all the various molecules that I think exist on Mars and evaluate them from the point of view of what sterilization processes will affect which ones more readily. I clearly believe that stable isotope data of hydrogen, oxygen, carbon, nitrogen, silicon, calcium, etc. will be extremely useful in helping understand the various processes that go on on Mars and the temperature under which they are going on. The preservation of the integrity of these isotopic abundances in the various phases would be most critical. I think that it would probably be best preserved if the Mars sample is sealed and heated to 150°C. Another possibility would be to bring the samples back to Earth and subject them to other forms of sterilization

CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA CALIFORNIA 91109

Dr. E. K. Gibson, Jr. - 3 - March 11, 1974 RE: TN7

like soft X-ray radiation which might kill all biological life but still preserve the integrity of the chemical and isotopic compositions. Such a possibility is not mentioned in your letter and it seems to be that such should be considered in some cases.

I would probably be able to discuss this a little more intelligently in a face-to-face discussion. I would therefore be happy to get together with you perhaps at the lunar conference regarding this matter. In any case feel free to phone me.

Good luck on your Mars project. Best regards.

Yours truly,

Sam

Samuel Epstein
Professor of Geochemistry

SE:bac

TYPED COPY OF HANDWRITTEN LETTER

JPL Memorandum

TO: Larry Nyquist

FROM: Fraser Fanale

"Low temperature" mineralogy crucial/clay and iron hydroxide etc., as coatings on surfaces. These are easy to make in Martian environment and tell us more about surface condition than details of high T petrology.

This stuff is delicate, and would be destroyed at intermediate temperatures 300°-500°C. ∴ low T long time advisable.

We don't want to lose the gas coming off and we want to give the rock a chance to reconstitute itself; e.g., replacement of interlayer H_2O in montmorillonite. On other hand, we fear that an unaltered igneous rock might "stew in its own juice" and get altered during sterilization. Therefore, cold trapping of volatiles is best.

Obviously we need to put various mineralogies through these hoops. One neat way to do this would be to run various candidate assemblies through the various sterilization time/temperature cycles twice on a Differential Scanning Calorimeter/Evolved Gas Analyzer. Then one could tell the effect (from the endotherms and simultaneous EGA peaks) that the time/temperature cycles and volatile trapping mechanisms each have on various assemblages in terms of producing irreversible changes. I have such a setup and will let you know if I get around to getting any good data on this.

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Geologic Division
Branch of Experimental Geochemistry and Mineralogy
345 Middlefield Road, Menlo Park, California 94025

March 13, 1974

Mr. William C. Phinney
ATTN of: TN7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

I have just turned my attention to your memo of February 19 concerning possible effects of sterilizing a returned Martian sample prior to arrival on Earth. Owing to the lateness of this reply and pressure to prepare several other reports this week, I will have to make my comments short.

I assume that other consultants have enumerated the many reasons for wanting to determine the petrography, mineralogy, oxydation state, and degree of hydration of the various materials in the sample at the time of collection. My main area of expertise lies in the field of hydrothermal water-rock reactions, and I shall comment only on option C, "Heat sterilization in a sealed container with water added to produce 80% relative humidity above the sample." My opinions are based mainly on several experiments (unpublished data) in which I have reacted individual minerals and rocks with water and salt solutions for various lengths of time at temperatures ranging from 200° to 300°C and 100% humidity. Under those conditions, the amount of reaction depends in great part upon:

1. The temperature and duration of the experiment - a very rough empirical rule is that reactions double their speed with an increase in temperature of 10°C (at 300°K) (S. W. Benson, 1960, p. 66, The foundations of chemical kinetics, McGraw-Hill, N.Y. 703 p.)

2. The energy driving give reactions to occur - Phases that are not far from equilibrium or that require high activation energies will undergo little, if any reaction. On the other hand, highly metastable materials such as glasses tend to react very quickly. Glass hydrates, devitrifies, and reacts with adjacent crystalline phases to form new minerals, generally zeolites and clays.

In regard to the Martian sample, I think that there generally would be more reaction at 300-350°C in one day than at 200-250°C for one week. Similarly, there would be more reaction at 200-250°C for one week than at 150°C for one month. However, in all cases, there could be drastic changes in the oxidation state of [redacted]. All of the original iron oxide minerals might be destroyed and new ones formed. Any glass in the sample (volcanic and meteor impact melt) would certainly hydrate and probably would devitrify (especially at 200°C+). There is a good chance that the glassy material would react with crystalline silicate rock fragments as well as carbonates and sulfates. Alteration products are likely to be many different zeolites. Any original sublimates are not likely to survive. Montmorillonite may react with carbonates and sulfates to yield new calcium and magnesium silicates. This would be particularly true above 250°C.

I hope that these brief and sketchy comments will be of some help to you.

Sincerely,

Robert O. Fournier

HARVARD UNIVERSITY
DEPARTMENT OF GEOLOGICAL SCIENCES

CLIFFORD FRONDEL
Professor of Mineralogy
Curator, Mineralogical Museum

GEOLOGICAL MUSEUM, 24 OXFORD STREET
CAMBRIDGE, MASSACHUSETTS 02138

March 8,1974

Dr. Robin Brett,TN7
Manned Spacecraft Center,
Houston, Texas,77058

Dear Robin :

With respect to the Martian sample,I will confine my remarks to the sampling,adsorptive nature and sterilization of particulate material in the sub-micron and colloidal range of size.

The Martian surface environment must act as an efficient colloid mill. The high wind velocities, low atmospheric pressure and very low temperature should reduce the surface particulate material in part to sizes far below those attainable by natural processes on Earth or on the Moon. The low temperature produces embrittlement and restrains chemical attack. On Earth, very fine material is ultimately removed by chemical attack,although it may have a relatively long life span in very dry and/or very cold environments. On the Moon, where very fine material could be produced attending impacts the high temperatures tend to destroy it by coalescence or vaporization.

The Martian fines are of interest because of the possible content of microscopic spores of biological origin. They are of great interest both mineralogically and,in particular,in their content of surface adsorbed material.

Particulate material in the sub-micron range, especially below about 1000A,because of the large surface area relative to the volume of the particles,stores a relatively large amount of adsorbed material. What would be adsorbed depends on what was in the Martian atmosphere and on the chemical and physical nature of the adsorbent. Since adsorption can be highly selective,some things present in the atmosphere - possibly organic molecules - could be wholly removed and stored in this way.

---

(1). With regard to properties that should be measured on a returned Martian sample of sub-micron material

(a) Particle size and shape examined by SEM and TEM techniques.
(b) Identification of the specific mineral phases by electron diffraction,etc.
(c) Examination for spores or other biological materials
(d) Evaluation of biological hazards
(e) Bulk chemical analyses of the sample and of individualized fractions thereof.
(f) Study of amount and kind of adsorbed material

(2) Thermal sterilization involves the following matters :

(a) Desorption of material held on surfaces. The temperature needed for desorption depends on the nature of the adsorbent and adsorbate or,more generally,on the nature of the forces holding the material to the surface. Molecular compounds held by van der Waals forces would come off at temperatures probably well below 200°C; chemosorbed material may be retained at temperatures well over 200°C. Changes in the adsorbent itself brought about by thermal treatment are a factor here.

Thermal sterilization of the fines should be done stepwise,say at 25°C intervals upwards from room temperature,with removal of the desorbed material from the container at each step.

Sampling of the adsorbed gases,etc.,may perhaps be best done on the Martian surface. A relatively large sample could be heated in a sealed container brought for the purpose - the heat provided by a built in chemical source - with the desorbed material trapped out cryogenically in a receptacle that can be sealed,detached and returned. The Martian environment certainly is cold enough to trap out at least the heavier molecules.

(b) The particulate material presumably would be enriched in mineral components resulting from the chemical breakdown on the Martian surface of primary igneous minerals. They hence could be expected to contain H_2O, OH and CO_3 as essential primary constituents. Compounds containing such constituents in general are not very stable thermally. An upper limit for thermal sterilization precluding such decomposition is not easily stated, especially if the particle size is extremely small and if the pressure of the substances is not known beforehand. The lower the temperature of sterilization the better, with a maximum of 150°C probably OK, over 250°C probably bad, and over 350°C certainly bad. Because of the relatively large surface area entering effects also come into question at the higher temperatures. The thermal decomposition of any organic compounds present is an added problem.

(5). Studies of the following matters preparatory to [illegible] would be helpful :

(a) The samples of finely divided dirt borne particulate material is a well developed field in which [illegible] doubtless could get good advice from the AEC.

(b) The sampling of surface deposits of very finely divided particulate material, especially if incoherent, with preservation of internal layering, is not a well developed field. Impregnation by a liquid polymerizing at low temperatures might preserve some information.

(c) Laboratory studies should be made of the adsorption and desorption of O_2, H_2O, CO_2, CO and H_2O on powders of known particle size, using goethite, hematite, siderite, quartz, pyrolusite, kaolinite, diaspore, montmorillonite, plagioclase and pyroxene.

(d) Laboratory studies of the thermal decomposition of goethite, etc., as a function of particle size, both in vacuum and at 1 atm. CO_2 or air.

Finally, if the LRL is to be reconstituted with the original staff and equipment, and the Martian samples examined therein, research should be done on where to move Earth's population so that it has some chance of survival.

Best regards,

Clifford Frondel

ORIGINAL PAGE IS
OF POOR QUALITY

FACULTY OF ARTS AND SCIENCES
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15260

DEPARTMENT OF EARTH AND PLANETARY SCIENCES
506 Langley Hall

March 14, 1974

Dr. Robin Brett
NASA - Lyndon B. Johnson Space Center
Houston, Texas 77058 ATTN: TN7

Dear Robin:

I enclose the notes on the possible effects of various proposed sterilization procedures on the magnetic information carried by Martian samples. It is my understanding in doing this that others will consider the question of whether Martian samples should be returned to earth as opposed to being studied in some latter day sky lab, etc. Sorry these notes are, as usual, late. They slipped by in my schedule somewhere.

As a starting point, we may ask what we may learn from Martian samples by magnetic observations. By now it is clear from terrestrial, lunar, and meteoritic samples that if we can understand their primary NRM, or even secondary NRM associated with a particular event in the sample's history, we can obtain a record of ancient magnetic fields experienced by the rock. Hence, the principle aim in the Martian work would presumably be to get a record of the ancient Martian magnetic field. If we ever get bedrock samples, they may give results relevant to structural geology of one sort or another. In addition, we can use magnetic observations such as hysteres classification which characterize the magnetic phases to help our understanding of the rocks themselves.

Assuming that our aim is to obtain a record of the ancient field of Mars and to characterize the magnetic phases of the rocks, we now need to consider the necessary observations. These are, quite simply, the measurement of the NRM and its demagnetization characteristics, and of such basic rock magnetism parameters as saturation magnetization, saturation remanence, susceptibility, etc., which permit characterization of the magnetic phases.

At this point we need to make use of the current wisdom for the Martian surface to give us some idea of the nature of the probable carriers, and the environment in which they were formed. An important parameter for the magnetic observations is the diurnal temperature cycle. Unlike the lunar diurnal cycle, its maximum is not significantly greater than the temperature in the laboratories in which the rocks will be measured. This means that any heating will degrade the magnetic results. The Martian samples are unlike lunar samples which have been thermally cycled to 100°C in the present low surface fields of the moon, so that they have essentially been thermally demagnetized to approximately 100°C. Hence, subsequent heating of lunar samples to 100°C should not destroy useful information due to simple thermal demagnetization. In contrast, we will destroy potentially useful information by heating Martian samples since we will certainly thermally demagnetize them. Nevertheless, heating Martian samples to 150°C or even to 300°C may

still not be a disastrous treatment providing that the magnetic carriers are not seriously degraded by the heating. If the heating were carried out in a shielded region, then this could effectively be a first step in a thermal demagnetization, a procedure which would probably be carried out eventually anyway. Even if it were carried out in a magnetic field, this magnetization could possibly be unscrambled eventually.

The most difficult problem then is to assess the effect of heating on the magnetic phases themselves. If, as the current wisdom suggests, the NRM may be carried by hydroxides and hydrated salts, then heating even to 150°C, could be disastrous. The properties of the relevant mineral species are relatively well known; their Curie points and fields of stability are, in part, in this low temperature range (20-300°C). There does not seem to be much point in giving detailed consideration to particular minerals, in view of our very limited knowledge of Martian surface. Suffice it to say, that if these compounds are really important, then heating to even 150°C may be disastrous. If, on the other hand, current wisdom turns out to be unwisdom and most of the NRM is carried by iron and iron-nickel, or even Fe_3O_4 or Fe_2O_3 hematite, heating to 300°C will be a relatively unimportant problem and good magnetic data should be obtainable.

In summary:

	ASSUMPTIONS	
Heating	1) Magnetism carried by compounds of low temperature stability	2) Magnetism carried by Fe°, FeNi, Fe_3O_4 and Fe_2O_3
150°C	Bad	OK
200-250°C	Worse	OK
300-350°C	Probably disastrous	OK providing care is taken to avoid oxidation of these phases
Incandescent	Forget it!	Forget it!

dehydration

I hope these comments will be of some use to you. Perhaps we should get together with Dave or a few of the other members of the magnetism club and talk about this at the Conference next week.

All very best wishes,

Michael Fuller
Professor

lkt

cc: Dr. King

ORIGINAL PAGE IS
OF POOR QUALITY

University of Hawaii at Manoa

Department of Oceanography
2525 Correa Road • Honolulu, Hawaii 96822
Cable Address: UNIHAW

March 1, 1974

Dr. Robin Brett
Lyndon B. Johnson Space Center
NASA
Houston, Texas 77058

Dear Robin:

About the Martian samples: I should think drying part of them at 150°C, with splits heated with water vapor present, would be quite reasonable in terms of preserving most stuff. I don't think it would do much to montmorillonites, except take out the interlayer water. Too bad interlayer water can't be measured; at 25°C the last two water layers are lost at less than the saturation pressure for water -- in fact water content is a rather delicate measure of vapor pressure. Anyway, I assume direct measurements will be made of H_2O pressure in situ. And the montmorillonites will take it back up again.

Abundant iron oxide, as well as traces of O_2, would seem to preclude much $FeCO_3$. The CO_2 pressure is OK, but $FeCO_3$ oxidizes with more traces of oxygen at a pretty good clip. Color change of the samples with 150°C drying from brown to red would be good indication of goethite originally. By the way, it is still not clear whether FeOOH or Fe_2O_3 is the stable species at 25°C in presence of water. But on Mars, with low H_2O pressure, hematite would be expected.

It would be an interesting exercise, for which there is not time now, to calculate expected weathering phases at H_2O vapor pressures less than that for liquid H_2O at low temperature. I suspect people like Danny Milton already have played that game.

These are about all the comments I have at the moment. I could probably respond better to direct questions than make suggestions.

Cynthia and I send our best.

Sincerely,

Robert M. Garrels

UNIVERSITY OF OREGON

CENTER FOR ...

EUGENE, OREGON ...

Telephone ...

7 March 1974

Dr. Everett K. Gibson, Jr.
Code TN7
NASA L. B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

I am sorry to be so late in responding to your letter of 15th February, but with the end of the term upon me I have been seriously swamped with chores related to the two courses I am teaching. Consequently I have not had a chance to organize my thoughts on the sterilization problem very completely, nor have I put together supporting data of the kind you would like to have. Nevertheless, under the assumption that something is better than nothing, I would like here to respond to the very interesting questions you raise.

As background information, let me point out that our primary interest in a returned Martian sample would lie in the general area of petrogenesis and studies of clastic transport and mixing processes, as it does for the lunar specimens. We would like to know the compositions of the various types of soil particles and rock fragments present in the returned sample, reading "compositions" as meaning not only chemical but also mineralogical compositions, including such features as structural states of minerals and the degree and nature of abraison of grains. Others may well have other interests and inherent requirements, but I shall treat our requirements based on our interests. I think it is obvious that these properties are of extraordinary, perhaps primary, importance in drawing inferences about the planetary evolution of Mars.

Sterilization by heating to incandescence, even for a very short time, would be grossly destructive of a great deal of important information of this kind. I simply cannot envision that anyone could do control experiments adequate to tell us how such treatment would change the contents of elements like the alkalies, halogens, carbon compounds, water, etc., and these components are likely to be very informative in outlining a history of the Martian soil (see, for example, the arguments in the accompanying reprint; the history of water contents in the Martian shallow lithosphere are probably written in part at least in the hydrated minerals of the soil). Furthermore, heating to incandescence would certainly destroy the records originally held by the mineral phases in the soil, records of the kinds of rocks available for incorporation in the regolith and of the transport processes which moved them about. Clay minerals, which should be an important and very interesting component of the Martian soil, would be destroyed by such a treatment. I think it is simply unacceptable as an alternative.

Sterilization in a sealed container with 80% relative humidity would probably not change significantly the overall composition of the sample, but would grossly perturb both the mineralogical character and the distribution of elements among grains. It

would probably destroy micro-scale surface features which would if preserved help greatly to understand modes of transport of clastic materials. It goes without saying that such treatment would destroy any records of the history of f_{H_2O} in the Martian atmosphere that might be present in the sample, and it is easy to see that such records are at least of as much interest to exobiologists as to the rest of us. I conclude that while slightly less destructive than heating to incandescence, this approach is also unacceptable.

Heating in vacuum for any substantial period is likely to dehydrate clay minerals (but probably not goethite — see the arguments about kinetics in the enclosed reprint), but judging from the substantial amount of information which can be obtained from dehydrated or partly dehydrated clays in carbonaceous chondrites, that is not a major objection. I judge that, especially at 150 to 250 °C, there will be no significant destruction of information on chemical composition, and it is easy to predict that there will be no damage worth mentioning to microscale surface features. Consequently, I vote for one form or another of these treatments. Obviously we need to undertake control experiments to establish that a protocol of that kind will reliably sterilize the sample, and in so doing we could usefully test its effect on the properties I have mentioned. If I can be of assistance in carrying out such control experiments, such as by running INAA analyses before and after, please let me know. We would probably need minor funding to do very much of that kind of work, but could sneak a few comparison samples in under our lunar funding.

Best regards,

Gordon

Gordon Goles

StonyBrook

State University of New York
at Stony Brook
Stony Brook, New York 11790

Department of Earth and Space Sciences
telephone: (516) 246-6540

March 13, 1974

Dr. Laurence E. Nyquist - TN7
National Aeronautics and Space
Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Larry:

I am sorry this is going to be a bit late.

I will answer quickly the aspects particularly regarding sterilizing on Ar dating. My experience with heating of samples has been mainly in stepwise heating in vacuum for $^{40}Ar/^{39}Ar$ dating of basaltic rocks, biotite muscovite and hornblende (unpublished data) and a heating experiment in the atmosphere for the effects of heating on the loss of argon from biotite (Hanson 1971, see enclosed). In the biotite heating experiment it can be seen that biotite from a rock heated for 10 days at 600°C in N_2 atmosphere loses about 30% of its argon. In a vacuum furnace muscovite, biotite and hornblende heated to 700°C for one hour, less than 3% of their argon. Basaltic rocks lose up to 12% of their argon at 700°C for one hour, but generally less than 3%. Amirkhanoff, Bandt and Bartnitsky (1961, Radiogenic Argon in minerals and its migration, Annals of New York Academy of Science, V. 91, p. 235-275) have heated feldspars as well as Mias at low temperatures, 100-400°C.

From my experience, I would suggest that dry heating in nitrogen or vacuum at temperatures of 300°C and less for ten's of hours will give less than 1% loss of radiogenic argon from the above minerals and rocks. I would suspect that it would also have a negligible effect on Rb-Sr systematics as much higher temperatures are necessary to see any movement in Rb-Sr system, see Baadsgaard and Van Breeman, 1970, reference in the enclosed reprint. Enclosed is a table of our unpublished results on $^{40}Ar/^{39}Ar$ samples. I have given the first two temperature steps of one hour heating and the percent of argon lost at each step.

Sincerely yours,

Gilbert N. Hanson

GNH:hf

PS. I'd HAVE THIS RETYPED BUT I THINK YOU WOULD RATHER HAVE THE INFORMATION RIGHT AWAY

FROM $^{40}Ar/^{39}Ar$ STUDIES

SAMPLE	TEMP. °C	% Ar LOSS AT TEMP. STEP
MC 2531 B Basalt	700°C	1.3
	800°C	6.8
MC 2544 B Basalt	700°C	2.95
	800°C	9.37
MCB 87 Basalt	700°C	3.92
	800°C	5.64
AN 3-9 Basalt	700°C	2.79
	800°C	21.63
MN 9 Basalt	700°C	5.19
	800°C	13.26
ON 22 Basalt	700°C	4.79
	800°C	12.50
~~P 164 Basalt~~ TIGH BASALT	600 ~~600~~°C	1.45
	700°C	4.77
[illegible] BASALT	500 ~~800~~°C	1.71
	700°C	1.24
MN 38 Basalt	700°C	11.66
	800°C	22.24
LS 14 Basalt	700°C	3.38
	800°C	19.10
RP 1 Rhyolite	700°C	3.43
	800°C	11.94
MN 7 Hornblende	900°C	1.9
	1000°C	43.4
NL 25 Hornblende	700°C	.51
	900°C	.73
NL 25 Hornblende	700°C	.85
	900°C	.78

ORIGINAL PAGE IS
OF POOR QUALITY

M[illegible]254 Biotite	700°C	2.41
	800°C	14.33
M[illegible]252 Biotite	700°C	1.20
	800°C	16.37
M 7003 Biotite	700°C	1.62
	800°C	21.67
M 7001 Biotite	700°C	0.66
	800°C	16.39
M[illegible] Biotite	700°C	1.90
	800°C	16.54
[illegible] Biotite	700°C	2.87
	800°C	35.72
[illegible]250 Biotite	700°C	0.96
	800°C	24.87
M 7058 Biotite	700°C	1.91
	800°C	22.39
M 7061 Muscovite	700°C	2.41
	800°C	4.88
M 7047 Muscovite	700°C	0.93
	800°C	3.04
M 7045a Muscovite	700°C	0.90
	800°C	3.21
M 5222 Hornblende	700°C	1.73
	800°C	2.90
M 5220 Hornblende	700°C	0.50
	800°C	1.87
M 5217 Hornblende	700°C	0.50
	800°C	0.49

ORIGINAL PAGE IS
OF POOR QUALITY

CARNEGIE INSTITUTION OF WASHINGTON

DEPARTMENT OF TERRESTRIAL MAGNETISM

5241 BROAD BRANCH ROAD, N. W.

WASHINGTON, D. C. 20015

TELEPHONE: 966-0663
AREA CODE 202

March 7, 1974

Dr. Larry Nyquist
NASA
Johnson Space Center
Houston, Texas 77058

Dear Larry:

In reply to your request for comments on the possible effects of sterilization procedures on returned Martian samples, I can only offer brief comments based on areas of my own research, because of the tight time requirements you set forth.

Obviously Martian samples should be analyzed in much the same way lunar samples have been. Studies of various volatile gases have been very important in lunar studies and can be expected to be at least as important in Martian studies. All of these gases will be potentially adversely affected by any of the thermal sterilization procedures you outlined, with perhaps the least damaging of the procedures being the low temperature-long time dry sterilization. One solution would be to do the sterilization under conditions such that all the evolved gases could be collected (under ultra-clean conditions) for later measurement. This, of course, essentially requires duplication of the sophisticated state-of-the-art extraction equipment used by many investigators. This procedure will still destroy much crucial information, as it will mix gases from different phases so that the gas contents of individual mineral phases are no longer determinable. Overall, it would seem more sensible to develop techniques for evaluation of biological activity in space, before the samples are introduced to earth.

As a specific example, consider the K-Ar dating of returned samples. Many silicate phases will retain argon when heated to several hundred degrees for weeks, but there are also many phases, especially hydrous minerals, which will suffer significant Ar loss under these conditions. I have enclosed several reprints which deal with problems of thermal diffusion of argon. There is a very large body of published work on this subject, and I suspect most potential questions can be answered by reference to work already in the literature. On the other, the diffusion characteristics of the other rare gases, all of which are important (solar wind studies, xenon chronology, etc.) are very poorly known and would require further study before being useful in evalution of sterilization procedures.

As far as non-volatile elements (such as those used for major element chemistry, Rb-Sr dating, U-Pb isotopic studies, etc.), I would guess that 150°C dry for periods of several weeks would not produce serious mobility problems. Thus, a significant amount of research could still be carried out on such sterilized samples, but this work would still not in any way substitute for the gas studies, as far as answering many fundamental questions concerning the chronology of Mars.

I'm sorry I can't give your request a more thorough reply but March 8 isn't very many days away!

Sincerely yours,

Stanley R. Hart

Stanley R. Hart

Science Center
Rockwell International

P. O. Box 1085
1049 Camino Dos Rios
Thousand Oaks, California 91360
(805) 498-4545

March 7, 1974

Dr. Robin Brett/TL7
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

Enclosed is a write up of my initial thoughts on a set physical properties measurements which I think would be valuable on a Martian return sample. Initial thoughts regarding sterilization are also discussed and additional information which would be helpful in choosing between alternatives outlined. I hope this is helpful and look forward to further discussions.

Sincerely yours,

Bob Housley

Robert M. Housley

Enc.

SOME PHYSICAL PROPERTIES STUDIES ON A MARTIAN SAMPLE

The ultimate goals in studies of returned Martian material must be to learn as much as possible about the initial chemistry of Mars, about its subsequent chemical and physical evolution, and about its interactions with the rest of the solar system.

Although the Martian atmosphere is dense enough to prevent appreciable interaction of solar wind or solar flare particles and micrometeorites with the surface we must still anticipate that Martian surface material may be considerable more complex than lunar fines. At least the following primary constituents might be present;

1) Meteoritic debris including microtektites and spherules,
2) Volcanic ash,
3) Comminuted primary igneous rocks, and
4) Comminuted hydrothermally altered rocks exposed by erosion or large impacts.

These constituents may all have been altered by weathering and wind erosion processes in past and present Martian atmospheres and thermal regimes. The extent to which the original nature of particles can be recognized and the depth to which many questions can be answered depends on the severity of these weathering and erosional processes. On the other hand the weathering itself may contain information about past atmospheric compositions and temperatures.

In view of the varied possibilities it seems that any measurement that might give unique information about the physical or chemical state

of the sample must be seriously considered at this time. Several such experiments together with the type of information they might give are mentioned below.

Mössbauer Spectroscopy: Determines the valence state of Fe and the identity and relative abundance of major Fe containing phases. Can have unique value in the study of altered and/or amorphous phases and characterization of submicroscopic phases.

EPR: Can detect organic free radicals with high sensitivity. Can be useful in the study of magnetic phases and can detect magnetic remenance in very small samples.

Optical Spectroscopy: Useful for correlation with telescopic observations.

Magnetic Probing: If returned sample is a core this might provide quick information on stratigraphy.

Auger and ESCA Spectroscopy: Might detect evidence of any recent exposure of the grain surfaces to reactive gases, for example, gases associated with volcanic activity.

Gas Interaction Studies: Can be useful in characterizing clay minerals and might provide insight into the nature of Martian weathering processes.

Brief consideration of the temperature dependence of chemical reaction rates and diffusion rates suggests that heating option (a) 150°C (or less) for one month would always be preferable to a higher temperature treatment. The choice of atmospheric environment however does not seem to be as clear cut. Each option would protect certain possible information or constituents in the sample at the expense of others.

It appears that we really need experimental data which will allow us to reliably estimate weathering reactions and their rates on the probable primary sample constituents under reasonable past and present Martian conditions and in the sterilization chamber with the possible atmospheric environment options. A rough guess suggests that one month in a sealed chamber at 150°C might produce weathering effects similar to about 100,000 years on the Martian surface and hence would not lead to any great loss of information.

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF PHYSICS BERKELEY, CALIFORNIA 94720

March 12, 1974

Dr. Robin Brett
Chief, Geochemistry Branch
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

Please include the following as an addendum to my letter of 22 February 1974.

The thin Martian atmosphere and weaker (than terrestrial) gravitational field may permit relatively "soft landings" of cosmic dust that could be identified by means of solar wind coatings and solar flare tracks. In stagnant areas protected from dust storms there may be a sedimentary history of cosmic dust fluxes relating to fluxes of comets, etc.

Another aspect of the thin atmosphere is that most cosmic rays can build up "air showers" leading to muons, which in term will interact in Martian rocks before decaying. Muon archeology could be done by means of mass spectrometry of specific reaction products, and possibly also by track studies.

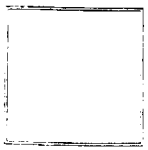
I believe it would be useful to calibrate minerals thought to form on Mars. Both accelerator bombardments and long-term annealing experiments would be worthwhile. Clay minerals have never been subjected to track studies before.

Yours sincerely,

P. Buford Price

PBP:mk

CASE WESTERN RESERVE UNIVERSITY · CLEVELAND, OHIO 44106



March 19, 1974

Dr. W.C. Phinney Attn: TN7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

Here are some comments on the treatment of Martian surface samples with respect to sterilization procedures and what properties should be measured in a returned Martian sample.

Because it seems possible that the Martian soil contains clay minerals that were hydrated in the past (or possibly hydrated somewhat even now) I think that the lowest temperature sterilization temperature possible would be the best. This is not, of course, to preserve any water that might be present, for that is out under any conditions of sterilization, but to preserve the structures intact as much as possible and to prevent dehydroxylation. The irreversibility of dehydration of terrestrial hydrated clays appears to be related largely to structural re-arrangements that take place at higher temperatures, rather than the simple removal of the interlayer water. I have enclosed a table showing the rehydration characteristics of montmorillonite and vermiculite after being heated to differing temperatures. These are all short-term (less than 24 hour) heating times, but the results certainly show that if the hydrated clays are heated much above 200°C for even a short time their hydration characteristics are irreversibly altered. I would choose the lowest temperature possible, heating in a sealed container at 80% relative humidity. Under these conditions virtually all terrestrial clays are refractory to any significant chemical reaction even for long times of treatment. For example, montmorillonite is unaltered by heating in a distilled water solution at 5 atm. at 165°C for as long as three months Eberl (1970). A small amount will, of course, go into solution, but the bulk phase remains nicely intact. The 80% RH will also help prevent either dehydroylation of structural (OH) or any interlayer hydroxy-metal complexes that might be present - these are very common in terrestrial hydrated clays (Rich, 1968).

The properties that should be measured include: (1) Mineral identification, of course. What the Martian surface material turns out to be like in terms of particle size will determine the techniques used. If much turns out to be very fine grained, a combined x-ray diffraction/petrographic study would probably be most beneficial. If clays are present, the x-ray diffraction method, supplemented by some infrared and electron microscopic work would be best. (2) Chemical analysis of the bulk sample, plus, if possible, chemical analysis of any mineral separates it is possible to make. (3) If enough

Department of Geology

material is present, K/Ar and, perhaps, Rb/Sr age measurements should be made. By analogy with terrestrial soils, chemical alteration of a parent rock to a soil often alters the age little or none ( ), because daughter and parent are lost at the same rate.

I think that if the sterilization procedure used is the lowest temperature possible and in a sealed container with a reasonable relative humidity it will be possible to say a considerable amount about the past availability of water at the Martian surface on the basis of the clay mineral assemblages present (assuming they are!). It would be good, however, to have some really long-term, low-temperature (100-200°C) heating experiments in a hard vacuum of the common clays (both hydrated and non-hydrated) to see what the effects will be on their structure - particularly the re-hydration characteristics of naturally hydrated clays.

Hope this will do you some good. Best wishes.

Sincerely,

John Hower,
Professor

JH:ab

enclosure

Eberl, D.D. (1970) Experimental diagenetic reactions involving clay minerals. unpub Ph.D. Thesis Case Western Reserve U

Rich, C.I (1968) Hydroxy interlayers in expansible layer silicates. Clays and Clay Min, 16, 15-30

ORIGINAL PAGE IS
OF POOR QUALITY

THE UNIVERSITY OF WISCONSIN

COLLEGE OF AGRICULTURAL AND LIFE SCIENCES
Madison, Wisconsin 53706

Department of Soil Science

March 8, 1974

Dr. Robin Brett
National Aeronautics and Space Administration
Lydon B. Johnson Space Center
Houston, TX 77058

Re: Your letter of Feb. 19, 1974

Dear Dr. Brett:

I enclose a brief outline of possible experimentation on Martian silts and clays that should be useful in tracing former planetary climates.

← Now Iowa State Soil Sci. Dept

Dr. Phil Helmke has an interest in trace element signatures which he can make with NAA, as he did in the lunar program, working with Dr. Larry Haskin.

Effects of the possible sterilization procedures are stated with reference to these types of study.

Dr. David M. Mickelson, glacialogist of the UW-MSN Geology and Geophysical Department, believes that a study of the particle surface morphology by scanning electron microscopy should be carried out to study abrasion patterns bearing on eolian and fluvial transport history.

We would appreciate your keeping us informed on your sampling proposal.

Cordially yours,

M. L. Jackson
Professor of Soil Science

MLJ/bp

Enclosure

Greetings to Dr. Johnson & Dr. Haskin
mlj

Evidence from Silts and Clays of Martian Paleoclimate

M. L. Jackson -- U. Wisconsin-Madison

Eolian effects on Mars were confirmed by Mariner 9 (Masursky et al., 1972) and changes in light and dark streaks were confirmed during the course of a dust storm (Sagan et al., 1972). Wind tunnel experiments simulated the light and dark streaks about craters, permitting differentiation of depositional from erosional features (Greeley et al., 1974).

Research: Expectation that the dusts are in the 1 to 100 μm range suggests that chemical isolation (Syers et al., 1968; Jackson, 1969; Henderson et al., 1972) would be needed for oxygen isotopic ratio determination of quartz silt, if indeed, quartz occurs in Martian silt (mainly basaltic composition is the common concept).

Variation of quartz isotopic ratio occurs in silts between Northern and Southern earth Hemispheres in the Pacific (Clayton et al., 1972) and adjacent continental areas (Jackson et al., 1973; Churchman et al., 1974). Higher values in the fine silt quartz in the Northern Hemisphere is attributed to a higher chert content (heavy oxygen) relative to that of igneous and metamorphic provenance (Jackson et al., 1971). The higher chert content reflects continental paleoclimatic history, i.e. residence time in reef-forming tropical and equatorial climates during continental drift northward. Whether Martian silt contains quartz which originated during past periods when liquid water existed (like earth lagoonal-weathering regimes) should be available from oxygen isotopic ratio of fine-grined monomineralic quartz isolates such as my laboratory has specialized in making (Henderson et al., 1972). Cross-correlation of this with the possible formation of clays such as montmorillonite from mafic rocks (Wildman et al., 1968) should be carried out, including oxygen isotopic ratio determination

(Henderson et al., 1971; Weaver et al., 1971). The fate of rare earth elements and transition elements during weathering should be determined (Haskin et al., 1973; Helmke et al., 1973).

The earth hemispheric variation observed in oxygen isotopic ratios concords with well-recognized paleomagnetically determined drifting of the Northern Hemisphere continents through reef-forming tropical and equatorial regions during 2 to 6 x 10^8 years involved in the sediment ages from which the shales, dusts, and soils were formed. Scarcity of limestones and dolomites in temperate latitudes of Southern earth Hemisphere continents attest to their not having passed through the equatorial region since the Precambrian; some intercalated strata of Precambrian marbles in Rio Grande du Sol suggest the possibility of earlier passages. Australia's Great Barrier Reef illustrates reef-building (later to be raised into a continent?) on entering the tropics from the south in the last 10^8 years or so. Isolates of quartz from Martian silty sediments should be studied and might help determine the plate tectonics involved thereon.

Sterilization: Sterilization of Martian silt at 150°C-350°C (conditions a, b, or c) would not have any effect on the quartz oxygen isotopic ratio (Syers et al., 1968; Sridhar et al., 1974), but ignition would. Fe-montmorillonite would be decomposed above 350-400°C, but not below. More common Al, Mg-montmorillonite would survive to 500-550°C. Extensive lunar work shows that 150°C sterilization would volatilize Hg, As, Na, K, and Pb; however, the more refactory elements would not be affected by the sterilization at 150°C and could be traced through any weathering regime that has occurred.

References:

Churchman, G. J., R. N. Clayton, K. Sridhar, and M. L. Jackson (1974) Source reservoir of aerosol-sized eolian quartz. To be submitted to J. Geophys. Res.

Clayton, R. N., R. W. Rex, J. K. Syers, and M. L. Jackson (1972) Oxygen isotopic abundance of quartz in Pacific pelagic sediments. J. Geophys. Res. 77:3907-3915.

Greeley, R., J. D. Iversen, J. B. Pollack, N. Udovich, and B. White (1974) Wind tunnel simulation of light and dark streaks on Mars. Science 183:847-849.

Haskin, L. A., P. A. Helmke, D. P. Blanchard, J. W. Jacobs, and K. Telander (1973) Major and trace element abundances in samples from the lunar highlands. Proc. 4th Lunar Conf., Supplem. 4, Geochim. Cosmochim. Acta 2:1275-1296.

Helmke, P. A., D. P. Blanchard, J. W. Jacobs, and L. A. Haskin (1973) Rare earths, other trace elements and iron in Luna 20 samples. Geochim. Cosmochim. Acta 37:869-874.

Henderson, J. H., M. L. Jackson, J. K. Syers, R. N. Clayton, and R. W. Rex (1971) Cristobalite of authigenic origin associated with montmorillonite in bentonites. Clays Clay Miner. 19:229-238.

Henderson, J. H., R. N. Clayton, M. L. Jackson, J. K. Syers, R. W. Rex, J. L. Brown, and I. B. Sachs (1972) Cristobalite and quartz isolation from soils and sediments by hydrofluosilicic acid treatment and heavy liquid separation. Soil Sci. Soc. Amer. Proc. 36:830-835.

Jackson, M. L. (1969) Soil Chemical Analysis--Advanced Course. 2nd Ed. Published by the author, Dept. of Soil Sci., Univ. of Wis., Madison, WI 53706.

Jackson, M. L., T. W. M. Levelt, J. K. Syers, R. W. Rex, R. N. Clayton, G. D. Sherman, and G. Uehara (1971) Geomorphological relationships of tropospherically-derived quartz in soils of the Hawaiian Islands. Soil Sci. Soc. Amer. Proc. 35:515-525.

Jackson, M. L., D. A. Gillette, E. F. Danielsen, I. H. Blifford, R. A. Bryson, and J. K. Syers (1973) Global dustfall during the Quaternary as related to environments. Soil Sci. 116:135-145.

Masursky et al. (1972) Science 175:294.

Sagan et al. (1972) Icarus 17:346.

Sridhar, K., M. L. Jackson, and R. N. Clayton (1974) Oxygen isotope variation with quartz grain size as a result of diversity of source. To be submitted to Soil Sci. Soc. Amer. Proc. (Agron. Abstracts 1973:150).

Syers, J. K., S. L. Chapman, M. L. Jackson, R. W. Rex, and R. N. Clayton (1968) Quartz isolation from rocks, sediments, and soils for determination of oxygen isotopes. Geochim. Cosmochim. Acta 32:1022-1024.

Weaver, R. M., M. L. Jackson, and J. K. Syers (1971) Magnesium and silicon activities in matrix solutions of montmorillonite-containing soils in relation to clay mineral stability. Soil Sci. Soc. Amer. Proc. 35:823-830.

Wildman, W. E., M. L. Jackson, and L. D. Whittig (1968) Iron-rich montmorillonite formation in soils derived from serpentinite. Soil Sci. Soc. Amer. Proc. 32:787-794.

Determination of the transport history of
Martian mineral grains by identification of
grain surface characteristics

R. H. Dott and D. M. Mickelson
Department of Geology and Geophysics
University of Wisconsin-Madison

Since the advent of the scanning electron microscope, several workers (Krinsley and Margolis, 1969; Krinsley and Smalley, 1972) have succeeded in identifying characteristic surface features on sand grains which were deposited in different sedimentary environments. Thus far, glacial, eolian, fluvial, and coastal environments have tentatively been identified on the basis of these surface features. This technique is presently being refined (by Dott and Mickelson as well as others) by the study of sand grains from modern sedimentary environments.

The application of the method is obvious for Martian samples. It has been suggested that running water, wind and perhaps other transport agents are responsible for erosional and depositional features seen on Mariner Photographs (Sagen et al., 1973; NASA Summary). Characteristics of grain surfaces should give indications of the relative importance of these sediment transport processes.

Further research must be done on silt sized particles. Until now nearly all research has been on sand grains. Also, most work so far has been on grains of quartz. Other minerals might be more abundant and therefore more appropriate for the Martian samples.

Sterilization should not affect surface features of grains unless grains are fused. We know of no experimental results on this aspect. Rapid temperature change may cause grains to shatter, destroying surface textures.

References cited

Krinsley, D. H. and S. V. Margolis, 1969. A study of quartz sand grains with the scanning electron microscope. Trans. N.Y. Acad. Sci., v. 31, p. 457-477.

Krinsley, D. H. and I. J. Smalley, 1972. Sand. Am. Sci., v. 60, p. 286-291.

Sagen, C. J., J. Veverka, P. Fox, R. Dubisch, R. French, P. Gierasch, L. Quam, J. Lederberg, E. Levinthal, R. Tucker, B. Eross and J. B. Pollack, 1973. Variable Features on Mars. 2. Global Results. J.G.R., v. 78, p. 4163-4196.

United States Department of the Interior
GEOLOGICAL SURVEY
12201 SUNRISE VALLEY DRIVE
RESTON, VIRGINIA 22092
Mail Stop #432

March 29, 1974

Dr. William Phinney, NASA
L.B.J. Space Center
Houston, Texas 77058

Dear Bill:

This will reach you under the oft-used cliche' "too little, too late," but in view of our move and attendant chaos, it is the first opportunity I have had to consider the problem, even feebly.

The only materials I can comment on are the clays and iron oxides. Basically, after mucking about with the stability data for Fe phases at low temperatures I subscribe to the Berner thesis (Geochimica Acta, 1969, p. 267-273) that the stable iron oxide will be hematite, with any sterilization procedure simply hastening the demise of metastable oxy-hydroxide. Similarly, the background material provided suggests that the montmorillonoid phase will be dominated by some sort of "iddingsite", that is, a mix of Fe oxide + nontronite. Others on your list may have more definitive data, but I would suspect that almost any heating performed on such material in the total absence of H_2O vapor will alter the nature of structural hydration, particularly if discrete Fe oxide interlayers, such as in the "dioctahedral vermiculites" of soils, are present. I would recommend experimentation with such materials to ascertain what atmosphere, if any, can compensate, with respect to structural hydration, for the heats applied. Another item with which I have had some specifically bad experience is amorphous silica coexistent with such a phase. Low temperature heating (60°C) caused irreversible dehydration of the silica, with resulting formation of aggregate impossible to disperse for oriented x-ray examination.

I was surprised as the author of the summary that available evidence indicates low abundance of carbonates. However, some calculations on aqueous CO_2 species and guesses for iron hydroxy-silicate (greenalite) suggests (with enormous temerity) that Fe silicate may be stable relative to siderite in the presence of condensate. The sterilization procedures raise the whole spectre of re-crystallization, but I have no idea of the consequences.

Sorry I don't have more.

Sincerely,

Blair

Blair F. Jones

TYPED COPY OF A HANDWRITTEN NOTE

Dr. Everett K. Gibson
NASA-JSC, TN7
Houston, TX 77058

Dear Ev,

I have given your letter of February 15 some thought. There are two major aspects which you wnat us to address ourselves to (1) what studies need to be undertaken on returned Martian samples and (2) how should samples be treated prior to their returned to Earth?

Studies on Mars Samples

It is obvious that no simple investigator can outline a detailed account of what needs to be carried out. A good model to follow is the studies presently being carried out on Lunar returned samples but also to include some of the studies which were initially carried out after Apollo 11 and 12 missions, when there was a possibility that organic coumpounds or traces of water may have been present. In particular, it appears important to concentrate on minerals which characteristically form at low temperatures out of on agneous environment. On earth, these usually become included in sedimentary rocks.

Such sediments may include chlorides, sulfates and carbonates. Lack carbonates would indicate very low pH of solution. Lack of sulfate may indicate low O_2 fugacity and lack of chloride would suggest a very brief period for water contact and leaching. Unlike the earth, where exchange occurs within the ocean, on Mars which many have contained only ephemeral bodies of water K and Mg may be as important as Na and Ca in forming salts.

In addition to soluble salts, one should find clays which arise from agneous weathering of acid volcanics as well as zeolites which form from the weathering of basalt and volcanic ash. Oxidizing conditions should show goethite rich sediment dominant, reducing conditions or anoxic conditions may show abundant troilite. Intermediate conditions may produce, pyrrhotite, greigite on pyrite. Such low temperature minerals could then be used to determine the partial pressure of oxygen in the Martian environment when the minerals formed.

Isotopic Measurements

A variety of isotopic measurements should be performed. (1) δO^{18} and δD separated from water in contact with sediment should be informative in determining exchange mechanisms between oxygen containing minerals and the water. Extrapolating backing the data, one should be able to find a δO^{18} - δD relationship which on earth is responsive to altitude and latitude. One should also be able to determine primitive δO^{18} and δD and compare these values with terrestrial values. (2) δC^{13} in various froms of carbon may tell us if there has been biological cycles. In meteorites, δC^{13} of organic compounds is ≈ -17 0/00, on earth values <-30 are known. If organic matter is found, it very important to identify the nature of the process by δC^{13} measurements. (3) $\delta S31$ is a very good indication for biological processess. Sulfide produced would be enriched in δS^{32}, contrary to what has been found in either lunar rocks or meteorites.

Effects of Sterilization

My belief is that low temperature heating experiments will do very little to alter the composition and characteristics of the minerals. From experiments carried out in my laboratory, we believe organic matter decomposes most speadily under dry heat. Heating to 200°C for one week produces CO_2 and other products equal to heating the sample for one worth at 150. It is probable that 150°C will be the minimum acceptable temperature of sterilization. I believe that prolonged heating (1 month or less) under dry conditions, will cause little isotopic exchange or sample distinction. On the other hand, heating in the presence of added water could cause substancial alteration and isotopic exchange in the mechanisms.

I would therefore suggest, that for maximum presentation of the original conditions of the Martian surface it is better to heat at (a) the lowest temperature possible and (b) under dry conditions. I believe that by heating to only 150°C, the ateration may be minimum on negligible in terms of inorganic substances.

Sincerely yours,

Original signed by Ian Kaplan

Ian Kaplan

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER
MOFFETT FIELD, CALIFORNIA 94035

REPLY TO
ATTN OF LPE:239-9

March 4, 1974

Dr. Everett K. Gibson, Jr.
NASA-Johnson Space Center TN7
Houston, TX 77058

Dear Everett:

Thank you for your letter of February 15, 1974, which finally reached me last week. As you know my major interests are in organic geochemistry and organic cosmochemistry, and the sorts of molecules that I have been concerned with are extractable in some kind of solvent and are usually classed as non-volatile organic compounds, (i.e., amino acids, fatty acids, hydrocarbons, etc.). Although your letter does not specify exactly, I presume that at the present time you are not soliciting comments with regard to the effects of sterilization on these kinds of substances but rather are asking me to focus my attention on the alteration in chemical properties of light, volatile elements. I assume this based on a copy of a memorandum by Larry Haskins, dated February 11, indicating the areas of research for which you and others at JSC will be responsible. If I assumed incorrectly please let me know, and I will provide whatever I can concerning changes in the organic chemistry upon sterilization treatments.

As you well know my knowledge about light, volatile elements is not extensive. I rely on Sherwood Chang for sophisticated detail in this area, and I presume that he will respond, as you requested, with a detailed consideration based on the work that you and he have done together. About all I can do at this time is state some generalizations which I think must be kept in mind throughout this research effort.

(1) Returned martian samples must be examined for the same light, volatile elements that have been sought in lunar samples.
(2) The same or similar techniques must be applied so that the data resulting from returned martian samples can be compared directly with what is known about the moon.

(3) Both the organogenic elements (C,N,H,O,S,P) and inorganic volatile elements should be examined, but I would stress the importance of the organogenic elements and their volatile compounds which might lead to information related to the organic history of Mars.
(4) Two general procedures have been used for volatile organogenic elements -- pyrolysis and hydrolysis. Application of these same procedures should be extended to martian samples.
(5) In studies of terrestrial and lunar samples heating as in dry heat sterilization is usually avoided except when contamination can be removed by the heating process. Therefore, there is little experimental data at present with regard to the effects of heat on the residual elements.
(6) For lunar samples your work suggests that heating (dry) at 150°C for 1 month would not alter greatly the results you obtain at higher temperatures in your pyrolytic gas released experiments. At 200-250°C for one week I would guess that the samples would still retain useful information for you. At higher temperatures undoubtedly severe alteration of the residual material would result. If carbides occur on Mars as they do on the moon, I would guess that they would remain fairly stable at conditions below 250°C for all time conditions listed.
(7) Wet heat sterilization would cause problems at all temperatures. Even at 150°C with water I would guess that significant carbide hydrolysis would take place. If carbides are not a significant constituent of martian samples perhaps wet sterilization at lower temperatures could be used, but I suspect that the inorganic geochemistry and mineralogy would suffer.
(8) Experiment must be designed to answer the specific questions you ask. As stated (5) the sort of treatment envisaged for martian samples is avoided in most geochemical studies. Therefore a series of martian analoguesshould be subjected to the prescribed treatments and the resulting alteration determined. For example industrial and meteoritic carbides should be examined in light of the sterilization protocol. A small amount of lunar sample should be sacrificed to see how its properties alter with sterilization.

3.

Other martian analogues might be terrestrial basalt, carbonaceous meteorites, etc. With these kinds of experiments it can be determined what sterilization protocols are acceptable and unacceptable.

I regret this little report is so sketchy and provides no hard data, but to me this suggests the need to acquire data to answer your questions. Rest assured that we are very much interested in the subject of returned martian samples and in their analyses. We would like to help in anyway we can to supply information needed at this time or in the future.

Best regards and good luck,

Keith A. Kvenvolden
Chief, Chemical Evolution
Branch

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING
WEST LAFAYETTE, INDIANA 47907

February 27, 1974

Dr. Everett K. Gibson, Jr.
Code TN 7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

Thank you for your letter of February 15 regarding questions relevant to the possible return of Martian samples to earth. Before attempting to answer these questions let me give you a little background information regarding some of our recent experiments supported by NASA Grant NGL 15-005-140.

As you know, for some years we have been concerned with measuring certain elements, particularly volatile ones, by a combination of neutron activation analysis and atomic absorption spectrometry. The samples studied have been mostly primitive meteorites (i.e. carbonaceous, enstatite and unequilibrated ordinary chondrites) and from the abundance patterns and patterns of interelement relationships we have been examining various models for the formation and evolution of solid material condensed from the solar nebula. About 14 months ago we began a series of investigations dealing with the effects of extended heating of primitive material to simulate thermal metamorphism. Since we had no idea of the possible effects we decided to concentrate upon one primitive meteorite, the C3 chondrite Allende. We have been heating samples of this chondrite in closed systems at 100° increments over a temperature span of 400-1000°C. In most experiments the duration of heating has been arbitrarily set at 1 week (in one case we heated samples at 500°C for 29 days) and the ambient atmosphere has been H_2, initially at $\sim 10^{-5}$ atm (we are currently analyzing separate runs at 1000°C in which O_2 and He were the ambient gases at $\sim 10^{-5}$ atm initially).

In our studies (in some cases in collaboration with others) we are investigating effects of thermal treatment upon: trace element abundances; mineralogy and petrology; stable oxygen isotopic composition; nature of the organic compounds evolved. We are arranging to have the retention of noble gases examined also and to extend these studies to temperatures up to 1500°C when a suitable reaction vessel is successfully tested. From the trace element standpoint we have been analyzing for Co, Ga, Se, Bi, Tl and In (listed in order of increasing depletion, i.e. presumed volatility, in equilibrated ordinary chondrites relative to C1 chondrites) in both 100 mesh powder and chunks (~5-8 mm) of Allende. We are now extending these studies to other primitive meteorites and will determine an additional 5 elements (Ag, Cs, Te, Zn and Cd) together with the 6 elements listed above.

With that lengthy introduction let me now proceed to the questions you raised.

1. Properties to be measured in returned Martian samples. Clearly a number of important experiments could be suggested and I will enumerate those which I personally feel to be the most important and interesting. It would be desirable to determine all of the chemical elements in each sample. Since this probably cannot be done I would suggest that the following would be the most important: volatile/chalcophile elements - noble gases, halogens, Ag, Bi, C, Cd, Co, Ga, Ge, In, N, Pb, S, Se, Te, Tl, Zn; siderophile elements - Au, Co, Cu, Ir, Ni; lithophile elements - alkali metals, rare earth elements, Al, O, Th, U; major elements - e.g. Ca, Fe, Mg, Mn, Si. It will be essential to investigate the mineralogy and petrology of the samples and their ages. It will also be necessary to investigate the isotopic composition of stable isotopes of C, H, O, Pb and S and it would be useful to determine amounts of molecular gases (e.g. H_2O, CO, CO_2, etc.) present in the samples.

2. Importance of measurements. Determination of the elements listed above should permit establishment of the main Martian geochemical fractionation processes including core formation and mineral formation. Information on volatile/chalcophile and siderophile elements should permit assessment of meteoritic contribution to the Martian surface although weathering effects may complicate the picture. The prevalence of fumaroles should also be indicated by data for these elements. The importance of age determinations (Rb/Sr, Pb/Pb, U, Th/He, K/Ar) are self-evident as are mineralogic and petrographic investigations. Investigation of the composition of stable isotopes of the elements listed may lead to an understanding of the meteorological conditions on Mars and/or the formation temperature of various minerals.

3. Effects of thermal sterilization. Sterilization will affect some of the parameters listed above to a greater or lesser extent depending on the conditions used. From our experiments we know that the retention of Ga, Se, In, Bi and Tl

ORIGINAL PAGE IS
OF POOR QUALITY

decreases (in that order) with heating. At 1000° all 5 are lost to some extent while at 400° only Tl is lost (all heating times 1 week) from Allende. We guess that in other primitive samples similar results will occur; we should have further information on this by May 1974. We guess that the other volatile/chalcophile elements listed in answer to question 1 will also be lost by heating; in some cases we will have information on this in May. We know that the mineralogy and petrology of Allende is altered by heating at temperatures ≥ 700°C and we guess that such effects would be evident at lower temperatures for such clay minerals as montmorillonite. We guess that the ages of samples would be affecte by thermal treatment because of loss of noble gases. We guess that re-equilibration of stable isotopes of C, H, O, Pb and S will occur as a result of steril ization (we should have information on this shortly) and that molecular gas concentrations will also be affected. Naturally carbon-based organic compounds wil be affected since that is the purpose of the heating. I guess that magnetic properties and other physical properties (thermoluminescence, etc.) will also be affected by heating.

4. Further research needed. If a decision to proceed is made it would be enormously helpful for a decision to be made on the sterilization mode to be use since this would reduce the number of necessary experiments. From the standpoin of "damage" to the samples I feel that dry heat sterilization in a sealed container at the lowest temperature would be least harmful. If this can be decided upon it will be necessary to conduct experiments on likely geologic samples to assess effects upon the various parameters. As mentioned we will be doing some of these experiments shortly under the aegis of our NASA grant. In addition we presently have a proposal under consideration by the NSF to conduct similar investigations on some terrestrial geologic samples.

I hope that the above is of use to you. If you have any further questions please feel free to ask them and I'll try to answer them promptly. I look forward to seeing your report to the Administrator.

With best regards,

Michael E. Lipschutz
Professor of Chemistry
and Geosciences

cc: Dr. Hosterman, NASA
Dean Andrews, Purdue
Dr. Benkeser, Purdue
Dr. Davis, Purdue
MEL:JHB

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY
REVELLE COLLEGE

POST OFFICE BOX 109
LA JOLLA, CALIFORNIA 92037

March 19, 1974

Dr. L. Nyquist, TN7
NASA/Johnson Space Center
Houston, Texas 77058

Dear Larry:

As a follow-up of our telephone conversations, I will summarize below my opinion and recommendations with regard to the type and temperature history of returned samples from the Martian surface.

1. A sample return from Mars requires the consideration of possible biological contamination of Earth by harmful organisms. This question appears to be more appropriate than in the case of lunar sample return.

2. With regard to possible sterilization, I think nobody has any idea as to what kind of organisms have to be considered, and, therefore, it seems to be extremely hard to specify a maximum temperature and time for the sterilization. To be absolutely safe, a very high temperature would be required.

3. A high sterilization temperature would scientifically degrade the Martian samples to a very large degree (this applies to physical, chemical, isotopic properties and others).

4. A minimum of gas phase and gas-solid reactions is obtained if the sterilization is carried out in a sealed container in a vacuum or near-vacuum. Also this makes it possible to analyse the reaction products in the gas phase and also diffused gases.

5. Since the gas phase of a sealed sample container will almost certainly differ from the composition of the Martian atmosphere, a sample of the Martian atmosphere should be taken in a sealed container. I would like to stress the scientific importance of such a sample.

6. Based on the arguments discussed above, I suggest the following scheme of sample return. At least three sealed containers should be returned; two sample containers, one with a sample of the Martian atmosphere. The first sealed sample container should be heated to a high temperature to effectively sterilize the samples.

The second sealed sample container should not be sterilized. A sterilization of the second container, which would be stored in the sealed condition, should be made contingent on the results obtained from the sterilized samples. It is possible that only a mild or no sterilization will be required, therefore maximizing the scientific information available from these samples. I will be glad to discuss any of the above suggestions and others in more detail with you.

Sincerely yours,

Kurt Marti

KM/mls

ORIGINAL PAGE IS
OF POOR QUALITY

TO: Dr. Larry Nyquist, TN7
JSC

24 March 1974

FROM: Dr. Kurt Marti

Here are some additional comments on the Martian samples you requested:

7. A biological sterilization would release an unknown percentage of radiogenic, spallogenic and implanted gases. This would, of course, invalidate radiogenic ages and exposure ages based on gas concentrations. On the other hand, ages based on isotopic data of a single element such as ^{39}Ar-^{40}Ar, ^{81}Kr-Kr are expected to be unaffected by sterilization. Information on extinct elements should be extractable, even if the samples have been heated.

8. A sample of atmospheric gases is expected to give important information such as a) composition of early atmosphere, b) solar wind contribution to the Martian atmosphere, c) diffusion of gases into the atmosphere.

9. Sterilization will affect information on regolith dynamics. However, parameters such as hardness of irradiation, neutron effects and shielding can now be obtained from the isotopic composition of heavy rare gases and therefore will be little affected.

XC: K. Marti

ORIGINAL PAGE IS
OF POOR QUALITY

D. McKay

INTRODUCTION

In 1965 NASA negotiated a small contract with Bendix Corporation and the University of Michigan to study the effects of the lunar surface environment (mainly the heating and cooling cycle) on certain minerals. The results of this study are summarized in a report to NASA and are given in more detail in a Master's Thesis by Franklin F. Foit, Jr. in the Geology Department at the University of Michigan. As it turned out, the results of this study were not particularly pertinent to lunar minerals (with the possible exception of Geothite) but may be much more applicable to Martian minerals.

The study consisted of two parts. First all available thermodynamic data was used to estimate the stability field of 10 selected minerals under temperature conditions of -180 to +130°C and at high vacuum. Secondly, actual minerals were heated in vacuum in a mass spectrometer and volatile species were monitored as a function of temperature to determine the kinetic stability of each of the 10 mineral groups.

Results

Some of the more pertinent results are as follows:

Goethite decomposes to hematite and H_2O at about 130°C in a matter of minutes at moderate pressures (10^{-6} torr).

Calcite: Under high vacuum (10^{-12} mm Hg of CO_2 pressure), calcite breaks down at about 200°C. However, in short heating runs (~2 hours), calcite did not break down until temperatures of about 500°C were reached.

Calcium montmorillonite: This layer mineral loses its interlayer water under moderate temperatures (100-300°C) at 1 atmosphere. If the mineral is not completely dehydrated, it becomes hygroscopic and readily absorbs water when reexposed. Under moderate vacuum conditions (10^{-5}) considerable water is lost even at 100°C.

Gypsum: At 100°C and 1 atm., gypsum will dehydrate to hemihydrate and at slight vacuum (1 mm) will dehydrate to anhydrate. Under moderate vacuum (10^{-6}) gypsum dehydrates at quite low temperatures ± 30°C.

Other minerals that may decompose under 200°C vacuum conditions include Serpentine, Natrolite, and possibly actinolite.

SUMMARY: Many common low temperature environment minerals were shown by this study to be unstable at moderate heating under vacuum. It is likely that some of these minerals may be present on Mars and it is equally likely that they would be seriously degraded by the proposed sterilization techniques. A study should be made of the actual effects of these breakdown reactions. This study should include X-ray diffraction on a hot stage and scanning electron microscope observation on a hot stage. Only with this kind of detailed study will all the effects of heating become apparent.

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO

Branch of Isotope Geology

February 27, 1974

Dr. Robin Brett
N. A. S. A.
Johnson Space Center
Houston, Texas 77058

Dear Robin:

Enclosed you will find a short report on the effects of proposed sterilization on charged particle tracks.

I hope this will be helpful to you.

Sincerely,

Charles W. Naeser

1. Materials suitable for charged particle track studies should be present on the Martian surface. Carr (1973) has pointed out a number of features on the Martian surface which are volcanic in origin. Most minerals present in the volcanic deposits are capable of recording charged particle tracks. Probable minerals would be; pyroxenes, feldspars, olivine, and accessory zircon and apatite. Impact events are also common on the Martian surface (Hartmann, 1973). The glass produced during the impact can also be used as a charged particle track recorder. Only montmorillonite, a probable component, would probably not be useful as a track recorder. The expandable nature and fine grain size of montmorillonite make it almost impossible to etch.

2. Studies of charged particle tracks in returned lunar material have provided important information on the history of the lunar surface. Fleischer and others (1971) were able to reconstruct the post crystallization history of rock 12017. This was accomplished by looking at the charged particle track record in pyroxene, feldspar and glass phases that made up this rock. By looking at the tracks in the green glass spherules, Fleischer and Hart (1973) were able to determine that the glass has been at the surface for a relatively short time. Fleischer and others (1970) were able to say that down to a depth of at least 12 cm, the lunar surface is constantly being stirred. This was determined by looking at the fossil track densities in anorthite, glass, and augite grains found in the lunar soil.

than (2), considering the reported observation that goethite is more stable than hematite at activity of water greater than 0.6 (Schmalz, 1956). Unfortunately, only values for unstable $Fe(OH)_3$ are found in standard reference sources. The reaction is within the realm of possibility on Mars.

The fourth alternative is that the oxidation was caused by preferential escape of hydrogen originated by the thermal dissociation of water in the late magmatic to duteric stage. Formation of ferric oxide probably due to this mechanism was observed and described in Hawaii (Sato and Wright 1966) and elsewhere. There are other pieces of evidence which suggest that oxidation by this mechanism is prevalent in magmas which contain water. Sato et. al. (1973) pointed out a possibility that the difference in the oxidation state between terrestrial and Lunar igneous rocks is due primarily to the difference in the initial water content of magma, which in turn is due to the difference in total mass between the two planets. The smaller Moon lost much of water (a light-weight molecule) at the time of formation because of its small gravitational field, whereas the larger Earth retained a considerable amount of water.

The oxidation state of the Martian rocks is of extreme interest because the mass of this planet and probably the water content fall between the Earth and the Moon. The escape of hydrogen would be easier if a planet is smaller. On the other hand, the internal water content would be less if a planet is smaller, as discussed earlier. It may turn out that Mars represents the optimum planetary size for the oxidation of magma by hydrogen loss.

The intrinsic oxygen fugacities of mafic minerals indicate the course of change in oxidation state of a magma (Sato 1972). Terrestrial basalts show a tendency of increasing oxidation with decreasing depth (Sato unpublished data), whereas lunar basalts show an opposite tendency (Sato et. al. 1973). Examination of the intrinsic oxygen fugacities of Martian igneous minerals would show which way the oxidation state of Martian magma changes with depth (or at least with the degree of crystallization). This information would most likely be a crucial clue to the understanding of the mechanism of control of the oxidation state of magmas in the Solar planets.

iv) The composition of volatiles in any rock is an important information to obtain. Volatile compounds control the origin of atmosphere, hydrosphere and life. Photosynthesis requires the availability of CO_2 and H_2O to produce high-energy compounds such as carbohydrates. Without these photosynthetic products, higher organisms may not operate.

Volatiles also play an important role in controlling the oxidation state of igneous and metamorphic rocks as partly pointed out by Sato et. al. (1973). Volcanic activities depend heavily on the volatile components in magma. Explosive volcanic eruptions and ash falls would not occur without volatiles. Geothermal heat transfer would be very ineffective without volatiles. Valuable mineral deposits may not form without them.

3. Sterilization is simply undesirable for any measurements mentioned above except possibly category (ii) (chemical composition). It would be ideal if the samples are returned to a Sky-Lab type space station first for biological testing and quarantine for 3 months or so, and then shipped intact to the Earth receiving lab. The samples need be quarantined regardless of whether they are sterilized or not, because nobody

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO

Branch of Isotope Geology

February 27, 1974

Dr. Robin Brett
N. A. S. A.
Johnson Space Center
Houston, Texas 77058

Dear Robin:

Enclosed you will find a short report on the effects of proposed sterilization on charged particle tracks.

I hope this will be helpful to you.

Sincerely,

Charles W. Naeser

1. Materials suitable for charged particle track studies should be present on the Martian surface. Carr (1973) has pointed out a number of features on the Martian surface which are volcanic in origin. Most minerals present in the volcanic deposits are capable of recording charged particle tracks. Probable minerals would be; pyroxenes, feldspars, olivine, and accessory zircon and apatite. Impact events are also common on the Martian surface (Hartmann, 1973). The glass produced during the impact can also be used as a charged particle track recorder. Only montmorillonite, a probable component, would probably not be useful as a track recorder. The expandable nature and fine grain size of montmorillonite make it almost impossible to etch.

2. Studies of charged particle tracks in returned lunar material have provided important information on the history of the lunar surface. Fleischer and others (1971) were able to reconstruct the post crystallization history of rock 12017. This was accomplished by looking at the charged particle track record in pyroxene, feldspar and glass phases that made up this rock. By looking at the tracks in the green glass spherules, Fleischer and Hart (1973) were able to determine that the glass has been at the surface for a relatively short time. Fleischer and others (1970) were able to say that down to a depth of at least 12 cm, the lunar surface is constantly being stirred. This was determined by looking at the fossil track densities in anorthite, glass, and augite grains found in the lunar soil.

3. There is every reason to believe that charged particle track studies on returned Martian samples would provide valuable information. The proposed thermal sterilization of the Martian samples would anneal (erase) the charged particle tracks in some or all of the material depending on the temperature used.

Table 1 shows the approximate temperature at which annealing would begin after a one hour heating.

Table 1

Track reduction would begin after one hour at:		
100°C	Basaltic glass	MacDougall, 1973
	Lunar impact glass	Fleischer and others, 1971
200°C	Feldspar glass	Fleischer and others, 1968
	Basaltic glass	Fleischer and others, 1969
300°C	Apatite	Naeser and Faul, 1969
	Lunar impact glass	Fleischer and Hart, 1973
400°C	Phlogopite	Maurette and others, 1964
	Muscovite	Fleischer and others, 1964
500°C	Pyroxene (pidgeonite)	Fleischer and others, 1965a
	Olivine	Fleischer and others, 1965b
600°C	Sphene	Naeser and Faul, 1969
	Epidote	Naeser and others, 1970
700°C	Zircon	Fleischer and others, 1965b
	Feldspar	Fleischer and others, 1965a

Lower temperatures for longer times would have a similar effect. For example, apatite held at 225°C for 10^4 minutes (6.9 days) would also be partly annealed (Naeser and Faul, 1969).

If thermal sterilization must be used on the Martian samples, the lowest possible temperature for the shortest possible time would be best. Incandesence would remove all tracks in all phases present. The higher and higher the temperature, more and more phases will become unsuitable for charge particle track studies.

4. Research is needed on the track retention properties of clay minerals. While it is unlikely that montmorillonite can be etched, some research should be done on it and other clay minerals to determine if any useful track data can be derived from them if they should be present in the returned Martian samples.

References

Carr, M. H., 1973, Volcanism on Mars: Jour. Geophys. Res., v. 78, p. 4049-4062.

Fleischer, R. L., Haines, E. L., Hart, H. R., Jr., Woods, R. T., and Comstock, G. M., 1970, The particle track record of the Sea of Tranquility: Proc. Apollo II Lunar Sci. Conf., Geochim. et Cosmochim. Acta, Suppl. 1, v. 3, p. 2103-2120. Pergamon.

Fleischer, R. L., Hart, H. R., Jr., Comstock, G. M., and Evivaraye, A O., 1971, The particle track record of the Ocean of Storms: Proc. Second Lunar Sci. Conf., Geochim. et Cosmochim. Acta, Suppl. 2, v. 3, p. 2559-2568. MIT Press.

Fleischer, R. L., Price, P. B., Symes, E. M., and Miller, D. S., 1964, Fission track ages and track annealing behavior of some micas: Science, v. 143, p. 349-351.

Fleischer, R. L., Price, P. B., and Walker, R. M., 1965a, Solid state trace detectors: Applications to nuclear science and geophysics: Ann. Rev. Nuc. Sci., v. 15, p. 1-18.

Fleischer, R. L., Price, P. B., and Walker, R. M., 1965b, Effects of temperature, pressure, and ionization on the formation and stability of fission tracks in minerals and glasses: Jour. Geophys. Res., v. 70, p. 1497-1502.

Fleischer, R. L., Price, P. B., and Walker, R. M., 1968, Charged particle tracks: Tools for geochronology and meteorite studies: E. Hamilton and R. M. Farquhar, Radiometric Dating for Geologists, Interscience, p. 417-435.

Fleischer, R. L., Viertl, J. R. M., and Price, P. B., 1969, Age of Manicouagan and Clearwater Lake Craters: Geochim. et Cosmochim. Acta, v. 33, p. 523-527.

Fleischer, R. L., and Hart, H. R., Jr., 1973, Particle track record of Apollo 15 green soil and rock: Earth Planet. Sci. Lett., 18, p. 357-364.

Hartman, W. K., 1973, Martian Cratering, 4, Mariner 9 initial analysis of cratering chronology: Jour Geophys. Res., v. 78, p. 4096-4116.

MacDougall, D., 1973, Fission track dating of oceanic basalts: EOS. Trans. Am. Geophys. Union, v. 54, p. 987-988.

Maurette, M., Pellas, P., and Walker, R. M., 1964, Étude des traces de fission fossiles dans le mica: Bull. Soc. Franc. Minner, Crist., v. 87, p. 6.

Naeser, C. W., and Faul, H., 1969, Fission track annealing in apatite and sphene: Jour. Geophys. Res., v. 74, p. 705-710.

Naeser, C. W., Engels, J. G., and Dodge, F. C. W., 1970, Fission track annealing and age determination of epidote minerals: Jour. Geophys. Res., v. 75, p. 1579-1584.

State University of New York
at Stony Brook
Stony Brook, New York 11790

StonyBrook

Department of Earth and Space Sciences
telephone: (516) 246-6540

20 February 1974

Dr. Everett K. Gibson, Jr.
Code TN7
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Gibson:

I am writing in response to your letter of 15 February regarding the scientific results that might be expected from a returned Martian sample. In accord with our prior telephone conversation, I will confine my remarks primarily to those aspects related to the Martian atmosphere.

We will clearly be in a much better position to address this whole question after the Viking missions when we know more about Mars and more about our ability to learn about Mars by means of experiments sent to the planet. Nevertheless, it is already obvious that we can do a much better job of atmospheric analysis on a sample brought to our laboratories than we can hope to achieve with miniaturized instruments sent to Mars. The main problem with sterilization in this area is the chemical reactions that would occur between the solid sample and the atmosphere. We will even be in a better position to assess this problem after Viking, since the heating of samples in ovens for analysis by the GCMS is similar to the sterilization procedures being suggested. Lacking all this vital information, I have attempted to answer the points raised in your letter in fairly general terms.

1. Proposed methods of sterilization

I would prefer dry heat in a sealed container in order to retain all evolved gases and to avoid additional chemical reactions. A helpful addition to this protocol would be an independently gathered and sterilized atmospheric sample that could serve as a control. The temperature regime is harder to evaluate, but the two extremes (a) and (d) are certainly less desirable than (b) or (c). We will have specific information for use in evaluating this question after running the GCMS experiment on Mars.

2. Present knowledge of atmospheric composition

I am enclosing a table from a forthcoming paper (in Comments on Astrophysics and Space Physics) that gives my best current estimate of the relative abundances of gases in the Martian atmosphere. In your informal compilation "Nature of the Martian Surface" there are some errors and redundancies in item 3 that should be clarified by

this table. In particular, it is the mean total (not H_2O) pressure that is 5-6 millibars; the H_2O content is highly variable with season and location on the planet (ranging from < 2 to > 40 precipitable micrometers) and ozone has definitely been detected--also in variable amounts.

3. Properties to be measured in returned sample (gas)

The basic quantities desired are the relative abundances of all constituents, including isotopic forms. We will get a good first cut at this with Viking. To improve on these preliminary results, one will want to use a very high resolution mass spectrometer and/or sophisticated methods of separating constituents (e.g., by gas chromatography) in order to provide better data on ^{20}Ne in the presence of ^{40}Ar (doubly charged in MS), N_2 and CO in each other's presence and in all that CO_2, and other possible mass/charge overlaps that may occur with trace constituents.

Two exciting isotopic problems that are unlikely to be solved by in situ analysis are

D/H in Martian water and
$^{13}C/^{12}C$ in Martian organic compounds.

We may have difficulty with neon and nitrogen isotopes in our initial analysis if these gases are present in very small amounts. Here again a returned sample would help.

Another interesting problem concerns the composition of gases trapped in the rocks. The temperatures achieved in the Viking GCMS ovens will not be high enough to perform this experiment adequately on Mars. We also lack the capability of detecting and measuring gases with molecular weights less than 12. Both of these constraints could be removed with ground-based instrumentation.

4. Significance of measurements for understanding Mars

The role of terrestrial atmospheric studies in the development of our knowledge about the Earth is well known. We expect similar progress to be made with an understanding of the Martian atmosphere, as I have attempted to demonstrate in the enclosed papers.

I hope these remarks are useful; I am certainly interested in the possibility of a returned sample and will be happy to do what I can to support your efforts in this direction. I have passed your letter along to others in our department who may be interested.

With best wishes,

Sincerely,

Toby Owen

Tobias Owen

TO:pm
Encl.

TABLE I

Composition of the Martian Atmosphere

Gas	Abundance (cm am)	Relative Abundance	Reference
CO_2	7500 ± 1000	≥ 900,000 ppm	A
CO	13 ± 8	1,600	B
O_2	9 ± 2	1,100	C
H_2O*	2.5 ± 1.5	300	D
O_3*	2.5 ± 1.5 x 10^{-4}	0.03	E

*These constituents are known to vary with seasonal and diurnal cycles.

References

A. L. D. G. Young, J. Quant. Spectrosc. Radiat. Transfer 11, 1075 (1971).

B. ———, ibid. 11, 385 (1971).

C. E. S. Barker, Nature, 238, 447 (1972).
N. P. Carleton and W. A. Traub, Science, 117, 988 (1972).

D. R. A. Schorn, in Planetary Atmospheres, ed. C. Sagan, T. C. Owen, and H. J. Smith (Dordrecht: D. Reidel) p. 223 (1971).

E. C. A. Barth, C. W. Hord, A. I. Stewart, A. L. Lane, M. L. Dick, and G. P. Anderson, Science, 179, 795 (1973).

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA CALIFORNIA 91109

DIVISION OF GEOLOGICAL AND PLANETARY SCIENCES

TELEPHONE (213) 795-6811

March 7, 1974
RE: TN7

Dr. Laurence E. Nyquist
National Aeronautics and
Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Nyquist:

The chemical composition and molecular structure of most nitrogenous, carbonaceous, and hydrated substances in the Martian samples would probably be seriously altered by temperatures substantially above 25°C. Heat treatment of the samples would probably negate most chemical measurements bearing on surface chemical conditions of Mars by forming, in the samples, compounds that did not exist on Mars and destroying many of those that did. The comments that follow do not deal with the above problems at all, but relate instead to the effects of heat treatment on the trace metal composition of the samples, with particular reference to lead.

Great care must be exercised to minimize trace metal impurities of the metals or plastics used in the sample collecting apparatus, together with trace metal contaminations of the surfaces of these materials from the time they have been cleaned to the time they are used to collect a sample.

I won't go into details about this matter here. It is sufficient to say that the steps that must be taken to control heavy metal contamination on a reliable basis are both unbelievable and incomprehensible to engineers and scientists outside this restricted field of study, and it is not possible to set down instructions and advice for controlling contamination which engineers and scientists outside the field can use. Even after procedures for construction and assembly have been worked out, a scientist used to working at ultra low levels of heavy metal contamination must supervise the entire operation from fabrication to liftoff, in order to insure optimum contamination control.

Two substances that have been proven by bloody experience to be most trustworthy with respect to trace metal contamination are (1) fused quartz made from ultra fine grade crystals, with the stock being handled during fabrication with new, clean graphite tools, with the quartz subsequently being cleaned successively with HF, HNO_3, and ultra pure acidified water; and (2) FEP teflon in fabricated form being boiled with prolonged, successive treatments of pure aqua regia, HNO_3, and ultra pure slightly acidified water. It is probable that the use of other substances, such as

stainless steel, TFE teflon, or polyethylene for materials that would contact the Mars samples would introduce sufficient amounts of trace metal contamination to substantially degrade the scientific integrity of the samples.

A fused quartz liner could be heated up to 350°C without damage. FEP teflon could only be heated safely to 150°C for a month, with higher temperatures being unsafe.

There are two serious drawbacks to heating the samples: (1) volatile metallic substances may be driven out of the samples and lost; and (2) volatile metallic contamination, originating from heated materials outside the sample container lining, may be carried inside the sample container. The probability of both of these effects operating at significant levels is high enough, by themselves, to seriously compromise the scientific integrity of the samples.

It should be clear that geochemists look with horror on heating their samples, and for valid reason.

Sincerely,

C. C. Patterson

CCP:bac

State University of New York
at Stony Brook
Stony Brook, New York 11790

StonyBrook

Department of Earth and Space Sciences
telephone: (516) 246-6540

March 13, 1974

Dr. William Phinney
Chief, Geology Branch
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

Reference is made to your February 19th communication, concerning the degree to which studies of a Martian sample will be compromised by the proposed sterilization procedures. We will not remark in detail on the effect of heating to temperatures of 350°C on such minerals as hydrous iron oxides, carbonates, hydroxides, etc. Others have given input to you on these minerals. We will only add that even if the sterilization procedure tends to dehydrate or oxidize some of these minerals, most important crystal chemical information should remain intact and an accurate prediction of the nature of these minerals on the Martian surface should be possible.

Most of our work to date has been on silicates such as amphiboles, pyroxenes, feldspars, etc., and the Fe-Mg-Ti oxides, and these phases are likely to occur on Mars. We will be especially interested in the nature of these phases when they occur in Martian volcanic rocks. Our studies will concern the near surface chemical and thermal evolution of these rocks and after selecting candidates for primary liquids, we will address the problem of their source regions. It is likely that these rocks will already be compromised (weathered) by exposure to the CO_2-rich Martian atmosphere. However, we should be able to see through this alteration overprint and determine the character and petrogenetic history of these rocks. It is unlikely that reasonable sterilization treatment ($T < 350°C$, inert atmosphere) will compromise these rocks significantly. Judicious choice of an inert atmosphere (e.g., N_2) is particularly important. We do not believe that other accepted sterilization techniques (e.g., infrared radiation) would compromise the samples seriously. In summary, I would state that the important (at least to us) petrologic aspects of origin of Mars such as the nature of the crust, genesis of volcanic rocks and the nature of the Martian interior will not be unduly compromised by the proposed sterilization procedures. On the

other hand, clues to the details of Martian surface weathering and alteration could be greatly obscured by any sterilization procedure which dehydrates or changes the oxidation state of iron in the low-temperature mineral assemblages. However, we repeat, the basic petrologic information concerned with planetary formation and differentiation will probably still be intact.

Sincerely yours,

JJP;AEB:sk

J. J. Papike

A. E. Bence

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF PHYSICS BERKELEY, CALIFORNIA 94720

February 22, 1974

Robin Brett
Code TN7
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

I am responding to your letter of February 15, 1974, concerning the effects of sterilization on Mars samples.

1. Track studies that could be carried out on Mars samples.

The present Martian atmosphere shields surface soil grains from all but the penetrating cosmic rays - in the case of Fe nuclei such as are responsible for the majority of tracks in lunar samples, energies must be higher than ~500 MeV/nucleon. Amorphous coatings on grains due to solar wind irradiation will be absent. Microerosion and mass wastage erosion will be absent. Track densities will be much lower than in lunar grains. Fission track dating will be easy, with such a drastically reduced track background. One ought to be able to determine absolute solidification ages of very small samples without having to search for the rare, uranium-rich phases. Paleovolcanism and soil transport could be studied by fission track dating of individual grains.

One could search for rare grains with steep gradients, which, if found, must have been produced when there was no Martian atmosphere. Contamination of the soil by fragments of gas-rich meteorites could also contribute, but could be distinguished from indigenous grains.

I am sure that several minutes more thought could turn up other interesting problems that can be tackled by track techniques.

2. Effects of sterilization on tracks

a) "Clay" minerals. Not much is known. Assuming mica to be a representative layer-lattice silicate, we can say that 150°C for 1 month would have no effect, but that 250°C for 1 week or 300°-350°C for 1 day might cause some fading of tracks.

b) Basaltic minerals. Very track-retentive minerals such as sphene, zircon, diopside, garnet and some feldspars can stand temperatures up to ~600 or even 700°C for 1 hour and perhaps 100° lower temperatures for 1 month. Less retentive minerals such as apatite, whitlockite and olivine will begin to lose tracks at temperatures as low as 400°C in 1 hour.

Yours sincerely,

P. Buford Price

PBP:mk

ARGONNE NATIONAL LABORATORY

8 March 1974

Dr. Everett K. Gibson, Jr.
ATTN: TN7
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

We recommend that the biological sterilization of Mars samples be restricted to either ambient temperature ethylene oxide treatment or to dry or wet heat limited to 150°C in a closed system. Our rationale is as follows.

Several elements and compounds must be considered as volcanic emanations and/or weathering products: (1) highly volatile reactive agents such as H_2O, HCl, HBr, HF, and H_2S; (2) highly volatile non-reactive elements such as Hg and the rare gases and (3) moderately volatile, relatively non-reactive elements (compounds) such as Pb, Bi, Tl and Os.

Stepwise heating and aqueous leaching experiments on lunar samples have established that a number of elements, which terrestrially may be associated with fumarolic activity, are present on surfaces. All of the halogens in lunar samples, except possibly F, are mobile. Some Br is volatilized at 150°C; leaching experiments for I and release of ^{128}Xe (produced from I) at low temperatures indicate that I will also volatilize. The element Hg is possibly one of the most abundant volatiles on the lunar surface and must be present as a component of the atmosphere at lunar day time temperatures. Pb can be leached at pH 5-6 and volatilized at temperatures as low as 450°C.

Since these elements will provide important information of Martian vulcanism and surface weathering processes, the samples should be compromised as little as possible. We suggest that: (1) both sterilization procedures be employed assuming that at least two sample containers will be returned. This should satisfy both organic and inorganic interests; (2) the ethylene oxide treated samples should not be heated; (3) the heat treated samples should be maintained at temperatures of <150°C. If wet-heat is recommended

9700 South Cass Avenue, Argonne, Illinois 60439 · Telephone 312-739-7711 · TWX 910-258-3285 · WUX LB, Argonne, Illinois

then deuterated H_2O should be used. The atmosphere of the container should not be vented to space but be maintained intact for tapping at the receiving laboratory and (4) obviously, containers and reagents should be selected for freedom from contaminants and should be passive to possible compounds released during the sterilization process, for instance HCl.

Sincerely,

George W. Reed, Jr.
Chemistry Division

GWR/ljc

C-2

The following information was supplied by

Dr. R. C. Reedy
Los Alamos Scientific Laboratory
of the University of California
Los Alamos, New Mexico

in response to a question regarding the expected production rates of certain nuclides by cosmic-ray interactions in the Martian atmosphere. The production rates are based on calculations used in the paper "Interaction of Solar and Galactic Cosmic Ray Particles with the Moon" by R. C. Reedy and J. R. Arnold (Jour. of Geophys. Res., 77, pp. 537-555, 1972). The cosmic ray fluxes used are the values at 1 A.U. These fluxes will not be drastically different at the Martian orbit for galactic cosmic rays, the only ones considered here. Permission to include the following information in this report was verbally given by R. C. Reedy to L. E. Nyquist. The original notes were transcribed by L. E. Nyquist, any errors in transcription are his.

I. Productuion rate by galactic cosmic rays in 100% CO_2 atmosphere (atoms/min per kg of oxygen).

Depth (g/cm^2)	0	20	40
^{3}H	203	206	191
^{10}Be	16	17	16
^{14}C	34	48	52

II. Neutron capture production of ^{14}C from ^{14}N.

i. 95.8% of total captures in ^{14}N produce ^{14}C.

ii. 5% N captures 98.9% of total neutrons in a 95% CO_2 (by weight) atmosphere.

iii. 0.5% N captures 89.5% of total neutrons in a 99.5% CO_2 atmosphere.

iv. Using the Lingenfelter, Canfield, and Hempel Model (Earth Planet. Sci. Lett. 16, 355, 1972) for neutron production yields the following capture and production rates:

Depth (g/cm^2)	LCH captures / kg min	atoms ^{14}C / kg min (5% N)	atoms ^{14}C / kg min (0.5% N)
0	120	51	5.1
5	225	96	9.6
10	327	139	14.0
20	516	220	22.0

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO — SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF PHYSICS — BERKELEY, CALIFORNIA 94720

March 8, 1974

Dr. Laurence E. Nyquist
Code TN-7
NASA Johnson Space Center
Houston, Texas 77058

Dear Larry:

As usual these days I am late in replying and even so have not spent the time on this that it deserves. Thus you are getting an off-the-top-of-the-head answer and I am reasonably sure that everything I have said here will have been anticipated by you.

From the standpoint of rare gas research I think it is clear that a temperature run of irradiated and unirradiated material maximizes the possible information obtained. One gets from these experiments an Argon-39/Argon-40 age for almost anything, possible xenon from extinct radioactivities, indications whether this xenon from extinct radioactivities was produced in situ or not, information about the trapped rare gases in the sample, certain of the trace elements - namely Br, I, Ba, U, exposure ages from the ^{81}Kr-^{80}Kr relationships and from the ^{38}Ar-Ca relationships.

It is also obvious that the lowest temperature sterilization among your proposed regimes is the most favorable from the standpoint of the rare gas analyses. In almost any sample the long low temperature heating will release less gas than the shorter high temperature heating. If there is a choice to be made between heating the sample in a closed container or in vacuum it would be better from the standpoint of rare gas research to heat it in a closed container. The gases driven off can then be examined. It is important to have a sample of the Martian atmosphere as well but if possible this ought to be a separate sample, not mixed with the gases released in the sterilization. By the same token it would be better if the sample, or at least part of it, were evacuated before the sterilization process began.

I hope this information is of some use to you. Clearly the detailed design of an experiment would require knowing all the various limitations on the sample and the uses to be made of the sample.

Sincerely yours,

John H. Reynolds
Professor of Physics

JHR/ek

Motoaki Sato
U.S. Geological Survey

This is in reply to your inquiry on the possible effects of biological sterilization on returned Martian samples. The questions asked are so sweepingly broad and time to answer is so short that I feel a little uneasy about making written statements, but in view of urgent circumstances you described, I will jot down whatever that have come up in my mind at a risk of mixing up speculations with facts and established principles.

1. The properties that should be measured or studied within the realm of petrology and geochemistry are as follows:
   - i) Mineral assemblages and textural relations.
   - ii) Major and trace element composition.
   - iii) Oxidation state (Fe^{3+}/Fe^{2+} ratio and intrinsic oxygen fugacities).
   - iv) Composition of volatiles.
2. The reason for studying the above properties are briefly described below in the same sequence.
   - i) Minerals, singly and in assemblage, reflect the chemical and physical factors of various environments they have been exposed to. Regardless of whether a sample is an igneous rock, soil or something else, detailed examination of individual minerals and mineral assemblages tells us a lot, needless to say.
   - ii) This is more or less routine and one of the first things one would try to find out.
   - iii) The state of oxidation of Martian rocks is a subject of more than passing interest. It will probably give us a strong clue as to the mechanism of control of the oxidation state of igneous rocks on various planets. The reddish albedo of Martian soil or lavas, which is believed to be due to ferric iron on the basis of spectral correspondence, may be produced in four different ways.

The first possible way is oxidation by atmospheric free oxygen similar to the formation of lateritic soils on Earth. This mechanism would require the presence of photo-synthetic plants or bacteria to liberate free oxygen from carbon dioxide and water, if the Martian magmas were similar to terrestrial or lunar magmas. The gases extracted from deep sea pillow basalts at high temperatures exclude the possibility of presence of free oxygen at equilibrium (Sato et. al. unpublished data). Oxygen fugacity values of relatively uncontaminated magmatic gases are significantly below that of the hematite-magnetite assemblage (Sato and Wright 1966, Sato and Moore 1972).

The second alternative is that the Martian interior was extremely rich in oxygen and the Martian magmas were oxidized from the start, and as the result hematite or other high ferric minerals crystallized directly out of magma as primary igneous minerals. This mechanism would require an extraordinary setting for the origin of Mars. The cosmic elemental abundance favors reduced states for iron at high temperatures. Iron in chondrites occur in reduced states.

The third alternative is that magnetite was attacked by CO_2-rich water and reacted to form hematite (or ferric hydroxide) and siderite:

$$Fe_3O_4 + CO_2 = Fe_2O_3 + FeCO_3 \quad \Delta F^\circ_{298} = -1.50 \text{ Kcal} \qquad (1)$$

$$Fe_3O_4 + CO_2 + 3H_2O_{(l)} = 2\,Fe(OH)_3 + FeCO_3 \quad \Delta F^\circ_{298} = +3.97 \text{ Kcal} \qquad (2)$$

The free energies of reaction were computed on the basis of data in Latimer (1952), except for $Fe(OH)_3$ which is based on JANAF (1971). Reaction (1) requires partial pressure of CO_2 greater than 80 mb at 25°C to proceed. Reaction (2) should have more negative free energy of reaction

ORIGINAL PAGE IS
OF POOR QUALITY

than (2), considering the reported observation that goethite is more stable than hematite at activity of water greater than 0.6 (Schmalz, 1956). Unfortunately, only values for unstable $Fe(OH)_3$ are found in standard reference sources. The reaction is within the realm of possibility on Mars.

The fourth alternative is that the oxidation was caused by preferential escape of hydrogen originated by the thermal dissociation of water in the late magmatic to duteric stage. Formation of ferric oxide probably due to this mechanism was observed and described in Hawaii (Sato and Wright 1966) and elsewhere. There are other pieces of evidence which suggest that oxidation by this mechanism is prevalent in magmas which contain water. Sato et. al. (1973) pointed out a possibility that the difference in the oxidation state between terrestrial and lunar igneous rocks is due primarily to the difference in the initial water content of magma, which in turn is due to the difference in total mass between the two planets. The smaller Moon lost much of water (a light-weight molecule) at the time of formation because of its small gravitational field, whereas the larger Earth retained a considerable amount of water.

The oxidation state of the Martian rocks is of extreme interest because the mass of this planet and probably the water content fall between the Earth and the Moon. The escape of hydrogen would be easier if a planet is smaller. On the other hand, the internal water content would be less if a planet is smaller, as discussed earlier. It may turn out that Mars represents the optimum planetary size for the oxidation of magma by hydrogen loss.

The intrinsic oxygen fugacities of mafic minerals indicate the course of change in oxidation state of a magma (Sato 1972).

Terrestrial basalts show a tendency of increasing oxidation with decreasing depth (Sato unpublished data), whereas lunar basalts show an opposite tendency (Sato et. al. 1973). Examination of the intrinsic oxygen fugacities of Martian igneous minerals would show which way the oxidation state of Martian magma changes with depth (or at least with the degree of crystallization). This information would most likely to be a crucial clue to the understanding of the mechanism of control of the oxidation state of magmas in the Solar planets.

iv) The composition of volatiles in any rock is an important information to obtain. Volatile compounds control the origin of atmosphere, hydrosphere and life. Photosynthesis requires the availability of CO_2 and H_2O to produce high-energy compounds such as carbohydrates. Without these photosynthetic products, higher organisms may not operate.

Volatiles also play an important role in controlling the oxidation state of igneous and metamorphic rocks as partly pointed out by Sato et. al. (1973). Volcanic activities depend heavily on the volatile components in magma. Explosive volcanic eruptions and ash falls would not occur without volatiles. Geothermal heat transfer would be very ineffective without volatiles. Valuable mineral deposits may not form without them.

3. Sterilization is simply undesirable for any measurements mentioned above except possibly category (ii) (chemical composition). It would be ideal if the samples are returned to a Sky-Lab type space station first for biological testing and quarantine for 3 months or so, and then shipped intact to the Earth receiving lab. The samples need be quarantined regardless of whether they are sterilized or not, because nobody

could possibly be sure that a certain sterilization procedure is foolproof, except perhaps (d) heating to incandescence, a procedure which would destroy practically all useful information for which the samples will be brought back. This procedure would probably not destroy the bulk chemical composition, but for that there would be no need to bring the samples back. Just send an analyzer to Mars.

If we have to live with sterilization, procedures (a) and (c) must be rejected. Heating in vacuum would result in loss of volatiles, resulting in oxidation or reduction of samples, dehydration or decarbonation of hydrous minerals and carbonates, and change in volatile composition, as discussed earlier. Addition of water would obliterate information on volatile contents and degree of hydration of minerals. The presence of water vapor also tends to accelerate reactions among co-existing phases and thus likely to obliterate the memory of Martian environments locked in minerals. It does not make sense to deliberately help erase valuable recording of the Martian environment and substitute it with a recording of the environment in the sterilization chamber, even for 18 1/2 minutes!

The only procedure reluctantly acceptable is (b) dry heat sterilization in a sealed gold container. No base or ferrous metal container would be acceptable because of possible reaction with the sample. Platinum group metals are not acceptable because they are permeable to hydrogen.

Should water vapor exist in the sample, the rise in vapor pressure would result in hydrogen osmosis and resultant change in volatile composition and oxidation of the sample. This would be particularly so if the container is exposed to the high vacuum of space. Single crystal sapphire container may be acceptable as an alternative to gold.

The times and temperatures should be in such a combination that the reactions within a sample should be minimal. Natural samples are normally disequilibrium assemblages at any temperature. That is why we can decipher their geologic histories by carefully studying them. Now if we assume that a reaction is a first-order reaction and proceeds at a rate of k, the amount of change that would occur, x, in time t is:

$$x = a(1 - e^{-kt}) \qquad (3)$$

where a is the initial concentration. The rate constant k is a function of absolute temperature:

$$k = Ae^{-Ea/RT} \qquad (4)$$

where A is a constant and Ea the activation energy of the reaction. From (3) and (4), it can be seen that the amount of change that would occur during the sterilization will be the smallest if the temperature-time combination is such that the quantity, $e^{-(Ea/RT)} \cdot t$, is the smallest. The relative values of this quantity depend on the magnitude of the activation energy as shown in Table 1.

Table 1. Relative amounts of reaction that would occur for given temperature-time combinations.

			Ea (Kcal)				
	Temperature (°C)	Time (Days)	2	5	10	20	30
(a)	150	30	1	1	1	1	1
(b)	250	7	.368	.728	2.27	22.08	2.03×10^{4}
(c)	350	1	.072	.225	1.52	69.25	7.94×10^{41}

The table indicates that if the activation energy is low, a combination of higher temperature and shorter time would produce a relatively smaller amounts of reaction, and vice versa. Gaseous reactions

between stable molecules have values of Ea ranging from 2.5 to over 40 Kcal/mole, and reactions between ions and neutral molecules from 9 to 23 Kcal/mole (Frost and Pearson, 1953). Reactions in solid bodies range from 12 to 180 Kcal/mole (Budnikov and Ginstling, 1968). The majority of these inorganic reactions have activation energies around 20 Kcal/mole or higher. Therefore, combination (a) (low temperature and longer duration) is obviously the best sterilization plan to preserve inorganic disequilibrium relations of Martian samples. We can hope that organic reactions with low activation energies (life processes) reach equilibrium state(dead state), while inorganic record is still preserved through this sterilization procedure.

References

Budnikov, P. P. and Ginstling, A. M. (1968) Principles of Solid State Chemistry -- Reactions in Solids. Gordon and Breach Science Publishers, New York, p. 240.

Frost, A. A. and Pearson, R. G. (1953) Kinetics and Mechanism. John Wiley, New York, p. 101, 136.

Sato, M. (1972) Intrinsic oxygen fugacity of iron-bearing minerals at low total pressure. John W. Gruner Volume, Geol. Soc. Amer. Memoir 135, 289-307.

Sato, M. and Wright, T. L. (1966) Oxygen fugacities directly measured in magmatic gases. Science, v. 153, 1103-1105.

Sato, M. and Moore, J. G. (1972) Oxygen and sulfur fugacities directly measured in magmatic gases in active vents of Mt. Etna. Phil. Trans. Royal Soc. London A. 135-144.

Sato, M., Hickling, N., and McLane, J. E. (1973) Oxygen fugacity values of Apollo 12, 14, and 15 lunar samples and reduced state of lunar magmas. Proc. Fourth Lunar Sci. Conf. (Suppl. 4, Geochim. Cosmochim. Acta) Vol. 1, 1061-1079.

Radiation Center Oregon State University Corvallis, Oregon 97331 (503) 754-2341

March 4, 1974

Dr. Everett K. Gibson, Jr.
TN7
NASA/JSC
Houston, TX 77058

Dear Everett:

Dr. Laul and I cannot add much new information that you are not already familiar with concerning the present state of volatility studies with a variety of elements. You and Norm have essentially done the classic experiments that should be helpful as significant background data for the Martian sample protocols.

We can only emphasize the extreme importance of complete measurements of the entire chemical composition of both bulk and separated "minerals" on such returned samples. Such measurements are basic to all other proposed experiments on these samples. It seems doubtful whether large fractions of many volatiles will be lost for the 150°C and 200-250°C sterilizations. Certainly no lithophiles or refractories will be lost in heating even up to 350°C for one day. However, it seems probable that appreciable fractions of trace elements such as Tl might be lost at 350°C.

We would be willing to participate in a detailed study of volatile bulk and trace elements loss in a variety of samples that might approximate hypothesized Martian soil. See our latest Ap 17 boulder-2 papers for a list of elements. It seems pointless to invest any time in the analyses of refractory bulk and trace elements in such samples, since these elements will not be lost. May I suggest that the sample load for analyses of these volatile elements be shared by the Anders, Wasson and our group or any other group that has such capability.

Best regards,

R. A. Schmitt
Professor of Chemistry

jmw

UNIVERSITY OF CALIFORNIA, LOS ANGELES

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF GEOLOGY
LOS ANGELES, CALIFORNIA 90024

March 11, 1974

Dr. William C. Phinney
NASA - L.B.J. Space Center
Houston, Texas 77058
Code TN7

Dear Dr. Phinney:

In response to your letter of 19 February, the following are opinions (guesses) only, supported by some experience but not by a great deal of data. Obviously, properly designed experiments must be performed to agument and extend the limited data currently available.

1. Properties to be measured.

Clearly, measurement of various physical properties (water content, mineralogy, etc., etc.) will be important. Depending on sterilization regime, such properties can be preserved, and measured, relatively easily.

It is at least equally important -- and in my opinion, absolutely imperative -- that attempts be made to detect evidence of biologic organization. Severe sterilization regimes (e.g. "heating to incandescence"/sic./) will destroy such evidence and, thus, must be avoided. However, less severe regimes (relatively low temperatures for relatively long periods of time) can be employed which will have the desired sterilization effects while, at the same time, preserving the morphology and some biochemistry of hypothetical Martian microbes. In short, the desired goal should be one of providing sufficient energy of activation to break important organic bonds (e.g., C-C bonds, in straight-chain hydrocarbons about 58,000 cal/mole; ABELSON, 1959), and thus kill whatever organisms may be present, while at the same time not destroying the physical form of such organisms. Evidence of such organisms, whether recently dead or fossil, should be sought using "usual" paleobiologic techniques (optical and electron microscopy of powdered preparations, thin sections, acid-resistant organic residues, etc.)

2. Importance.

The "probability" of living systems occurring on Mars, now or in the geologic past of that planet, appears low (although it must be recognized that "probability statements" of this type

are very nearly meaningless since they presuppose the existence of substantive knowledge that is not, in fact, available, knowledge relating to such matters as (i) conditions, processes and events required for the origin of living systems; (ii) the nature of the primitive Martian environment and the evolution of that environment over geologic time; (iii) the evolutionary flexibility and adaptability of biologic systems; etc.) Nevertheless, it is obvious that the discovery of firm evidence of the present or past existence of living systems on Mars, and the characterization of such life forms, would be of tremendous significance. Every effort should be made to avoid the destruction, during sterilization, of possible evidence of Martian life.

3. Potential effect of sterilization.

Paleobotanists, palynologists and coal petrographers have long recognized that both the fidelity of cellular preservation and the color of carbonaceous plant fossils and particulate organic matter ("kerogen") preserved in ancient sediments vary as a function of metamorphic history and degree of coalification. Both in laboratory studies and in nature, a continuum of irreversible color changes (generally from yellow, through shades of amber, reddish brown and brown, to black) occurs during very low grade "metamorphic" alteration of carbonaceous material; temperatures extrapolated from known geothermal gradients or measured in boreholes or in laboratory heating experiments have been correlated with the color of preserved palynomorphs to yield "thermal alteration indices" (for a summary of these indices, see OEHLER, AIZENSHTAT & SCHOPF, 1974) which, in turn, have been used for mapping the distribution of eometamorphic facies and for predicting the potential gas and oil productivity of fossiliferous strata (e.g., GUTJAHR, 1966; STAPLIN, 1969; BURGESS, 1970; CORREIA, 1971; WILSON, 1971; TEICHMUELLER, 1971). Contrary to some reports, it has recently been established (OEHLER, AIZENSHTAT & SCHOPF, 1974) that these changes in color and fidelity of cellular preservation are dependent on both time and temperature -- the same transformations that occur at relatively low temperatures and long periods of time (e.g., 150°C, 2000 hr) also occur in shorter periods of time at higher temperatures (e.g., 300°C, 0.5 hr); the changes are accompanied by increases in C/H ratios, in the percent of fixed carbon, and in the degree of aromatization of the preserved organic matter and alteration occurs more rapidly in the presence of oxygen than under anoxic conditions (OEHLER, AIZENSHTAT & SCHOPF, 1974).

Based on the limited data available on alteration of modern plant material (pollen, spores, and one microorganism -- the blue-green alga Lyngbya), and on observations of preserved microorganisms in ancient sediments, I would evaluate the four suggested sterilization regimes as follows:

ORIGINAL PAGE IS
OF POOR QUALITY

(a) 150°C, 30 days (1.3×10^6 secs)

Anoxic: modern microorganisms would be structurally well preserved, fairly easily detectable (especially if stained with appropriate dyes), and would retain a considerable degree of intracellular organization (e.g., membranes, organelles, etc., would be relatively well preserved).

Oxygenic: preservation would be roughly comparable to that under anoxic conditions but alteration would be somewhat greater and dyes would be less useful for detection of microorganisms.

Fossils would be unchanged under this regime.

(b) 200°C, 7 days (3×10^5 secs)

Anoxic: modern microorganisms would be structurally degraded but still identifiable; intracellular organization would be very largely destroyed.

Oxygenic: more degraded (but still identifiable) than under anoxic conditions.

Fossils would be largely unaffected (depending on their mode of preservation and the nature of the surrounding matrix).

(c) 300-350°C, 1 day (4.3×10^4 secs)

Anoxic: modern microorganisms very largely destroyed, probably not identifiable.

Oxygenic: modern microorganisms destroyed, not identifiable.

Fossils probably somewhat altered, but may still be identifiable.

(d) incandescence, 10^2-10^3 secs

All conditions: organic matter volatilized, evidence lost.

Please note that the above are largely guesses; few hard data are available.

4. Further research.

Only one, reasonably applicable study has been published (OEHLER, AIZENSHTAT, & SCHOPF, 1974). This study, of one modern alga, is the only published report of the effect of time-temperature relationships in the degradation of the morphology and biochemistry of a modern microorganism of which I am aware. Clearly, extension of this work -- including investigations of the chemical changes involved and the possible effect of mineral-organic interactions -- is needed. Techniques should be designed to facilitate detection of dead microorganisms following sterilization (e.g., staining

procedures). Alteration of intracellular organization should be monitored by transmission electron microscopic studies. And, studies will be needed to define the effect of the sterilization procedure on fossils, as well as on representative modern microorganisms (it should be noted that studies of this sort, if appropriate modern "taxa" are chosen, can have applicability to geologic problems -- e.g., the mapping of eometamorphic facies in petroleum exploration -- so that the research performed could have much broader applicability than solely the matter of looking for Martian "bugs").

I hope all this is of some help to you. Please let me know if you have any further questions (213-825-1170).

Sincerely,

J. William Schopf
Professor of Geology

References:

ABELSON, P. H., 1959, Geochemistry of organic substances, in P. H. Abelson, ed., Research in geochemistry: N.Y., Wiley, p. 79-103.

BURGESS, J. D., 1970, Microscopic examination of kerogen (dispersed organic matter) in petroleum exploration: Geol. Soc. Amer. Abs. with Programs, v. 2, p. 508-509.

CORREIA, M., 1971, Diagenesis of sporopollenin and other comparable organic substances: application to hydrocarbon research, in J. Brooks et al., eds., Sporopollenin: N.Y., Academic Press, p. 569-620.

GUTJAHR, C. C. M., 1966, Carbonization measurements of pollen grains and spores and their application: Leidse Geol. Meded., v. 38, p. 1-29.

OEHLER, J. H., AIZENSHTAT, Z., & SCHOPF, J. W., 1974, Thermal alteration of blue-green algae and blue-green algal chlorophyll: Amer. Assoc. Petrol. Geol. Bull., v. 58, p. 124-132.

STAPLIN, F. L., 1969, Sedimentary organic matter, organic metamorphism, and oil and gass occurrence: Canadian Petroleum Geologits Bull., v. 17, p. 47-66.

TEICHNUELLER, M., 1971, Anwendung kohlenpetrographischer Methoden bei der Erdol- und Erdgasprospektion: Erdol Kohle, v. 24, p. 69-

WILSON, L. R., 1971, Palynological techniques in deep-basin stratigraphy: Shale Shaker, v. 21, p. 124-139.

ORIGINAL PAGE IS
OF POOR QUALITY

Yale University *New Haven, Connecticut 06520*

DEPARTMENT OF GEOLOGY AND GEOPHYSICS

Box 2161, Yale Station

March 4, 1974

Dr. Robin Brett
NASA - Johnson Space Center
Houston, Texas 77058

Dear Robin:

Your letter of February 15th concerning the effects of sterilizing procedures on Martian samples opens a complex bag of worms. I can address myself to the effect of heat on three probable kinds of materials to be encountered in the samples:

1) sulfide compounds present as primary minerals
2) condensed sublimates from volcanic processes
3) materials deposited as efflorescences in the Martian.

In addition to these classes of materials I can forsee vast problems associated with any clays, hydroxides, sulfates and similar materials that have formed by surficial alteration, but I presume you have sought advice other than my own on such problems.

1. Sulfides. All igneous rocks contain sulfide minerals and considering the geochemical abundance of sulfur, Martian rocks must be expected to do the same.

The most likely sulfides, regardless of primary igneous or secondary origins, are those of iron and copper. The likely mineral species, in order of probable abundance, are pyrrhotite, chalcopyrite, bornite and chalcocite. It is clear from the attached diagram (Fig. 1) taken from Barton and Skinner (1967), ("Sulfide Mineral Stabilities" in Geochemistry of Hydrothermal Ore Deposits, edited by H. L. Barnes, published by Holt, Rinehart and Winston) that all of the proposed sterilization heating times will produce reactions in sulfides and that for options at 200°C or higher, the reactions will probably proceed to completion and will obliterate most evidence contained within the minerals. The kinds of evidence to be anticipated are cooling rates of primary igneous rocks and because sulfides are the most sensitive group of primary minerals to secondary reactions, evidence of atmosphere induced chemical weathering.

The questions of closed versus open containers and humid versus dry atmospheres is obvious in the case of sulfides. Any heating in the presence of water vapor will produce reactions to form hydroxides and possibly oxides.

Vapor pressures will depend on the mineral species present. Figure 2, also taken from Barton and Skinner, shows that the assemblage pyrrhotite-iron (commonly seen in lunar rocks) would generate such a low sulfur pressure that even up to 300°C, sulfur loss would be small in an open container. However, if pyrrhotite coexisted with pyrite, the vapor pressure of S_2 would be about 10^{-12} atm. at 300°C and we would have to anticipate a significant loss of sulfur in a sample heated for an hour or more. Any heating should therefore be in a closed container.

The most vital information lost by either vapor loss or mineralogical reactions would probably be isotopic. This could be of two kinds. Small fractionations can be anticipated from a variety of inorganic processes such as fumarolic outgassing of volcanoes and atmosphere-rock interactions. If primitive life forms have or do exist on Mars, they may have given rise to sulfur isotope fractionations analogous to those on Earth. Soil and primary rock samples may have large differences in their isotopic ratios as a consequence.

The lower the temperature, the less drastic will be the degradation of sulfide minerals. Of the choices offered, clearly a temperature below 150°C for a month is preferable. A temperature of 100°C would be below most phase inversions and would reduce both reaction rates and vapor pressures to manageable levels. The difference between 100° and 150°C is particularly apparent from Figure 1. It is the difference between little change and drastic changes if copper-bearing minerals are present.

2. Condensed sublimates. Two kinds of materials can be anticipated. If volcanic processes on Mars cause permafrost water to be melted, then sublimates formed by reactions between water and hot magmatic rocks must be anticipated. These materials are common in and around volcanoes and volcanic fields on Earth, but they only persist for a short time because they are soluble and removed by rain. On Mars they would presumably remain and might become soil constituents by physical erosion processes. The kinds of materials likely to be present are gypsum ($CaSO_4 \cdot 2H_2O$) and the hydrous sulfates of iron and aluminum.

The second kind of sublimate is material given off by magmas and the most likely substances are native sulfur, sodium, calcium and iron chlorides.

Regardless of origin, the sublimates will all be influenced by the proposed heatings. The hydrous compounds would all dehydrate, at least partially, and native sulfur would melt. The only species that would be little influenced would be sodium chloride.

All compounds would react with water vapor of an 80% humid atmosphere and all have sufficient vapor pressures so that heating in an open container would lead to a partial or total loss of the material. Sulfur would be particularly vulnerable.

3. Efflorescences. If water or liquid carbon dioxide move in the Martian crust, the question of surface efflorescences arising from their evaporation and consequent precipitation of dissolved materials must be considered as a possibility. An analogy on Earth is the Atacama Desert with its carbonate, nitrate and halide efflorescences. In the case of Mars, nitrates are unlikely, but carbonates and halides must be considered possible. Presumably compounds of the most abundant elements are the most likely salts, so that Na_2CO_3, $CaCO_3$, NaCl, $CaCl_2$, $MgCl_2$ and similar compounds can be anticipated.

Heating in a humid atmosphere would cause a near total disintegration of all compounds except $CaCO_3$. Dry heating in a sealed container should not cause much change provided the temperature did not exceed 100°C. If the salts were present in their hydrated forms, however, even heating at 100°C would lead to release of water.

It seems to me that the "importance of each of these properties", as your letter states, is self-evident. We are dealing with materials that have been degraded physically and chemically on the surface of a planet at temperatures no greater than 25°C. Heating at any temperature will cause degradation products to react with each other and with more abundant rock and soil particles. Heating will also produce vapors containing S, H_2O and CO_2 as a result of mineral breakdowns and reactions. The sulfide minerals are in pretty good shape as far as our understanding of them is concerned. The same cannot be said for many of the possible sublimate and efflorescence compounds and I believe further work on their stabilities and interactions is indicated. Work should involve both isotopic chemistry and mineralogy.

I hope these remarks help you. Given more time I suspect I could have produced a more literate and better documented report.

Kind regards,

Brian J. Skinner

BJS/pk

ORIGINAL PAGE IS
OF POOR QUALITY

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF THE GEOPHYSICAL SCIENCES
5734 SOUTH ELLIS AVENUE
CHICAGO · ILLINOIS 60637

February 21, 1974

Dr. W. C. Phinney
NASA-JSC
Houston, Texas 77058

Dear Bill:

Here are our quick and dirty thoughts on heating the Mars sample to 275°C for one month. Input was provided by J. R. Goldsmith, A. T. Anderson and I. M. Steele.

Serious damage would occur for various types of minerals, but many would survive untouched. The vapor released by heating should be measured after heat treatment (e.g. the reaction $Fe^{2} + OH^{-} - Fe^{3} + O^{2-} + \frac{1}{2}H_2$ would release H_2, while decomposition of carbonates would release CO_2). The magnetic properties should be recorded during heat treatment. In general we believe that we could reconstruct the mineralogy of the sample from sophisticated mineralogical studies plus knowledge of the total gas emitted and the change in the magnetic properties.

Now for details:

(1) anhydrous silicates. No significant changes. Diffusion is trivial below 500°C.

(2) hydroxylated silicates. Amphibole may undergo internal oxidation-reduction between Fe and OH but the basic structure would survive. Chlorite would probably undergo a similar change.

(3) zeolites. Would lose water when hot and regain it when cold. Would also sorb CO_2 and H_2 emitted by other minerals. The released water might enter other minerals causing hydration. Could be tricky. Some zeolites would retain their aluminosilicate framework (e.g. analcime) but others might collapse (e.g. stilbite).

(4) silicate glass. Should survive intact except perhaps for devitrification if basaltic. Rhyolitic glass would survive easily.

(5) sulfide. Bulk composition should survive, but diffusion between sulfides and phase changes (e.g. in pyrrhotite) might occur.

(6) carbonates. Calcite stable, magnesite fairly stable, $FeCO_3$ would probably decompose in vacuo. Stability depends on CO_2 content of atmosphere.

(7) hydroxides. Iron oxide-hydroxides would go to hematite in air. Might be more stable in vacuo. Could be interaction with gases released from other minerals.

(8) phosphates. Apatite stable. Basic iron phosphates might undergo complex reactions. Too difficult to spell out here.

(9) sulfates. Annydrous ones might be stable, but hydrated ones would lose water.

(10) clay minerals. Very complex, but much would survive if heat treatment not too intense.

(11) sublimates. Many possibilities with many possible effects.

(12) CO_2-hydrate (clathrate structure). Would break down under any heat treatment above 10°C.

It is not easy to spell out all the possibilities, but you can see that there would be no difficulty in identifying high-temperature rock fragments such as basalt and rhyolite. Almost certainly we could identify hydroxides and carbonates either directly or from their remains. The worst problem would be sublimates and clathrate structures which would decompose totally even at room temperature. A key experiment on Mars would be to observe the sample with a stereomicroscope as the temperature was raised slowly up to 50°C.

Hope this is of some help.

Yours sincerely,

Joseph V. Smith

JVS/lb

copy: Dr. E. King
Dept. of Geology
University of Houston,
Houston, Texas

A. T. Anderson
J. R. Goldsmith
I. M. Steele

Memo TO: R. Brett

FROM: D. W. Strangway

RE: Some Measurements to be Made on Martian Samples (Physical Properties)

1) Was there an ancient Martian magnetic field?

A number of rock chips need to be measured for magnetic remanence and stability to alternating field and thermal demagnetization. From lunar experience it is difficult to make meaningful measurements on chips much smaller than one gram, and 5 gram chips are preferable. This measurement is of prime importance and is compromised strongly by heating. Even 100-150°C may have serious effects if very fine-grained particles (~100Å) of magnetic material are present, since these may grow in size (or change depending on the environment) and acquire stable magnetization of non-Martian origin. Goethite, a leading contender for Martian material, has a Néel point of about 120°C and it could be magnetized by heating above this temperature, to 350°C (or less depending on grain size) will alter it to hematite and again confuse the magnetic result.

2) What are the magnetic minerals on Mars?

Leading contenders are goethite, lepidocrocite, hematite, magnetite, iron, iron-nickel, etc. Magnetic identification of these, together with a feeling for the grain size, can readily be done magnetically. It is probably safe to do some heating - as follows -

goethite → hematite
in air -- 350°C in 1/2 hour or so

iron-stable in vacuum to 800°C or more

fine-grained iron + iron oxides
in air as low as 100-150°C
magnetite + iron
~500-600°C in vacuum

In other words, heating even over 100°C or 150°C will start to modify some of the magnetic minerals so they cannot be recognized magnetically in the returned samples. In view of the importance of the iron hydroxides in the Mars situation, it does not appear wise to heat the samples much over 100-150°C.

3) What are the dielectric properties of the Martian materials? (at radar frequencies)

Since this has been one of the main tools telling us about the surface of Mars we must study these properties in detail. The indications are that dielectric constant varies with altitude, tentatively implying that the mountains are rock and plains are soil. The amount of moisture present on Mars is not likely to have a major effect on the dielectric properties, but it is important to establish this, with careful experimental work on the Martian samples. This would simply bring back the samples under frozen conditions for the greatest relevance. Exposure to water and heating would certainly jeopardize the relevance of these measurements..

4) Do the surface materials have the optical properties detected from earth-based and orbital studies and can these observations be used to confidently map Mars?

The spectral reflectance properties of Martian materials

ORIGINAL PAGE IS
OF POOR QUALITY

also seems to be important. The controversial interpretations of its red color seem to make it particularly important to specifically tie down the properties of the surface and subsurface materials. If limonite is a serious contender, heating above 200 to 300°C would totally destroy this record. If glass has an important effect on optical properties (as it does in lunar materials), it should be kept below 700°C where major effects start to occur (or less if water vapor is present).

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

March 8, 1974

Dr. Laurence E. Nyquist
Planetary and Earth Sciences Division
Code TN7
NASA/JSC
Houston, Texas 77058

Dear Larry:

This is a reply to your letter of Februray 15,1974 regarding a possible method of biological sterilization for Martian samples. I do not have much to add to Bruce Doe's "top of the head" suggestions, but I would like to restate it from a Pb researcher's eye.

1. Properties to be measured: I believe age determination studies of Martian samples are among the most important subject to be studied and I expect that the U-Th-Pb method will be included in the dating, because the $^{207}Pb/^{206}Pb$ ratios and related ages are not affected by very recent events (i.e. not dependent of the observed U/Pb ratios).

2. Effects of sterilization: We unfortunately do not have enough knowledge of sterilization procedures to know what is the best procedure for the U-Th-Pb system, and carefully designed experiments are needed. Our recent experiments show that about 58% of the total Pb was extracted from the "orange soil" 74220 when heated to 500°C for 12 hours in vacumm. Soils 12033, 12070 and 14259 released about 10%of their total Pb when heated 600 C in vacumm. Although we have not done a precise stepwise-heating experiment such as Ar workers have (e.g. Dr. Signer's experiments), I presume from the above stated results that some of the Pb migrates among minerals at 300°C heating. In any case, we must study carefully the sterilization effects on the U-Th-Pb system in minerals and rocks Which are most likely to occur on Mars.

Some attractive sterilization methods to me are (in order of preference):
i) Sterilization by rader waves.
ii) Incandenecent instant heating.
iii) The 150 C degree (or lower)heating for one month.

I would like to participate in the study group for testing effects of sterilization on the U-Th-Pb systems of minerals of Martian-like rocks, if NASA plans such experiments.

Sincerely,

M. Tatsumoto

ORIGINAL PAGE IS
OF POOR QUALITY

WASHINGTON UNIVERSITY
ST. LOUIS, MISSOURI 63130

DEPARTMENT OF PHYSICS

March 15, 1974

Dr. Robin Brett
Code TN7
NASA/Johnson Space Center
Houston, TX 77058

Dear Robin,

This will supplement the enclosed letter to S. Dwornik discussing Martian samples.

Speaking generally, practically all the measurements that have been made on lunar samples should be made on Martian samples, plus a few more based on the fact that Mars has an atmosphere. Concerning our three major experimental thrusts, I would rate the track and rare gas studies as high priority and thermoluminescence (TL) as a rather low priority. The TL might be interesting but it is difficult to prove that it is at this time.

Concerning the problem of alternative time-temperature treatments of the samples, it is clear and easily demonstrable that science is best served by keeping the temperature as low as possible, even at the expense of longer treatment times. For just about any process that would dissipate the information carried in the distribution of atoms in the samples (track annealing, gas diffusion, isotopic equilibration, TL annealing, etc.), the rate of the process would be proportional to $e^{-Q/kT}$. The activation energy Q would characteristically be of the order of 1 or 2 electron volts. For the proposed heating temperatures kT is a small fraction of a volt (room temperature is $\frac{1}{40}$ volt) and thus $Q/kT >> 1$. A relatively modest change in temperature gives a very large change in rate. For a specific example, if Q = 1 volt, T_1 = 350°C, and T_2 = 250°C, $Q/kT_1 \approx 19$ and $Q/kT_2 \approx 22$, so the process goes $e^3 \approx 20$ times faster at 350°C than at 250°C. Thus, a week at 250°C does less damage than a day at 350°C. Similarly, for the same Q, the process goes about 100 times slower at 150°C than at 250°C, and a month at 150°C is clearly preferable to a week at 250°C, and so on. The differences are more pronounced for higher Q, less for lower Q, e.g. for Q = 2 ev, the difference between 350°C and 250°C is more like a factor of five hundred. In general, any damage that has not already been done by the temperatures on the Martian surface would be minimized by using the lowest temperatures possible.

The real situation, of course, is more complicated and should be regarded as a composite of processes characterized by a range of activation energies. For the rare gases, for example, adsorbed gases (low Q) would probably be completely lost even at moderate temperatures like 150°C, while gases

embedded in the crystal structure (radioactive decay products, spallation products), with relatively high Q, would probably not be seriously affected by temperatures less than ~500°C on any reasonable time scale. Similarly, we showed that tracks in lunar feldspars and pyroxenes are ~50% annealed in 1 hour at 500°C, and we estimate that the same loss would occur in ~60 days at 350°C. However, even low temperature annealing influences the tracks to some extent and modifies, for example, the track length distributions. By and large we would not expect large effects at 150°C (equivalent to the temperatures reached in lunar rocks) but would expect very noticeable effects at 350°C for a day. The latter treatment would degrade the information obtained but would not wipe it out. The TL degradation has the lowest Q and most of the scientific information obtainable from TL would probably be lost even by the 150°C treatment and almost surely be completely wiped out by 350°C.

In summary, the highest priority measurements (track and rare gases) would be only slightly affected by the 150°C treatment and could survive the 350°C treatment with some loss of scientific information. The TL would be severely affected at all heating temperatures. Whenever the choice is presented, heating for longer times at lower temperatures is clearly the way to go.

As a final thought, I wonder if the biologists have considered radiation sterilization? Prodigious doses of γ-rays in the 1 to 5 MeV range would of course destroy any scientific information that derives from the study of trapped electrons (e.g. thermoluminescence) but would leave most other properties unaffected. This is probably something that should be looked into very seriously.

I have not discussed the proposal to "heat the samples to incandescence." The phrase has a certain ring to it but is imprecise. If you mean to vaporize the sample and break it down into its constituent ions, I guarantee that this will destroy any living organism. Are you kidding?

Best regards,

Bob Walker

Robert M. Walker
Professor of Physics

RMW:hk
Enclosure

MAX-PLANCK-INSTITUT FÜR CHEMIE
(OTTO-HAHN-INSTITUT)

FERNSPRECHER 25044
MAINZER VOLKSBANK 28567
Abteilung Kosmochemie
Direktor: Professor Dr. H. Wänke

6500 MAINZ, DEN
SAARSTRASSE 23
SCHLIESSFACH 3060

Dr. Larry Nyquist
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058
U.S.A.

March 7, 1974

Code: TN 7

Dear Dr. Nyquist:

In the exploration of mars as of any other planet for a geochemical point of view element correlations will be of major importance. From the research on lunar samples the significance of element correlations became evident. All lunar samples showed identical values for many element ratios like Fe/Mn, K/La, K/Ba, W/La and to a somewhat smaller degree Fe/Sc and several others. One should therefore take great care to avoid any possible contamination for these elements. The W/La-ratio is of special interest as W is only partially lithophile and actually the major portion of W on the moon must reside in a metal core or layer. Hence, we have an ideal case to estimate the metal/silicate ratio of planets. (The samples of Luna 16 and Luna 20 for example showed high contamination in W).

As for the moon, for the parent planet of the eucrites and to some extend for the earth, the correlated elements will provide a geochemical frame-work for the estimation of the bulk chemical composition of mars.

The sterilization procedures should ,of course, avoid all possible contamt-nations. Dry heat sterilization in sealed containers should be preferred. Sterilization with addition of water vapour is the worsest what could be done. As far as time-temperature relation for the sterilization is concerned, case a) - long time-low temperature - will do least harm to the problems in mind which in general rely on trace element concentrations and distributions.

This is in short what I can say at the moment in this respect.

Yours sincerely,

H. Wänke

ORIGINAL PAGE IS
OF POOR QUALITY

THE UNIVERSITY OF UTAH
COLLEGE OF MINES AND MINERAL INDUSTRIES
SALT LAKE CITY 84112

DEPARTMENT OF GEOLOGY
AND GEOPHYSICS
717 Mineral Science Building

March 4, 1974

Dr. Robin Brett
National Aeronautics and
Space Administration
Mail Code: TN7
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Robin:

Last week we held a meeting of W. E. Glenn, W. P. Nash, W. J. Peeples, R. W. Shorthill, W. R. Sill, R. C. Wilson, and myself for the purpose of preparing a report to you on Martian sample sterilization. The attachment is a summary of the properties which might be measured, their priority in terms of understanding Mars, and our guess of degradation by elevated temperature environments.

We would recommend that the most acceptable treatment, of those you list, is "Dry heat sterilized in a sealed container at 150° for 1 month".

The needed research is simple: develop simulated Martian materials, subject them to one or more of the proposed environments, and evaluate the degree of degradation of knowledge -- for each property -- by application of the environment.

Our preference would be to avoid any sterilization by returning the samples to a space shuttle station for measurements. Alternatively, make the key measurements in Martian orbit and then sterilize the sample.

I hope that this brief report will assist you.

Kindest regards,

S. H. Ward
Chairman

SHW:mm

PROPERTIES TO BE MEASURED ON A RETURNED MARTIAN SAMPLE

			Priority
I.		Petrology - directed toward knowledge of interior of Mars	
	Δ	1. primary mineralogy	2
		2. petrographic texture	3
		3. petrofabrics	3
*		4. geochronology (K-Ar Sr-Rb)	1
		5. glass component	4
II.		Surficial material - directed toward study of surface processes	
		1. Weathering products	
	Δ O	a) oxides and hydroxides - mineralogy and chemistry	3
**	Δ O	b) clays - mineralogy and ion exchange capacity	2
*	Δ O	c) other hydrates such as opal - mineralogy and chemistry	3
*	Δ O	d) contained liquids and gases	3
		2. Soil mechanical properties	5
		3. Sediment petrography	
		a) grain size	4
**	Δ O	b) clay composition	2
**	Δ O	c) mineralogy	4
III.		Other Properties	
		A. Geophysical	
		a) density	5
*	Δ O	b) electrical properties	4
	Δ O	c) thermal conductivity	2
*	Δ	d) elastic parameters	2

		Priority
**	e) magnetic properties	2
Δ O	f) optical spectral reflectance	3
	B. Geochemical	
	a) radioactive spectrum	2
*	b) isotopes	2
Δ O	c) gas content	2

Legend:

* Degraded by sterilization at 200^{0}C and above.

** Possibly degraded by sterilization at 150^{0}C and above.

O Degraded by exposure to interplanetary vacuum.

Δ Degraded by adding water.

We assume slow heating and cooling.

ORIGINAL PAGE IS
OF POOR QUALITY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF GEOLOGICAL
AND PLANETARY SCIENCES

TELEPHONE 213-795-6811

30 January 1974

Dr. Stephen E. Dwornik, Chief
Planetology Program
Planetary Programs, Office of
Space Science
NASA Code SL
Washington, D. C. 20546

Dear Dr. Dwornik:

This letter is in response to your letter of 20 December regarding a study by the Planetary Programs Office to determine the feasibility of a Mars surface Sample Return mission.

Let me first indicate that this laboratory is very interested in participating in isotopic experiments to determine the extent of sample degradation which may be caused by various sterilization procedures. There are two critical studies which should be made in this area. One is the extent of rare gas loss by simple heating, and the other is X-irradiation. These studies should include the range of heating and/or X-irradiation in the realm of those considered for sterilization procedures. These analyses should also be done on a variety of materials including terrestrial, meteoritic, lunar and also, possibly, synthetic materials which might resemble a martian soil (both hydrous and anhydrous). In addition, studies of Rb, Sr and Pb should be carried out on the same samples, in order to assess the effects on these elements in the constituent mineral phases. We would be willing to undertake such studies on a contract or grant basis, and would be willing to distribute samples with other workers who would undoubtedly be studying mineral degradation as a result of sterilization.

There are several other laboratories throughout the world with people of such competance which could contribute effectively to the program as proposed in your letter. These include Dr. Peter Signer (ETH-Mineralogical Institute, Zurich, Switzerland), Johannes Geiss (Universitat Berne, Physikalisches Institut, Berne, Switzerland), Edward Anders (The Enrico Fermi Institute for Nuclear Studies, The University of Chicago), Kurt Marti (Department of Chemistry, University of California, La Jolla, California), Roman Schmitt (Department of Chemistry, Radiation Center, Oregon State University), Larry Haskin (Planetary and Earth Sciences Division, Johnson Space Center, Houston), Ray Siever (Department of Geological Sciences, Harvard), Cliff Frondel (Geological Sciences Department, Harvard), Robert [illegible] (Department of Physics, Washington University, St. Louis, Missouri), Robert Fleischer (Research Laboratory, General Electric Company, Schenectady, New York), John Philpotts (Planetology Branch, Goddard Space Flight Center), John [illegible] (Institute of Geophysics, University of California, Los Angeles), and Gordon Eaton (University of Oregon, Center for Volcanology, Department of Geology).

CALIFORNIA INSTITUTE OF TECHNOLOGY [illegible]

Dr. Stephen E. Dwornik, Chief
Planetology Program

30 January 1974

Page two

I am certain that there are many others who could contribute significantly to the solutions of the problems which you have posed in your letter. I would certainly hope that capable people, knowledgeable in the alteration of fine grain terrestrial sediments would be among the participating members.

I have just spoken with Professor Hans Eugster of the Johns Hopkins University who is extremely knowledgeable about processes and problems regarding [illegible] sedimentation. He indicated that he would be quite willing to participate in a Mars study, as indicated. He is uniquely qualified to give new and imaginative insights.

In this laboratory, the prime person who would wish to carry for [illegible] researches would be John C. Huneke, Senior Research Fellow. He has indicated to me that he would be willing to participate in this problem and to aid in some of the planning stages of problem definition and analysis.

Very truly yours,

G. J. Wasserburg
Professor of Geology
and Geophysics

GJW:kr

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF GEOLOGICAL AND PLANETARY SCIENCES

TELEPHONE (213) 795 6811

15 November 1973

Dr. Michael B. Mc Elroy, Chairman PSC
Pierce Hall G3A
Harvard University
Cambridge, Massachusetts 02138

and

Members of PSC

Gentlemen:

This note is to report on the Mars Sample Return Symposium at Ames on 24 and 25 October. The "conference" lasted two days and was rather loosely organized, so that no proper motion or action was taken by the participants. nonetheless, it is my impression that a strong consensus existed on the basic issues. These basic items are as follows:

1. There was a strong desire to pursue a Mars sample return mission with sterilization. No "in principle" opposition to a sterilized sample return was evident from the participants, including both Josh Lederberg and Carl Sagan.

2. The definition of sterilization and the mechanism by which sterilization could be accomplished (thermal, time, chemical, irradiation . . .) is uncertain and requires adequate definition.

3. The effects of possible sterilization procedures on the science ontent of a returned sample (both Inorganic, physical, "biochemical" and morphological) are unknown and must be assessed.

4. The Agency must aid ICBC in seeking and defining legitimate, operable sterilization and quaranteen requirements for the "importing" of extraterrestrial materials. The lunar quaranteen fiasco, which subjected lunar samples to enormous risks, whould not be repeated.

Dr. Michael B. McElroy
Members of PSC

15 November 1973

Page two

The above conference conclusions also implied action items which required prompt response from the Agency and the general science community if the matter of sample return is to be pursued.

1. A range of possible operable definitions of sterilization must be stated by a small group of knowledgeable scientists. This group would have to consist predominantly of non NASA personnel.

2. Experiments must be undertaken by scientists specializing in "biochemical", chemical, physical and organic life form (morphology) fields for the purpose of ascertaining the extent of sample degradation by various sterilization procedures (see 1 above) on model Mars materials. Again, this should not be carried out solely by NASA personnel.

3. The ICBC requirements for sterilized sample return and quaranteen must be defined so that only a small part of a Mars sample is used for ICBC protocol. The ICBC must re-evaluate the lunar experience and adequately define the circumstances under which the quaranteen restriction may be satisfied.

Very truly yours,

G. J. Wasserburg
Professor of Geology
and Geophysics

GJW:kr

x. c. J. Naugle
D. Young

United States Department of the Interior

GEOLOGICAL SURVEY
WASHINGTON, D.C. 20242

March 6, 1974

Dr. W. C. Phinney
Chief, Geology Branch
Johnson Space Center Code TN7
Houston, Texas 77058

Dear Bill:

We had our discussion on the Martian sterilization procedure. Ed Roedder has a separate report to Elburt King which I shall not reiterate here.

The general feeling is that any heating might be deleterious to carbonates and clay minerals, both to their composition and morphology. We feel that rate studies on carbonates and clay minerals should be done in conjunction with the organic decomposition rate studies to obtain optimum heating-time integrals.

George Faust felt that you would run a good chance of forming siderite from limonite + CO rich atmosphere if you heated it up. There are a wide variety of hydrous metastable carbonates that could form from exposure to a humid CO_2 rich atmosphere. George also felt that fluorine could form enamel-like compounds if very fine grained fluorides are present.

Moto Sato felt that most of the mineral assemblages on the Martian surface would be metastable and hence very susceptible to any maltreatment like heating.

Mac Ross and I are very concerned about auto-oxidation effects caused by heating in vacuo or inert gases and preferentially driving off hydrogen from ferrous iron-hydroxyl compounds (clays, micas, amphiboles, hydrous phosphates, carbonates and sulfates) leaving the ferric compound as the residua. This would negate H/D isotopes studies, H_2O bulk chemistry, Fe^{2+}/Fe^{3+} ratios, densities, and any spectral work which involved charge transfer processes (visible, ESR, Mossbauer, etc.).

Rosalind Helz came up with the best suggestion of all. Collect two samples. Sterilize one and check it for beasties. If it is clean, then open up the pristine sample for sample analysis.

I will be glad to amplify any of these, if needed, but I feel the kinetics program is the best positive suggestion, along with Ros' idea.

See you next week, especially the 19th.

Best regards,

David R. Wones

APPENDIX III

Progress Report

Preliminary Study of Dry Heat Sterilization Effects on Inorganic Science for a Returned Mars Surface Sample

Department of Geology
University of Houston
Houston, Texas 77004

March 27, 1974

Preliminary Study of Dry Heat Sterilization Effects on Inorganic Science for a Returned Mars Surface Sample

Summary

The brief study has involved eight laboratories and a number of different analytical techniques to characterize five model samples which are possibly analagous to some fraction of the Martian surface. The object of the study is to attempt to estimate, based on the analyses and data in the literature, the seriousness of sample inorganic degradation resulting from dry heat sterilization of the very short time available for this study, all results should be considered as preliminary. Also, it is obvious that the general conclusions reached are applicable only to the materials studied and will not apply to other samples.

A number of changes in chemistry and mineral phases present were noted in most of the samples as a result of heating to as much as 275°C. The changes mostly involve loss of volatile components. U. S. Geological Survey rock standard diabase W-1 was the least affected by heating.

The sterilized sample still retains an immense amount of inorganic science information and is of extreme scientific interest. If the temperature profile of the sterilization is well known, much of the information lost can be reconstructed. Also, if the identities of the gaseous species that are lost can be determined, the chemical and mineralogical sample changes can be interpreted rather completely.

If there are trade offs to be made on sterilization conditions, it appears that the lowest possible temperature is desirable from an inorganic point of view, even though the time required for sterilization may be longer.

Further work on other samples and the same samples is in progress, but it does not appear that an extensive program of experimental work of this type is justified until there is much better information on the chemistry and/or mineralogy of the Martian surface and the actual conditions of sterilization that will be required.

APPENDIX B1

National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
Houston, Texas
77058

NASA

CALL FOR INPUT TO A MARS SAMPLE-SCIENCE DOCUMENT

Reply to Attn of SN2-87-L084

February 10, 1987

Dear Colleague:

Analysis of geologic samples collected from Mars should be considered one of the key elements of a vigorous program for planetary exploration. Although the case for a Mars sample-return mission has been made in various ways over the past two decades, there remains a need for a self-contained and up-to-date summary of the scientific goals and requirements for collecting Martian samples and returning them to Earth for detailed study. I am asking for your assistance in preparing such a report that can be used in planning future Mars sample-return missions.

The foundation of this report is an unpublished document entitled, "On the Petrological, Geochemical, and Geophysical Characterization of a Returned Mars Surface Sample and the Impact of Biological Sterilization on the Analyses," that was prepared in 1974 at NASA/JSC and which may have also benefited from your participation or advice. Although most of the rationale in the 1974 report has not changed, important information obtained later from the Viking missions (1976-77) and from the putative Martian meteorites was not represented. The new report will incorporate those later advances and will also address requirements for biological studies of the samples. Much of the emphasis, though, will remain on defining modes of sample preservation that are needed to achieve the goals for sample analysis. A draft outline for the new document is enclosed, along with a copy of the "Conclusions" section of the 1974 report.

For your areas of special interest and expertise, please provide me with written responses to the following questions:

(1) What aspects of Martian history can be uniquely (or best) addressed by direct analysis of samples returned to Earth?

(2) What types and quantities of samples are needed to support the analyses related to (1)?

(3) What degrees of sample degradation can be tolerated without defeating the analysis goals? (Specify, if possible, upper limits for temperature, pressure, radiation, acceleration/shock, etc.).

(4) What <u>in situ</u> measurements should be made on Mars to supplement or replace information that might be lost from degraded samples?

In addition to your specific responses to the questions listed above, your general comments and suggestions are welcome. I am seeking input from a broad cross-section of the planetary geoscience community so feel free to distribute copies of this letter and the enclosed pages to your interested colleagues who might not have received them directly. In formulating your reply, please keep in mind that the purpose of this project is to summarize the case for material analyses of returned Martian samples. Landing site selection and on-orbit science are clearly important, and deserve mention, but will not comprise the central theme of this report.

In order to make the completed report available to mission planners by the end of 1987, I need your written opinions, advice, and suggestions as soon as possible but no later than May 1987. As was done in 1974, I plan to preserve all written responses as one or more appendices to the report.

I look forward to hearing from you.

Sincerely,

James L. Gooding

James L. Gooding
Space Scientist

Enclosures

Reply to: Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058 USA

Telephone: (713) 483-5128

Enclosure

MARS SAMPLE-SCIENCE DOCUMENT

DRAFT OUTLINE (% EMPHASIS BY CHAPTER)

PREFACE AND LIST OF CONTRIBUTORS (~ 1%)

1. INTRODUCTION (5%)
   - 1.1. SCIENCE GOALS FOR THE STUDY OF MARS
   - 1.2. MARS SAMPLE-RETURN MISSION AS PART OF MARS EXPLORATION
   - 1.3. RELATIONSHIP OF SAMPLE SCIENCE TO LANDING SITE SELECTION
2. IMPORTANCE OF MARTIAN SAMPLES (25%)
   - 2.1. INFORMATION CONTAINED IN PIECES OF MARS
   - 2.2. RELATIVE MERITS OF LABORATORY AND *IN SITU* ANALYSES
   - 2.3. LESSONS FROM THE *VIKING* LANDER EXPERIMENTS
   - 2.4. MARTIAN METEORITES: WHAT THEY MIGHT AND MIGHT NOT TELL US ABOUT MARS
   - 2.5. NEED FOR DOCUMENTED SAMPLES
3. SAMPLE PRESERVATION REQUIREMENTS (55%)
   - 3.1. INCIDENTAL DEGRADATION: REMOTE COLLECTION AND RETURN TO EARTH
   - 3.2. DELIBERATE DEGRADATION: BIOLOGICAL STERILIZATION
   - 3.3. TEMPERATURE AND PRESSURE EFFECTS
   - 3.4. RADIATION, ACCELERATION, AND SHOCK EFFECTS
   - 3.5. INFORMATION LOST FROM DEGRADED SAMPLES
     - 3.5.1. ICES AND ADSORBED VOLATILES
     - 3.5.2. MINERALS OF LIMITED STABILITY
     - 3.5.3. STABLE ISOTOPE TRACERS AND GEOTHERMOMETERS
     - 3.5.4. LABILE ORGANISMS OR FOSSIL REMAINS
   - 3.6. LOW-TEMPERATURE GEOCHEMISTRY, BIOLOGY, AND CLIMATOLOGY
   - 3.7. IGNEOUS PETROLOGY AND GEOCHRONOLOGY
   - 3.8. PHYSICAL PROPERTIES
   - 3.9. INFORMATION RECOVERY BY *IN SITU* ANALYSES ON MARS
4. CONCLUSIONS AND RECOMMENDATIONS (5%)

REFERENCES AND APPENDICES (10%)

ORIGINAL PAGE IS
OF POOR QUALITY

CONCLUSIONS OF 1974 JSC REPORT ON MARS SAMPLE RETURN

GENERAL CONCLUSIONS

Mike Carr (Appendix II) points out the great importance of returned samples for understanding planetary evolution.

> "The analysis of returned lunar samples has completely transformed our concepts of how the Moon formed and what its subsequent history has been. Our present knowledge of the timing of events that led to the Moon's present configuration, the evolution of the crust, the bulk and trace element geochemistry and how it differs from that of the Earth have all been derived from examination of returned samples. The degree to which this understanding could have been achieved solely by remote analysis is a matter of conjecture but there is ample reason to be skeptical. Having lunar samples in hand allowed the complete analytical and intellectual capability of the scientific community to focus on the problem of the Moon's evolution. Instead of having a small pre-determined set of analytical techniques applied to the samples, the approach could be both all-encompassing and flexible, the analytical emphasis shifting as the meaning of each set of results become better appreciated. There is no reason to believe that these enormous advantages of returned samples should be any less for Mars. Indeed the apparently more complex geology of Mars enhances the importance of the kind of comprehensive examination that a returned sample allows."

This is not to demean the value of remote analysis. It is assumed that the mission design and execution will take cognizance of all available data relevant to the composition, physical state and geologic context of the Martian surface and the site from which the sample will be collected.

A. <u>Sample Acquisition and Supporting Data</u>

It is difficult to envision a returned Mars sample whose study would not add greatly to our knowledge and understanding of the planet and the Solar System. On the other hand, judicious selection and processing of the sample during acquisition may enormously enhance its scientific value. Although some of the improvements over a single, simple device suggested below may be incompatible with one another, each has sufficient merit to warrant serious consideration. We have not attempted to prioritize these alternatives; that must wait until more is known about Mars (from Viking, principally) and the actual constraints to be imposed on a sample-return mission.

If the returned Martian sample is sterilized, much potential information will be lost. However, some of that information may be recovered if the time-temperature-pressure conditions are continuously

monitored during sterilization and on the entire Earth return trip. Every effort must be made to keep the sample at its temperature of collection on the Mars surface. If sterilization is necessary, the sample should be cooled afterward to that temperature for the duration of the flight to Earth.

Experience with both lunar and terrestrial rocks has shown that particles greater than about 2 mm in diameter are required to yield sufficient details to permit truly fruitful interpretations, even if the rocks are texturally quite fine-grained. On the other hand, very large fragments are often wasteful of sample mass in terms of information returned. The chief constraints appear to be that some fragments must be large enough for mineral separation for age dating and for determining their petrologic textures. A 2-cm fragment meets these requirements. Relatively few experiments are eliminated or seriously compromised if fragments larger than 2 cm are not included in the returned sample, and the loss of those is more than offset if a variety of smaller fragments is returned instead of one or two larger ones. In order to assure that the sample contains abundant fragments of useful size (assuming that they are present in the vicinity of the lander), we strongly recommend that the sample-acquisition mechanism have the capability to enrich the collected material in particles 2-20 mm in diameter. This might be accomplished by a sieving or raking device, when used in conjunction with a more general sampler, because acquisition of a sample with a more nearly representative size distribution is also essential (i.e., a typical soil sample).

The keys to many important questions regarding near-surface processes and the recent erosional-depositional history of Mars may lie in the fine-grained stratigraphy of surface materials. Some specific questions and properties include depth of weathering, cosmic-ray studies, thermoluminescence, turn-over rate, and the depth of condensation of volatiles. The mode of collection most likely to preserve the stratigraphic details sufficiently well to permit such studies is coring. We recommend the consideration of a coring device capable of obtaining as long a core as possible (of the order of 1 m).

For several reasons, it would also be desirable to collect a variety of sub-samples from different locations and depths in the immediate vicinity of the lander and, if possible, to maintain these samples separately from one another. One mechanism for accomplishing this might be a scoop-type sampler similar to that to be used on Viking '75. This capability helps to insure the acquisition of a useful sample even if sampleable material is but sparsely and erratically distributed in the sampler field. Used in conjunction with an imaging system, it would also permit selection of sample characteristics for maximum scientific return.

CONCLUSIONS OF 1974 JSC REPORT ON MARS SAMPLE RETURN

It is clear that thermal treatment may release substantial quantities of adsorbed and chemically bound volatiles to the Martian atmosphere enclosed with solid samples. The most crucial measurements to be made on the atmospheric portion of the sample are the isotopic ratios of H and C (Appendix II, letter from T. Owen), and these would be the most severely affected. It is therefore important to provide for a separate sample of the Martian atmosphere that is kept separate from the solid surface sample.

Although auxillary scientific investigations should obviously be subordinated to the prime goal of obtaining and returning a sample of Mars surface material, we feel that much valuable science will be gained with the addition of landed imagery and the capability to direct the sampling device in response to it. Not only would imagery of the sampled environment greatly enhance the scientific interpretation of laboratory studies, but it could prove essential to assuring that a usable sample is obtained. It is needed in order to select different spots in the sample field for sampling. Visual imagery could also be important in assuring the safety of a sampling device if obstacles exist in the sample field.

The options listed above should be seriously considered as early planning for the mission is begun so that the constraints they impose on the mission can be better understood. Under no circumstances should our desire for the above-mentioned devices, valuable as they would be, be construed as implying that a lesser mission would not be of great scientific value. The scientific return from the 5 grams of lunar material from the Luna 16 and 20 missions acquired by American scientists (Earth and Planetary Science Letters, 1972, vol. 13, no. 2, 244 pages; Geochimica Cosmochimica Acta, 1973, vol. 37, no. 4, 390 pages) is clear testimony to the value of even a very small, undocumented sample. It is nevertheless hoped that the mission to collect a Martian sample will be designed to assure the highest feasible scientific return.

B. Landing Site: Conditions and Constraints

While it is obviously premature to make specific recommendations of areas or localities on Mars from which a sample should be obtained, certain general characteristics of sample sites can be recognized, and their consequences inferred. We recommend that a Martian sample return mission be targeted to collect as wide a variety of materials as possible. This type of sample would allow the study of a wide range of Martian processes and materials. We further recommend that every effort be made to assure that the sample contains volcanic rocks (in order to study Martian interior structure, chemistry and time scales for vulcanism) and materials that display a wide range of weathering conditions (in order to study Martian surface processes and environments).

If a capability for precise targeting and pre-landing site certification exist, it may be useful to consider briefly the site characteristics that would have desirable properties. The site should have a heterogeneity of surface materials, and indications that it represents a locus of accumulation of transported debris. Based on our current understanding of Mars, a canyon-mouth area would be such a site. Other things being equal, the vicinity of apparently young volcanoes would seem to favor the acquisition of fresh volcanic materials. We emphasize that these criteria are based on our current knowledge of the planet, and should be continuously updated as we learn more about Mars.

C. Effect of Possible Biological Sterilization

It would probably not be possible to destroy all of the interesting information in a Martian sample by any method of biological sterilization. The value of the sample can be severely compromised, however, depending on the nature of the sterilization process. The effects are complicated and depend on the nature of the sample. The reader must consult the body of this report in order to understand the scope of the problem. Some brief comments are given below.

If the returned Martian sample consisted or primary, dry silicate minerals (such as feldspars, pyroxenes, olivines, and oxides), the sample could withstand moderate temperatures of sterilization (about 200 to 300°C) without major loss of information. At slightly higher temperatures (about 400 to 500°C) oxidation-reduction reactions would begin and the more volatile elements would migrate. As sterilization temperatures increased, more and more chemical and isotopic systems would become unstable, until melting occurred at about 1100 to 1300°C, when all data except those on bulk composition would be lost.

Further consideration of the effects of sterilization is highly model dependent and must be constantly re-evaluated as new and improved data concerning the surface of Mars become available. Materials such as secondary hydrates, carbonates, organic compounds, "ice," various water-soluble or effluorescent minerals, and hydrated amorphous and glassy materials will start to break down under various pressure conditions temperatures as low as 100 to 200°C (see table in section on Mineralogy and Petrology). The products of these breakdowns would react with the primary silicates and oxides and, in the process, could seriously disrupt the various chemical, isotopic and physical systems. The extent of the damage is strongly dependent on the temperatures and times of sterilization as well as on the exact nature of the materials in the sample.

CONCLUSIONS OF 1974 JSC REPORT ON MARS SAMPLE RETURN

D. Recommendations for Sterilization Procedures

Hopefully, sterilization will not be required. From the point of view of extracting scientific information, sterilization is at best a necessary evil regardless of the method used. More acceptable than sterilization of the whole sample would be the return of a split sample, half of it sterilized and the other half not, to be opened after an evaluation of the biological hazard could be made. The following guidelines apply to a sterilized sample.

We believe that the following important features can be satisfied by a sterilization procedure, independent of the exact times and temperatures of heating that are finally deemed necessary.

1. The container should probably be made of some tough, durable material such as stainless steel. It should have as foolproof a seal as is possible to make and should be able to withstand internal pressures of at least a few hundred bars. The gases evolved during heating must be preserved in some manner. Inert chemical liners such as fused quartz or gold (or teflon, assuming sterilization temperatures are low enough) should be considered. Differential loss of hydrogen during sterilization is an important consideration, because changes in the state of oxidation of the sample would severely impair interpretation of magnetic and of certain mineralogical properties. Such changes can be minimized with a gold liner. No single liner material is acceptable for the whole range of scientific experiments. Gold is best for hydrogen retention, but it entails contamination with siderophile elements, and so on.

   In any case, material used to line the interior of the container must in no way interfere with the ability to provide a reliable seal.

   Whatever material is used for the container, it should be thoroughly degassed by thermal cycling prior to use and should be as free as possible from any source of contamination of important trace elements. Some mechanism should be incorporated to allow withdrawal of gases after sample return, and the container should be designed in such a way that volatile coatings condensed on the interior walls as a result of sterilization can be recovered and examined.

2. The container must, of course, have some pressure release mechanism for safety if there is any danger whatsoever that internal pressures will exceed the strength of the seal. Retention of the gases evolved during sterilization has extremely high priority, but it obviously must not be allowed to interfere with preservation of the solid sample.

   Gases released after break of the inner seal should be absorbed on a series of appropriate getters present within the larger, sealed sample container.

3. Some attention should be paid to the possibility of chemically or physically removing the evolved gases from contact with the solid sample during the sterilization procedure. This may be desirable to prevent dissolution, re-hydration, re-carbonation and possible formation of new chemical compounds in the sample. Such a feature might make a pressure-release safety valve unnecessary, but it is not essential, and it must not be allowed to interfere with preservation and recovery of the evolved gases in such a way that isotopic and chemical information is lost.

4. A sample of the Martian atmosphere should be obtained and should be kept physically separate from the solid sample and from the gases evolved from the solid sample during sterilization.

5. Whatever the conditions of the sterilization procedure, the temperature-time history should be kept as simple as possible and should be carefully monitored and recorded. Ideally, this would involve heating at a single, specified temperature for a fixed length of time. Knowledge of the temperature-time history of the sample is critical in evaluating the original character of the Mars sample prior to sterilization, inasmuch as similar laboratory experiments will have to be carried out on analogous materials on Earth.

6. The temperature of sterilization should be kept as low as possible. Longer times are preferable to shorter times at a higher temperature.

7. No extraneous material of any kind should be added to the sample in some misguided effort to promote sterilization. This most particularly applies to addition of H_2O. Dry heating is preferable to wet heating even if slightly higher temperatures must be used. Heating in a humid atmosphere would promote isotopic and chemical exchange among minerals, would tend to destroy some minerals and form new ones, and in general would result in greater alteration of the original sample and more loss of scientific information. We realize that dry heating will dehydrate certain clay minerals irreversibly, but this is by far the lesser evil, because it should be possible to reconstruct the nature of the original clays from their decomposition products, provided that the volatiles released during sterilization are retained for analysis.

CONCLUSIONS OF 1974 JSC REPORT ON MARS SAMPLE RETURN

Of course, the sample collected could itself be very humid or contain ice and large amounts of thermally unstable materials. This could result in considerable pressure build-up during heating which would be undesirable (see Min-Pet report, Table II). To prevent this, the pressure release mechanism in the inner container should be set to a maximum of no more than a few dozen bars.

E. Experimentation in Preparation for a Returned Mars Sample

Preparations for the investigation and analysis of the returned Mars sample fall into two general categories as follows: 1) improvement and up-grading of analytical techniques and 2) simulation experiments to help interpret sample data. The identification of all of the reasonable areas of effort for development of analysis techniques is a large task and probably is worthy of a separate study. A partial list of these investigations is included below. No priorities should be inferred from the order in which the tasks are listed.

Many of the techniques used for the study of lunar samples will have to be modified to consume less material or be improved to gain more information from smaller particles in this small and extraordinary sample. It is, therefore, critical that laboratories presently doing the best job of petrological, geochemical, and geophysical analysis continue to be supported, both to keep a knowledgeable, up-to-date community of scientists and to further the state-of-the-art in analytical capabilities of all pertinent types. The tasks listed in the accompanying table are a few that need extra impetus at this time. The value of those development efforts are not greatly dependent on any special model of the Martian surface but are generally applicable

Pre-return Analytical Development

1. Chemical analysis of H_2O, CO_2, N_2, S, halogens, and platinum group elements.

2. Facility and techniques to handle and analyze (chemically and physically) small (1 to 10 micron) fragments.

3. Design and construction for a Mars sample return container. This study should include the material(s) that the container is constructed from, the nature of the seal, the nature of pressure release valves, mechanisms for temperature control, and gas adsorbers.

4. Mineral separation techniques to avoid elemental exchange, structural modification and sample degradation during separation.

Simulation studies should be limited to the most critical until more is known about Mars. After the actual sample return, a rather complete series of experiments to determine the effects of sterilization on the sample would then be done and would aid significantly in the reconstruction of the chemical and physical properties of the sample prior to sterilization. Some suggestions are included in the following table.

Pre-return Experiments

The following experiments are important in a general way to assessment of the value of a returned Martian sample.

1. Studies of rates of decomposition of carbonates as a function of temperature and partial pressure of carbon dioxide.

2. Experiments to determine the actual redistribution processes of elements involved in the three different isotopic dating techniques to heating in sterilization environments and in natural environments to temperatures both above and below those required for structural transitions and reactions between phases. This will aid tremendously in the understanding and chronological interpretation of the isotopic systematics obtained on such samples.

3. Some of the minerals and mineral assemblages which are reasonably anticipated as significant Martian rock types have not been adequately studied by all (or any) of the isotopic dating techniques. This must be done to determine the nature of chronological information which can be obtained by each technique and the systematics for obtaining this information. This is particularly true for the $^{40}Ar/^{39}Ar$ technique, which is relatively new and where the proper interpretation of age spectra can be obscure. For this reason, it is recommended that each proposed sample type be thoroughly studied by all dating methods.

4. Careful studies of track annealing as a function of time and temperature.

5. Experiments on relevant minerals to determine the extent of isotopic ratio shifts corresponding to loss, gain, or exchange of structural volatile molecules (e.g. H_2O, CO_2) during sample return and sterilization. For example, comparison of D/H obtained in clays heated in sealed containers to D/H in unheated samples and similar studies for $^{12}C/^{13}C$ from carbonates.

6. Study of the effects of magnetic overprinting by heating for various lengths of time in various environments using fine-grained iron, iron oxides, and iron hydroxides.

APPENDIX B2

ADDRESSEES AND RESPONDENTS* TO 1987 "CALL FOR INPUT"

NAME	ADDRESS
William H. Abbott	Dallas, TX 75265
Philip Abelson	Washington, DC 20005
John Adams	Seattle, WA 98199
Stuart O. Agrell	Cambridge CB2 3EQ, U.K
T.J. Ahrens	Pasadena, CA 91109
Arden L. Albee	Pasadena, CA 91125
Joseph K. Alexander	Washington, DC 20546
E. Calvin Alexander	Minneapolis, MN 55455
Hannes Alfven	La Jolla, CA 92093
Lew Allen, Jr.	Pasadena, CA 91109
Judy Allton*	Houston, TX 77058
Edward Anders	Chicago, IL 60637
Don L. Anderson	Pasadena, CA 91125
Duwayne Anderson	College Station, TX 77843
George W. Andrews*	Washington, DC 20560
John Annexstad	Bemidji, MN 56601
D.E. Appleman	Washington, DC 20560
John T. Armstrong	Pasadena, CA 91125
James R. Arnold*	La Jolla, CA 92093
Gustav Arrhenius	La Jolla, CA 92093
Raymond E. Arvidson	St. Louis, MO 63130
Lewis D. Ashwal*	Houston, TX 77058
John R. Ashworth	Birmingham B47ET U.K.
Howard J. Axon	United Kingdom
Philip A. Baedecker	Reston, VA 22092
John R. Bagby	Jefferson City, MO 65101
Sturgis W. Bailey	Madison, WI 53706
Victor R. Baker	Tucson, AZ 85721
K. Banerjee	Minneapolis, MN 55455
Amos Banin	Rehovot, 72879 Israel
A. Bar-Nun	Tel-Aviv 69978, Israel
David J. Barber*	United Kingdom
Nadine Barlow*	Houston, TX 77059
Virgil E. Barnes	Austin, TX 78712
James E. Barrick	Lubbock, TX 79409
J. Paul Barringer	Princeton, NJ 08542
D. John C. Barru	Cambridge, MA 02133
V.L. Barsukov	Moscow, USSR
Charles A. Barth	Boulder, CO 80309-0392
Paul B. Barton, Jr.	Reston, VA 22092
Charles Baskerville	Reston, VA 22092
Abhijit Basu	Bloomington, IN 47405
Raymond Batson	Flagstaff, AZ 86001
Richard Becker	Minneapolis, MN 55455
R. Beerbower	Binghamton, NY 13901
F. Begemann	65 Mainz, Fed. Rep. of Germany
Jeffrey F. Bell	Honolulu, HI 96822
Peter M. Bell	Worcester, MA 01608-1446
A. E. Bence	Houston, TX 77252

NAME	ADDRESS
Timothy M. Benjamin	Los Alamos, NM 87545
William A. Berggren	Woods Hole, MA 02543
John L. Berkley	Fredonia, NY 14063
David Bermudes	Boston, MA 02215
Robert A. Berner	New Haven, CT 06520
L.F. Bettenay	Perth, Western Australia 6000
N. Bhandari	India
Klaus Biemann	Cambridge, MA 02139
Alan Binder	Houston, TX 77058
R.A. Binns	North Ryde, Australia 2113
David C. Black	Moffett Field, CA 94035
Thomas R. Blackburn*	Laurinberg, NC 28352
Douglas Blanchard	Houston, TX 77058
Milton Blander	Argonne, IL 60439
George E. Blanford	Houston, TX 77058
Karl Blasius	Pasadena, CA 91101
Robert B. Blodgett	Corvallis, OR 97331
Arthur L. Boettcher	Los Angeles, CA 90024
D.D. Bogard	Houston, TX 77058
Bruce F. Bohor	Denver, CO 80225
J.N. Boland	Australia
Jon Boothroyd	Kingston, RI 02881
Janet Borg	91406 Orsay, France
Penelope J. Boston	Boulder, CO 80307
David J. Bottjer	Los Angeles, CA 90007
A.J. Boucot	Corvallis, OR 97331
Joseph M. Boyce	Washington, DC 20546
William V. Boynton	Tucson, AZ 85721
J. Platt Bradbury	Denver, CO 80225
John Bradley	Chicago, IL 60616
Garrett W. Brass	Miami, FL 33149
Carol S. Breed	Flagstaff, AZ 86001
Robin Brett	Reston, VA 22092
G.A. Briggs	Washington, DC 20546
B.E. Britron	Mexico, D.F.
Philip E. Brown*	Madison, WI 53706
Kenneth Brown	Moraga, CA 94575
Dale Browne	Houston, TX 77058
Donald E. Brownlee	Seattle, WA 98195
William E. Brunk	Washington, DC 20546
Vagn F. Buchwald	2800 Lyngby, Denmark
Raymond J. Bula*	Madison, WI 53706
Ted Bunch	Moffett Field, CA 94025
Bonnie J. Buratti	Pasadena, CA 91109
Kevin Burke	Houston, TX 77058
A. L. Burlingame	Berkeley, CA 94720
Donald S. Burnett	Pasadena, CA 91125
R.G. Burns	Cambridge, MA 02139
Joseph A. Burns	Ithaca, NY 14853
Peter R. Buseck	Tempe, AZ 85287
D. A. Cadenhead*	Buffalo, NY 14214
Melvin Calvin	Berkeley, CA 94720

NAME	ADDRESS
A.G.W. Cameron	Cambridge, MA 02138
J.R. Cann	United Kingdom
Ian S. Carmichael	Berkeley, CA 94720
Michael Carr	Menlo Park, CA 94025
William A. Cassidy	Pittsburgh, PA 15260
Moustafa Chahine	Pasadena, CA 91109
Sherwood Chang	Moffett Field, CA 94035
Clark R. Chapman	Tucson, AZ 85704
Stillman C. Chase	Goleta, CA 93017
C.L. Chou	Champaign, IL 61820
Philip R. Christensen	Tempe, AZ 85287
Robert L. Christiansen	Menlo Park, CA 94025
Roy Christoffersen	Tempe, AZ 85287
Mark J. Cintala	Houston, TX 77058
Stanley M. Cisowski	Santa Barbara, CA 93106
Uel S. Clanton	Las Vegas, NV 89114
Benton C. Clark*	Denver, CO 80201
Roger N. Clark	Denver, CO 80225
Pamela E. Clark	Pasadena, CA 91109
Roy S. Clarke, Jr.	Washington, DC 20560
Donald D. Clayton	Houston, TX 77251
Robert N. Clayton	Chicago, IL 60637
W. H. Cleverly	Kalgoorlie, Western Australia 6430
Stephen M. Clifford*	Houston, TX 77058
Preston Cloud	Santa Barbara, CA 93106
Gary Clow	Menlo Park, CA 94025
A.G. Coats	Washington, DC 20053
Aaron Cohen	Houston, TX 77058
Alvin J. Cohen	Pittsburgh, PA 15260
D.W. Collinson*	NE1 7RU, UK
Jim Conel	Pasadena, CA 91103
Guy Joseph Consolmagno	Cambridge, MA 02139
Rex E. Crick	Arlington, TX 76019
John R. Cronin	Tempe, AZ 85287
G. Crozaz	St. Louis, MO 63130
James A. Cutts	Pasadena, CA 91101
Paul E. Damon	Tucson, AZ 85721
E.J. Dasch*	Corvallis, OR 97331-5506
D. W. Davidson	Ottawa, Canada K1A OR9
Merton E. Davies	Santa Monica, CA 90406
Don Davis	Tucson, AZ 85719
Phillip A. Davis, Jr.	Flagstaff, AZ 86001
Andrew M. Davis	Chicago, IL 60637
Raymond Davis, Jr.	Upton, NY 11973
Donald J. De Paolo	Los Angeles, CA 90024
Rene DeHon	Monroe, LA 71209
Donald DeVincenzi	Washington, DC 20546
Peter Deines	University Park, PA 16802
Jeremy S. Delaney	New York, NY 10024
John W. Delano	Albany, NY 12222

APPENDIX B2, con't

NAME	ADDRESS
Michael R. Dence	Ottawa, Ontario Canada, K1A 0Y3
D. J. Des Marais	Moffett Field, CA 94035
John Dietrich	Houston, TX 77058
Robert S. Dietz	Tempe, AZ 85287
Robert T. Dodd	Stony Brook, New York 11794
Bruce R. Doe	Reston, VA 22092
Thomas M. Donahue	Ann Arbor, MI 48109
J. Allan Donaldson	Ottawa K1S 5B6, Canada
Robert H. Dott, Jr.	Madison, WI 53706
Robert G. Douglas	Los Angeles, CA 90007
Eric Dowty	New York, NY 10024
Darrell M. Drake*	Los Alamos, NM 87545
Michael J. Drake	Tucson, AZ 85721
Gerlind Dreibus	65 Mainz, Fed. Rep. of Germany
James I. Drever	Laramie, WY 82071
Ananda Dube	Calcutta 29, India
Michael B. Duke	Houston, TX 77058
Saeed A. Durrani	Birmingham B 15 2TT, U.K.
J. Thomas Dutro, Jr.	Washington, DC 20560
Thomas C. Duxbury	Pasadena, CA 91109
Stephen E. Dwornik	Springfield, VA 22151
Palmer Dyal	Moffett Field, CA 94035
Robert F. Dymek	Cambridge, MA 02138
Daniel Dzuirsin	Vancouver, WA 98661
Alexander J. Easton	London SW7 5BD, U.K.
Dennis D. Eberl*	Denver, CO 80225
Peter Eberhardt	CH-3012 Bern, Switzerland
Burton Edelson	Washington, DC 20546
William D. Ehmann	Lexington, KY 40506
Henry L. Ehrlich	Troy, NY 12108
Farouk El-Baz	Lexington, MA 02173
Charles Elachi	Pasadena, CA 91109
Niles Eldridge	New York, NY 10024
Wolfgang Elston*	Albuquerque, NM 87131
Peter Englert*	San Jose, CA 95192-0101
Roy J. Enrico	Dallas, TX 75265
Samuel Epstein	Pasadena, CA 91125
W. Gary Ernst	Los Angeles, CA 90024
Tezer Esat	Canberra ACT 2600, Australia
Larry W. Esposito	Boulder, CO 80309
O. Eugster*	3000 Bern, Switzerland
John Evans	Richland, WA 99352
Diane L. Evans	Pasadena, CA 91109
A. E. Fallick	Glasgow, Scotland G75 OQU
Fraser P. Fanale	Honolulu, HI 96822
Tom G. Farr*	Pasadena, CA 91109
Hugo Fechtig*	Heidelberg 06221/5161
Mikhail A. Fedonkin*	Profsojuznaja ul., 113
William C. Feldman*	Los Alamos, NM 87545
Anthony A. Finnerty	Davis, CA 95695

NAME	ADDRESS
Edward L. Fireman	Cambridge, MA 02138
James Fletcher	McLean, VA 22102
Geo. James Flynn*	Plattsburgh, NY 12901
R. V. Fodor	Raleigh, NC 27650
Robert Fogel	Providence, RI 02912
Robert O. Fournier	Menlo Park, CA 94025
Carl A. Francis	Cambridge, MA 02138
P.W. Francis*	MK7 6AA, England
Philip B. Fraundorf	St. Louis, MO 63130
Kurt Fredriksson	Washington, DC 20560
Bevan French	Chevy Chase, MD 20815
Gerald M. Friedman	Troy, NY 12180
Louis Friedman	Pasadena, CA 91106
E. Imre Friedman	Tallahassee, FL 32306
Clifford Frondel	Cambridge, MA 02138
Robert Fudali	Washington, DC 20560
Takaaki Fukuoka	Tokyo 171, Japan
M. Fuller	Santa Barbara, CA 93106
Michael J. Gaffey	Troy, NY 12180-3590
Edward S. Gaffney*	Los Alamos, NM 87545
Robert M. Garrels	St. Petersburg, FL 33701
James B. Garvin	Greenbelt, MD 20771
Donald E. Gault	Murphys, CA 95247
Johannes Geiss*	3012 Bern, Switzerland
E.K. Gibson, Jr.*	Houston, TX 77058
R.H. Giese	Gab. NB-7, Fed. Republic of Germany
Billy P. Glass*	Newark, DE 19716
Parmatina S. Goel*	Kanpur 208016, India
Kenneth A. Goettel	Washington, DC 20008
Alexander F.H. Goetz	Boulder, CO 80309-0449
Edward D. Goldberg	La Jolla, CA 92093
Samuel S. Goldich	Golden, CO 80401
Joseph I. Goldstein	Bethlehem, PA 18015
Gordon Goles	Eugene, OR 97403
Andy M. Gombos, Jr.*	Houston, TX 77001
James L. Gooding*	Houston, TX 77058
Cyrena Goodrich	Tucson, AZ 85721
A. El Goresy	Fed. Rep. of Germany
J.N. Goswami	Ahmedabad, 380009 India
Jonathan C. Gradie	Honolulu, HI 96822
Monica M. Grady	Milton Keynes MK7 6AA, U.K.
Andrew Graham	London SW7 5BD, U.K.
Ronald Greeley*	Tempe, AZ 85287
Richard A.F. Grieve	Providence, RI 02912
Ralph E. Grim	Urbana, IL 61801
Pieter M. Grootes	Seattle, Washington 98195
Lawrence Grossman	Chicago, IL 60637
Timothy L. Grove*	Cambridge, MA 02139
Eberhard Grun	Fed. Rep. of Germany
J.E. Guest	United Kingdom

NAME	ADDRESS
Edward A. Guinness	St Louis, MO 63130
S. Haggerty	Amherst, MA 01003
Wendy S. Hale-Erlich	New Orleans, LA 70150
Ian Halliday	Ottawa, Ontario K1A OR6, Canada
Kenneth Hamblin	Provo, UT 84602
C.U. Hammer	Copenhagen, Denmark
Martha Hanner	Pasadena, CA 91109
Gilbert N. Hanson	Stony Brook, NY 11790
Robert E. Hanss	San Antonio, TX 78284
B. Hapke	Pittsburgh, PA 15260
Robert B. Hargraves	Princeton, NJ 08540
Alan W. Harris	Pasadena, CA 91109
Stanley R. Hart	Brookline, MA 02146
William K. Hartmann	Tucson, AZ 85719
Jack B. Hartung	APO New York 09012-5423
Museum of Comparative Zoology	Cambridge, MA 02138
Larry A. Haskin*	St. Louis, MO 63130
B. Ray Hawke	Honolulu, HI 96822
J.F. Hays	Washington, DC 20550
James W. Head	Providence, RI 02912
Grant Heiken	Los Alamos, NM 87544
K. F. J. Heinrich	Washington, DC 20234
Eleanor F. Helin	Pasadena, CA 91109
Karl G. Henize	Houston, TX 77058
Donald L. Henninger	Houston, TX 77058
Ulrich Herpers*	D5000 Koln 1, Fed. Rep. of Germany
Jan Hermeam	B-3030 Leuven, Belgium
Claude T. Herzberg	New Brunswick, NJ 08854
Gregory F. Herzog	New Brunswick, NJ 08903
K.G. Heumann	Fed. Rep. of Germany
Roger H. Hewins	New Brunswick, NJ 08903
Richard Hey	La Jolla, CA 92093
Dieter Heymann	Houston, TX 77251
L.J. Hickey	Washington, DC 20560
Michael D. Higgins	Quebec G7H 2B1, Canada
Noel W. Hinners	Greenbelt, MD 20771
Peter Hirsch	(D-2300) Keil/West Germany
JSC Historian	Houston, TX 77058
R.D. Hoare	Bowling Green, OH 43403
Carroll A. Hodges	Menlo Park, CA 94025
Charles M. Hohenberg	St. Louis, MO 63130
Heindrich D. Holland*	Cambridge, MA 02138
William T. Holser	Eugene, MA 02138
Henry Holt	Flagstaff, AZ 86001
Masatake Honda	Tokyo 156, Japan
Yin Hong-Fu	People's Republic of China
K. Horai	Palisades, NY 10964
Robert J. Horodyski	New Orleans, LA 70118
Norman H. Horowitz*	La Jolla, CA 91125
F. Horz	Houston, TX 77058

NAME	ADDRESS
Robert M. Housley	Thousand Oaks, CA 91360
Hatten Howard	Athens, GA 30602
J. Stephen Huebner	Reston, VA 22092
W.F. Huebner	Los Alamos, NM 87545
Robert Huguenin	Amherst, MA 01003
Glenn I. Huss	Denver, CO 80201
Gary R. Huss	St. Paul, MN 55108
Ian D. Hutcheon	Pasadena, CA 91125
Robt. Hutchison	London, S.W. 7, U.K.
Donald W. Hyndman	Missoula, MT 59812
Yukio Ikeda	Mito 310, Japan
Andrew P. Ingersoll	Pasadena, CA 91125
Trevor R. Ireland	Canberra 2601, Australia
Anthony J. Irving	Seattle, WA 98195
Andrei V. Ivanov	Moscow, USSR
Marion L. Jackson	Madison, WI 53706
Bruce M. Jakosky	Boulder, CO 80309
Odette B. James	Reston, VA 22092
Eugene Jarosewich	Washington, DC 20560
Raymond Jeanloz	Berkeley, CA 94720
J.A. Jeletzky	Ottawa, K1s 5B6 Canada
E.K. Jessberger	Fed. Rep. of Germany
William D. Johns	Columbia, MO 65211
Torrence V. Johnson	Pasadena, CA 91109
Blair F. Jones	Reston, VA 22092
Sheldon Judson	Princeton, NJ 08540
Anthony J.T. Jull	Tucson, AZ 85721
Anne Kahle	Pasadena, CA 91109
Ralph Kahn*	Washington, DC 20546
Gregory Kallemeyn	Los Angeles, CA 90024
I.R. Kaplan	Los Angeles, CA 90024
William J. Kaufmann, III	Danville, CA 94526
William Kaula	Los Angeles, CA 90024
Paul W. Keaton	Los Alamos, NM 87544
Klaus Keil	Albuquerque, NM 87131
James E. Keith	Houston, TX 77058
Walter D. Keller*	Columbia, MO 65211
Burton M. Kennedy	Berkeley, CA 94720
John E. Kennedy	Canada S7N 0W0
John F. Kerridge	Los Angeles, CA 90024
Joseph Kerwin	Houston, TX 77058
Hugh H. Kieffer	Flagstaff, AZ 86001
Makoto Kimura	Mita 310, Japan
Trude V.V. King	Denver, CO 80225
John S. King	Amherst, NY 14226
Elbert A. King*	Houston, TX 77004
T. Kirsten	Fed. Rep. of Germany
Margaret Kivelson	Los Angeles, CA 90024
Lisa C. Klein	Piscataway, NJ 08854

NAME	ADDRESS
Jens Martin Knudsen*	DK-2100 Copenhagen, Denmark
Michael Kobrick	Pasadena, CA 91109
Carl F. Koch	Norfolk, VA 23508
R. Craig Kochel	Carbondale, IL 62901
Christian Koeberl*	A-1010 Wien, Austria
Truman P. Kohman	Pittsburgh, PA 15213
Paul D. Komar	Corvallis, OR 97331
Alan S. Kornacki	Houston, TX 77001
Randy Korotev*	St. Louis, MO 63130
U. Krahenbuhl	CH-3000 Bern 9, Switzerland
Konrad B. Krauskopf	Stanford, CA 94305
William N. Krebs	Denver, CO 80202
David Krinsley	Tempe, AZ 85287
Gero Kurat	Vienna, Austria A-1014
Ikuo Kushiro	Tokyo, 113, Japan
Keith Kvenvolden	Menlo Park, CA 94025
Philip R. Kyle	Socorro, NM 87801
John De Laeter	Western Australia
C. W. Lagle*	Houston, TX 77058
D. Lal	India
Chris Lambertsen	Philadelphia, PA 19104-6068
Ed Landing	Albany, NY 12230
Carl Landuydt*	Krijgslaan 281, S8, Belgium
Bruno Lang*	02-089 Warsaw, Poland
Yves Langevin	Orsay, France
Chester C. Langway, Jr.	Amherst, NY 14226
John W. Larimer	Tempe, AZ 85281
J.C. Laul	Richland, WA 99352
Larry Lebofsky	Tucson, AZ 85721
Joshua Lederberg*	New York, NY 10021
W.P. Leeman	Houston, TX 75251
Douglas A. Leich	Livermore, CA 94550
Conway B. Leovy	Seattle, WA 98195
Gilbert V. Levin*	Rockville, MD 20852
Eugene H. Levy	Tucson, AZ 85721
John S. Lewis*	Cambridge, MA 02139
Byron J. Lichtenberg	Cambridge, MA 02139
Louis Lindner	1009 AJ Amsterdam, Netherland
Donald H. Lindsley	Stony Brook, NY 11794
David Lindstrom	Houston, TX 77058
Marilyn M. Lindstrom	Houston, TX 77058
Michael E. Lipschutz*	W. Lafayette, IN 47907
Gary Lofgren	Houston, TX 77058
John Longhi*	New Haven, CT 06511
Heinz A. Lowenstam	Pasadena, CA 91125
Baerbel K. Lucchitta	Flagstaff, AZ 86001
Gunter W. Lugmair	La Jolla, CA 92093
Maw-Suen Ma	Melville, NY 11747
J.D. MacDougall	La Jolla, CA 92093

NAME	ADDRESS
Glenn J. MacPherson	Washington, DC 20560
Ian Mackinnon	Albuquerque, NM 87131
Michael C. Malin	Tempe, AZ 85287
Rocco Mancinelli*	Moffett Field, CA 94305
Oliver K. Manuel	Rolla, MO 65401
Kurt Marti*	La Jolla, CA 92093
Ursula Marvin	Cambridge, MA 02138
Brian H. Mason	Washington, DC 20560
Akimasa Masuda	Nada, Kobe 657, Japan
Harold Masursky	Flagstaff, AZ 86001
Dennis Matson	Pasadena, CA 91109
Satoshi Matsunami	Tokyo 113, Japan
D. P. Mattey	Cambridge, U.K.
Michel Maurette	91406 Orsay, France
Ted A. Maxwell	Washington, DC 20560
Toshiko Mayeda	Chicago, IL 60637
John F. McCauley	Flagstaff, AZ 86001
Thomas B. McCord	Honolulu, HI 96822
James E. McCoy	Houston, TX 77058
Frank B. McDonald	Washington, DC 20546
J.A.M. McDonnell	Canterbury, Kent, CT2 7NT, U.K.
Lucy A. McFadden	College Park, MD 20742
James J. McGee	Reston, VA 22092
George E. McGill	Amherst, MA 01002
Gordon McKay*	Houston, TX 77058
Christopher P. McKay	Moffett Field, CA 94035
David McKay	Houston, TX 77058
Kevin McKeegan	St. Louis, MO 63130
Stephen W.S. McKeever	Stillwater, OK 74078
Harry Y. McSween, Jr.	Knoxville, TN 37916-1410
Charles L. Melcher	Ridgefield, CT 06877
H.J. Melosh	Tucson, AZ 85721
Wendell W. Mendell	Houston, TX 77058
A.E. Metzger	Pasadena, CA 91103
Tony Meunier	Reston, VA 22092
Henry O.A. Meyer	West Lafayette, IN 47907
Charles Meyer	Houston, TX 77058
Michael A. Meyer*	Tallahassee, FL 32306
Stanley Miller	La Jolla, CA 92093
Daniel J. Milton	Reston, VA 22092
Douglas W. Ming	Houston, TX 77058
David W. Mittlefehldt	Houston, TX 77058
Masamichi Miyamoto	Tokyo 153, Japan
Henry Moore	Menlo Park, CA 94025
Carleton B. Moore	Tempe, AZ 85287
J.W. Morgan	Reston, VA 22092
Richard Morris	Houston, TX 77058
Elliott C. Morris	Flagstaff, AZ 86001
David Morrison	Honolulu, HI 96822
D.A. Morrison	Houston, TX 77058
Peter J. Mouginis-Mark	Honolulu, HI 96822

NAME	ADDRESS
W.R. Muehlberger	Austin, TX 78712
Duane Muhleman	Pasadena, CA 91125
A.B. Mukherjee	W. Bengal, India
Frederick A. Mumpton	Brockport, NY 14420
Bruce Murray	Pasadena, CA 91109
M.T. Murrell	Pasadena, CA 91125
Charles W. Naeser	Denver, CO 80225
Hiroko Nagahara	Hongo, Tokyo 113, Japan
Hiroshi Nagasawa	Tokyo, 171, Japan
B. Nagy	Tucson, AZ 85721
Andrew F. Nagy	Ann Arbor, MI 48102
Noburu Nakamura	Nada-ku, Kobe 657, Japan
Douglas B. Nash	Pasadena, CA 91109
David F. Nava	Greenbelt, MD 20771
C.E. Nehru	Brooklyn, NY 11210
John M. Neil	Sacramento, CA 95825
Joseph A. Nelen	Washington, DC 20560
Robert M. Nelson	Pasadena, CA 91109
Gerhard Neukum*	W. Germany
H.E. Newsom	Albuquerque, NM 87131
Neil Nickle	Pasadena, CA 91109
John Niehoff	Schaumberg, IL 60195
Alfred O.C. Nier	Minneapolis, MN 55455
Kunihiko Nishiizumi	La Jolla, CA 92093
Gordon L. Nord, Jr.	Reston, VA 22092
Northrop Services, Inc.	Houston, TX 77058
Stewart Nozette	Austin, TX 78705
Dag Nummedal	Baton Rouge, LA 70803
Joseph A. Nuth	Greenbelt, MD 20771
Larry Nyquist	Houston, TX 77058
John O'Keefe	Greenbelt, MD 20771
Carol O'Neill	New York, NY 10024
Edward Olsen	Chicago, IL 60605
John Oro	Houston, TX 77004
Rolf Ostertag	West Germany
Tobias C. Owen*	Stony Brook, NY 11794
Vance I. Oyama	Moffett Field, CA 94035
David A. Paige*	Los Angeles, CA 90024
Thomas O. Paine	Los Angeles, CA 90024
Herbert Palme	Fed. Rep. of Germany
Kevin Pang	Pasadena, CA 91109
D. A. Papanastassiou	Pasadena, CA 91125
J.J. Papike	Rapid City, SD 57701
Julie Paque	Cambridge, MA 02138
E.M. Parmentier	Providence, RI 02912
Stanton J. Peale*	Santa Barbara, CA 93106
Paul Pellas	Paris 5, France
Robert O. Pepin	Minneapolis, MN 55455
Gordon Pettengill	Cambridge, MA 02139
Roger Phillips	Dallas, TX 75275

NAME	ADDRESS
Wm. Phinney	Houston, TX 77058
David C. Pieri	Pasadena, CA 91109
Carle Pieters	Providence, RI 02912
R.J. Pike	Menlo Park, CA 94025
C.T. Pillinger*	MK7 6AA, Buckinghamshire, U.K.
Charles W. Pitrat	Amherst, MA 01003
Harry N. Planner	Los Alamos, NM 87545
Jeffrey Plescia	Flagstaff, AZ 86001
C.W. Poag	Woods Hole, MA 02543
James B. Pollack	Moffett Field, CA 94035
C.A. Ponnamperuma	College Park, MD 20742
Wayne R. Premo*	Denver, CO 80225
Frank Press	Washingon, DC 20418
P. B. Price	Berkeley, CA 94720
Martin Prinz	New York, NY 10024
Wm. L. Quaide	Washington, DC 20546
R.S. Rajan	Pasadena, CA 91109
L. A. Rancitelli	Columbus, OH 43201
Kalervo Rankama	00170 Helsinki 17, Finland
M.N. Rao	Ahmedabed-380 009, India
A.S.P. Rao*	Hyderabad-500 007, India
U.R. Rao	Bangalore-560 009, India
Kaare L. Rasmussen	2200 Copenhagen, Denmark
David M. Raup	Chicago, IL 60605
D.G. Rea	Pasadena, CA 91109
S. J. B. Reed	Cambridge CB2 3EW, U.K.
George W. Reed, Jr.	Argonne, IL 60439
Robert C. Reedy*	Los Alamos, NM 87545
Arch M. Reid	Houston, TX 77004
Wolf Uwe Reimold	Johannesburg 2000, South Africa
John H. Reynolds	Berkeley, CA 94720
J.M. Rhodes	Amherst, MA 01003
Steven M. Richardson	Ames, IA 50011
Frans J.M. Rietmeyer*	Albuquerque, NM 87131
J. Keith Rigby	Provo, UT 84602
A. E. Ringwood	Canberra, ACT 2600, Australia
R.F. Rissone	Swinton, SN2 1ET, England
Barrett N. Rock	Pasadena, CA 91109
David J. Roddy	Flagstaff, AZ 86001
Edwin Roedder	Reston, VA 22092
Jeff Rosendahl	Washington, DC 20546
Lisa Rossbacher	Pomona, CA 91768
George R. Rossman	Pasadena, CA 91125
Ladislav Roth	Pasadena, CA 91109
Marvin W. Rowe	College Station, TX 77843
A. Ru Rozanov	Profsojuznaja ul., 113
Alan Edward Rubin	Los Angeles, CA 90024
Marvin L. Rudee	La Jolla, CA 92037
Keith Runcorn	United Kingdom NE1 7RU
C.T. Russell	Los Angeles, CA 90024
Pat Russell	Washington, DC 20001

NAME	ADDRESS
Graham Ryder	Houston, TX 77058
Carl Sagan	Ithaca, NY 14853
Jack Salisbury	Reston, VA 22092
Frank B. Salisbury	Logan, UT 84322-4820
Peter Salpas	Auburn, AL 36849-3501
Scott Sandford*	Moffett Field, CA 94035
M. Sato	Reston, VA 22092
R.S. Saunders	Pasadena, CA 91103
Norman M. Savage	Eugene, OR 97403
Samuel M. Savin	Cleveland, OH 44106
Gerald Schaber	Flagstaff, AZ 86001
Roman A. Schmitt	Corvallis, OR 97331
Harrison H. Schmitt	Albuquerque, NM 87191-4338
Charles Schnetzler	Greenbelt, MD 20771
J. William Schopf	Los Angeles, CA 90024
Henry D. Schreiber	Lexington, VA 24450
Gerald Schubert	Los Angeles, CA 90024
Peter Schultz	Providence, RI 02912
Ludolf Schultz	Fed. Rep. of Germany
Henry P. Schwarcz*	Canada L8S 4M1
Ronald F. Scott	Pasadena, CA 91125
Edward R.D. Scott	Albuquerque, NM 87131
David H. Scott	Flagstaff, AZ 86001
Derek W. Sears	Fayetteville, AR 72701
Tom See	Houston, TX 77058
J.J. Sepkoski	Chicago, IL 60637
Mark Settle	Plano, TX 75075
Robert P. Sharp	Pasadena, CA 91125
D. M. Shaw	Hamilton, Ontario, Canada L8S 4M1
Michael F. Sheridan	Tempe, AZ 85287
Masato Shima	Tokyo 110, Japan
Makoto Shima	Yokohama, Japan T240
Eugene M. Shoemaker	Flagstaff, AZ 86001
Nicholas Short	Greenbelt, MD 20771
Richard Shorthill	Salt Lake City, UT 84112
Peter Signer	Zurich, Switzerland
Godfrey Sill	Tucson, AZ 85721
Leon T. Silver	Pasadena, CA 91125
Tom Simkin	Washington, DC 20560
Steven Simon	Rapid City, SD 57701
Patrica A. Sims*	SW7 5BD, England
Robert Singer	Tucson, AZ 85721
C.S.P. Singh	Varanasi 221005, India
Brian J. Skinner	New Haven, CT 06520
Monty R. Smith	Richland, WA 99352
Brad Smith	Tucson, AZ 85721
Joseph V. Smith*	Chicago, IL 60637
Roger S. U. Smith	Austin, TX 78712
Roman Smoluchowski	Austin, TX 78712
Joseph R. Smyth	Boulder, CO 80309-0250

NAME	ADDRESS
John Snyder	Washington, DC 20550
Larry A. Soderblom	Flagstaff, AZ 86001
Sean C. Solomon	Cambridge, MA 02139
C.P. Sonett	Tucson, AZ 85721
Frank J. Spera	Santa Barbara, CA 93106
Cary R. Spitzer	Hampton, VA 23665
John Splettstoesser	St. Paul, MN 55114
Paul D. Spudis	Flagstaff, AZ 86001
Steven W. Squyres	Moffett Field, CA 94035
G.M. Stanley, Jr.	Washington, DC 20560
Ian M. Steele	Chicago, IL 60637
James B. Stephens	Pasadena, CA 91109
James H. Stitt	Columbia, MO 65211
Carol Stoker*	Moffett Field, CA 94307
Edward D. Stolper	Pasadena, CA 91125
Charles D. Stone	Austin, TX 78713
G. Stotzky	New York, NY 10003
Patricia A. Straat	Rockville, MD 20852
Melissa Strait	Alma, MI 48801
David W. Strangway	Vancouver, B.C., Canada V6T 2B3
Ed Strickland	Leander, TX 78722
Robert G. Strom	Tucson, AZ 85721
Hans Suess	San Diego, CA 92037
David E. Sugden	Aberdeen AB9 24F, Scotland
Naoji Sugiura	Ontario, Canada L5L1C6
Robert M. Sullivan	Boulder, CO 80309
Kathryn D. Sullivan	Houston, TX 77058
Steve Sutton	Upton, NY 11973
Gordon A. Swann	Flagstaff, AZ 86001
Peter Swart	Miami, FL 33149
Walter C. Sweet	Columbus, OH 43210
Nobuo Takaoka	Yamagoto, 990, Japan
Hiroshi Takeda	Hongo, Tokyo 113, Japan
Kim H. Tan*	Athens, GA 30602
Ken Tanaka*	Flagstaff, AZ 86001
Tsuyoshi Tanaka	Ibaraki, 305 Japan
Helen Tappan	Los Angeles, CA 90024
James Taranik	Washington, DC 20546
Mitsunobu Tatsumoto*	Denver, CO 80225
G. Jeffrey Taylor	Albuquerque, NM 87131
S.R. Taylor	Canberra, Australia
Lawrence A. Taylor	Knoxville, TN 37996
Klaus Thiel	Fed. Rep. of Germany
Mark H. Thiemens*	La Jolla, CA 92093
H.G. Thode	Hamilton 16, Ontario, Canada
David E. Thompson	Washington, DC 20546
Lonnie G. Thompson*	Columbus, OH 43210
Theodore W. Tibbitts	Madison, WI 53706
Allen Tice	Hanover, NH 03755
Shelby Tilford	Washington, DC 20546
Robert Tilling	Reston, VA 22092

APPENDIX B2, con't

NAME	ADDRESS
G.R. Tilton	Santa Barbara, CA 93106
M. Nafi Toksoz	Cambridge, MA 02139
T.A. Tombrello	Pasadena, CA 91109
Kazushige Tomeoka	Tempe, AZ 85287
Owen Brian Toon	Moffett Field, CA 94035
Priestly Toulmin, III	Reston, VA 22301
Kenneth M. Towe	Washington, DC 20560
Allan H. Treiman*	Boston, MA 02215
Jacob I. Trombka	Greenbelt, MD 20771
Akira Tsuchiyama	Kyoto 606, Japan
Karl K. Turekian	New Haven, CT 06511
Anthony Turkevich	Chicago, IL 60637
G. Turner	Sheffield S3 7RH, U.K.
F.C. Ugolini	Seattle, WA 98195
D.R. Uhlmann	Cambridge, MA 02139
James R. Underwood, Jr.	Manhattan, KS 66506
W.R. Van Schmus	Lawrence, KS 60044
David Vaniman	Los Alamos, NM 87545
Michael Anthony Velbel*	East Lansing, MI 48824
Geerat J. Vermeij	College Park, MD 20742
Joseph Veverka	Ithaca, NY 14853
Faith Vilas	Houston, TX 77058
R.D. Vis*	Amsterdam 1007MC, The Netherlands
Alex Volborth	Butte, Montana 59701
Tyler Volk	New York, NY 10003
W. VonEngelhardt	Tuebingen, Fed. Rep. of Germany
John F. Wacker	La Jolla, CA 92093
Robert M. Walker	St. Louis, MO 63130
Dave Walker*	Palisades, NY 10964
Steven D. Wall	Pasadena, CA 91109
Heinrich Wanke	6500 Mainz, Fed. Rep. of Germany
Stanley H. Ward	Salt Lake City, UT 84112
A. Wesley Ward	Flagstaff, AZ 86001
Bruce R. Wardlaw	Denver, CO 80225
David Wark	Tucson, AZ 85721
Jeffrey L. Warner*	La Habra, CA 90631
Paul H. Warren	Los Angeles, CA 90024
G.J. Wasserburg	Pasadena, CA 91125
John Wasson	Los Angeles, CA 90024
P.W. Weiblen	Minneapolis, MN 55455
D.F. Weill	Eugene, OR 97403
Michael K. Weisberg	New York, NY 10024
Paul R. Weissmann	Pasadena, CA 91109
David B. Wenner	Athens, GA 30602
G.W. Wetherill	Washington, DC 20015
W. Brian Whalley*	Northern Ireland, UK
Ian Whillans	Columbus, Ohio 43210
Fred L. Whipple	Cambridge, MA 02138
David C. White	Tallahassee, FL 32306
I.P. Wright*	Buckinghamshire, UK
J.L. Whitford-Stark	Alpine, TX 79832

NAME	ADDRESS
Don E. Wilhelms	Menlo Park, CA 94025
Laurel L. Wilkening	Tucson, AZ 85721
Richard Williams	Houston, TX 77058
John L. Williams	Denver, CO 80202
John Willis	Bethlehem, PA 18015
M.V.H. Wilson	T6G 2E9 Canada
S.L. Wing	Menlo Park, CA 94025
Donald Wise	Amherst, MA 01002
S.W. Wise	Tallahassee, FL 32306
Frank Wlotzka	D-65 Mainz, Fed. Rep. of Germany
Charles A. Wood	Houston, TX 77058
John A. Wood	Cambridge, MA 02138
Joe Wooden	Menlo Park, CA 94025
Dorothy S. Woolum	Fullerton, CA 92634
Alexander Woronow	Houston, TX 77004
Thomas L. Wright	Hawaii Natl. Park, HI 96718
Ian Wright	Buckinghamshire, UK
Sherman S.C. Wu	Flagstaff, AZ 86001
Peter Wyllie	Pasadena, CA 91125
Crayton J. Yapp	Albuquerque, NM 87131
Ellis L. Yochelson	Washington, DC 20560
Hatten S. Yoder, Jr.	Washington, DC 20008
Ed Zeller	Lawrence, KS 66045
Benjamin H. Zellner	Tuscon, AZ 85721
Aaron P. Zent*	Honolulu, HI 96822
Herman Zimmerman	Washington, DC 20550
E. Zinner	St. Louis, MO 63130
William Zinsmeister	Columbus, OH 43210
Mike Zolensky	Houston, TX 77058
Herbert Zook	Houston, TX 77058
Jack Zussman	Manchester M13 NPL UK

APPENDIX B3

NOV 5 1987

Basalt Waste Isolation Project
Westinghouse Hanford Company
Richland, WA 99352
November 2, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

Thank you for the opportunity to contribute to the Mars Sample-Science Document. My work includes the effects of elevated temperatures and radiation fluxes on the structural stability of smectite clay. This work was performed for the Department of Energy under the Basalt Waste Isolation Project. Reprints of two papers on these subjects are enclosed.

We studied a commercial Wyoming bentonite, composed of 85% Na-montmorillonite plus nontronite, silica, feldspar, illite, calcite and gypsum. Bentonite has been proposed as a part of the "packing material" intended to surround individual canisters in a nuclear waste repository. Experiments were performed to assess the effects of dry heating and gamma irradiation on montmorillonite. The results are applicable to the structural degradation of martian clays subjected to sterilization by heat and/or radiation.

The bentonite dehydration study reported in Allen et al. (1984) showed that sodium montmorillonite can be heated to 370°C for as long as 340 days without significant loss of structural water. The only effect of this heating was the rapid loss of interlayer water, which proved entirely reversible. Heating of this clay to 440°C for 365 days, however, resulted in the irreversible loss of structural water.

The effects of gamma irradiation, both at ambient and elevated temperatures, were reported by Allen and Rawson (1986). We cited work by Krumhansl (1985) in which clay derived from bentonite suffered no crystallographic changes after exposure to 3×10^{10} rad of ^{60}Co gamma radiation. In our own experiment, bentonite was exposed to 3.5×10^{9} rad and simultaneously heated to 300°C for a two-week period. The only detectable effect was reversible loss of interlayer water, similar to the effect of the high temperature alone.

The recommendations for treatment of a clay-bearing martian sample are as follows. If the material is known to be dry (ie no significant amount of ice), heat sterilization to 370°C for as long as a year may not result in serious degradation. As an alternative, sterilization by gamma radiation may prove a better alternative. An expanded program to test the effects of irradiation sterilization on candidate martian soil materials should be undertaken.

Sincerely,

Carlton C. Allen

ORIGINAL PAGE IS
OF POOR QUALITY

7/28/87

Jim –

If you are still accepting input, I would like to submit this. The deadline passed by so long ago, that I decided not to submit. Bill Lagle mentioned (earlier this month) that you may still be accepting papers – so I tackled it again.

Thanks,

Judy

7/28/87

Jim –

If you are still accepting input, I would like to submit this. The deadline passed by so long ago, that I decided not to submit. Bill Lagle mentioned (earlier this month) that you may still be accepting papers – so I tackled it again.

Thanks,

Judy Allton

RESPONSE TO INPUT FOR A MARS SAMPLE-SCIENCE DOCUMENT

J.H. Allton, Lockheed-EMSCO, 2400 NASA Rd. 1,
P.O. Box 58561, Houston, TX. 77358

Area of interest: the opening and preliminary description of returned regolith cores and the subdivision of sample for analysis.

Aspects of Martian history addressed by examination of returned regolith samples:

Near surface profiles of grain size, shape, mineralogy, chemistry, surface properties, surface volatiles, and radiation effects will be important in characterizing Martian volatile cycles, interaction of regolith and atmosphere, and depositional processes.

Types and quantities of sample needed:

Profiles of 10 to 20 cm depths in lunar regolith are useful for examining the effects of micrometeorite bombardment and solar radiation. Both of these effects would be reduced in Martian regolith. Soil cores from the Dry Valleys in Antarctica, often cited as an analog for Martian conditions, show sharp chemical and physical boundaries within the top 5 to 10 cm. An example is the salt enriched layer at 2 - 4 cm (Gibson et. al, 1984).

Because we do not know the significant depth range of the Martian profiles, a long, continuous regolith core is desired to ensure that all vital samples are returned. However, periodic sampling along the core length has been suggested to reduce the total sample weight returned, and yet obtain samples from the desired depths (Martin Marietta, 1980).

The upper few centimeters, which may be very active and for which larger sample sizes would be required to support more experiments, might be sampled using a trowel to scrape off discrete depth intervals. This would be most useful when layering is visible in images taken of a trench wall. The lunar analog to this technique was the taking of lunar soil trench samples. However, more information has been extracted from the more finely-sampled core tube samples than from the trench soil samples. A device to sample only the upper one millimeter of regolith was used on Apollo 16, but this 2 g sample has been little used after its return to Earth.

A continuous core in the upper few centimeters augmented by interval samples to greater depths is preferable. A ten-centimeter long core of 2 cm diameter would weigh about 50 grams (based on lunar drill core bulk densities). As the diameter of the coring device is narrowed more distortion of the sample will occur.

Degree of sample degradation that can be tolerated:

The continuous core sample should maintain the regolith stratigraphy. The core soil must be tightly packed in its container. Acceleration, shock, or vibrations should not dislodge hardware confining the soil. Several lunar soil core tubes had void space, due either to movement of confining hardware or settling of soil as it became more efficiently packed. Lunar ascent, zero-G, and Apollo capsule splashdown were probably the principal forces acting on the core containers. Nominal splashdown forces were 6.5 to 7 G (although it was possible to go as low as 1.5 to 3 G in a descending wave trough).

Some minor settling occurred in several of the Apollo lunar soil cores during five years of nearly static storage at the Lunar Curatorial Facility. This indicates that consideration be given to vibrations and motion both for the rover, as it wanders about rough terrain for months, and for the return vehicle during the long flight home.

In situ measurements needed:

Images are needed to show the site before and after coring and to show the depth to which the coring device was inserted into the regolith. After the core is taken, a trench should be dug so that a trench wall (corresponding to the core sample) can be imaged. Penetrometer measurements may also be helpful.

Additional comment:

Design of a soil coring device needs to consider not only the conditions of sampling and trans-Earth travel, but also the conditions under which a sample is opened and partitioned in the laboratory. Lunar soil cores were partitioned to $\pm$ 2 mm. Ways to open the drill cores and drive tubes were not developed until return of the samples from the moon.

References:

Gibson, E.K., Wentworth, S.J., and McKay, D.S. (1983) Chemical weathering and diagenesis of a cold desert soil from Wright Valley, Antarctica: An analog of Martian weathering processes. Proc. Lunar & PLanetary Sci. Conf. 13th, part 2, J. Geophy. Res. vol. 88 supplement, pp. A912-A928.

Martin Marietta (1980) Study of sample drilling techniques for Mars sample return missions, Final Report. MCR-79-615.

APR 13 1987

United States Department of the Interior

GEOLOGICAL SURVEY
RESTON, VA. 22092
970 National Center

April 9, 1987

Dr. James L. Gooding
EN2
NASA Johnson Space Center
Houston, Texas 77058

Attn: EN2-87-6084

Dear Dr. Gooding:

Your letter of February 10, 1987 regarding input to a Mars sample-science document has been received and given consideration. I do not know how much thought has, or should be, given to examining possible Martian sedimentary rocks for possible fossil content, but I would like to address some aspects of this problem.

My field of specialty is fossil diatoms, both marine and nonmarine, and it has occurred to me that diatoms as well as other siliceous microfossils (or possible Martian analogues) have some unique properties that may be favorable to a space research project. The shells of siliceous microfossils, composed of SiO_2, are relatively inert chemically, show great resistance to high or low temperatures and should not be affected by radiation. They are susceptible to mechanical breakage, but their small size somewhat reduces this problem. Diatoms range in size from about 5 µm up to about 2000 µm, but seldom exceed a few hundred µm in maximum dimension. A relatively small sample, therefore, if only moderately fossiliferous, may contain a great many specimens. A cubic centimeter of richly diatomaceous rock contains an incalculable number of specimens.

I shall now address the questions raised in your letter as follows:

(1) Probably the best way of determining whether life ever existed on Mars is the examination of water-laid sedimentary rocks for various groups of microfossils. Microfossils are more pervasive in terrestrial deposits than are macrofossils, and it would be highly fortuitous for a probe to encounter a Martian macrofossil deposit if indeed such a thing exists.

(2) Samples should be from sedimentary rock showing evidence for aqueous deposition. Diatoms require an aqueous environment for growth and reproduction, though theycan apparently survive dessication for extended periods and remain viable. A sample of about 2 to 4 cc in size should be sufficient for study. It should be composed of sedimentary particles that can be disintegrated and concentrated for study.

(3) As long as diatoms are not treated with hydrofluoric acid or hot concentrated solutions of alkali, they should not be damaged in the short term by chemical sterilization techniques. Diatom valves have been heated to redheat in the laboratory without noticeable degradation. They would seem to be immune to pressure changes and and effects of radiation. I have no information about their resistance to acceleration and shock.

(4) These samples would need to be examined by a compound microscope to determine their microfossil content. I do not see that anything could be done on Mars to offset possible sample degradation.

A search for siliceous microfossils, as well as other possible forms of life, in Martian sedimentary rocks could indicate if life ever existed on that planet. Any evidence for Martian life and its comparison with terrestrial life could produce clues concerning a common or parallel process of origin and development of life throughout the universe. The most feasible technique for providing concrete evidence for extraterrestrial life in the foreseeable future seems to be the Mars sampling program.

The following topic should probably be considered in this letter. In a recent paper entitled "Diatoms on earth, comets, Europa and in interstellar space" by R. P. Hoover, F. Hoyle, et al., (Earth, Moon and Planets, v. 35, p. 19-45, 1986) the hypothesis was set forth that terrestrial diatoms and bacteria were seeded on the earth at various times by comets. I do not know if this hypothesis has been taken seriously by the community of space scientists, and I am indeed skeptical of it myself. However, this report does contain considerable factual information about the tolerance of terrestrial diatoms to extreme environmental conditions. It provides additional data that may be useful in evaluation of a program of sampling for possible Martian siliceous microfossils, regardless of what one may think of the theoretical considerations.

I hope that the above comments may be of some use to you.

Sincerely,

George W. Andrews
Research Geologist

MAR 12 1987

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY (0317)
LA JOLLA, CALIFORNIA 92093

March 6, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

This is in reply to your request about Mars sample-science.

I assume my "special area of expertise" for purposes of this document is cosmic-ray-produced (cosmogenic) radionuclides, in particular ^{26}Al, ^{10}Be, ^{53}Mn, ^{36}Cl, ^{41}Ca, and ^{129}I. Given the small mass of the Martian atmosphere, these nuclides can be expected to be present in surface materials and in short cores at substantially meteoritic or lunar levels. However, the atmosphere is thick enough, unfortunately, to eliminate SCR products. It is imaginable that some species made in the atmosphere will be incorporated in surface materials -- this will have to be seen, but I suppose that the nuclides produced in situ will be the most instructive. The main objective would be erosion-deposition history. Impact gardening on a small (centimeter) scale should be suppressed by the atmosphere. It seems barely possible that historic fluctuations in atmospheric pressure could be detected in this way.

One development since 1974 which has major implications is AMS, which has brought sample size requirements for most nuclides into the milligram range, in striking contrast to counting methods used earlier.

As for the speciafic questions:

(1) Quantitative measure of erosion-deposition history (including possibly impact history), over the last 10^5-10^8 year period.

(2) For most nuclides (assuming suitable sample compositions), samples on the order of 10 milligrams will suffice -- in special cases less. For ^{129}I, which is unique in its time scale ($t_{\frac{1}{2}}$ - 16×10^7 years), samples of a few grams are still required.

Samples will be rock or soil material (core samples would be best), taken at well defined location and depth.

(3) From our Apollo experience it seems likely that we will have no special requirements except radioactive cleanliness, which cannot be taken lightly.

(4) Gamma ray and escape neutron maps of the surface, on a 100 km + scale will be available after the MO mission. It would be desirable to have neutron flux measurements of the Burnett-Woolum type (as a function of depth) at the sample site.

Sincerely yours,

James R. Arnold

JRA/fk

JUN 12 1987

LUNAR AND PLANETARY INSTITUTE

3303 NASA ROAD 1 HOUSTON, TEXAS 77058



MEMORANDUM

To: J. L. Gooding **Date:** June 11, 1987

From: L. D. Ashwal

Subject: Mars Sample Science Document

My contribution represents a suggestion for Mars sample handling protocol, specifically relating to thin section preparation. Samples returned from Mars will likely contain a wealth of information on the volatile budget and history of Mars. Fluid-filled inclusions within minerals, trapped at various stages in the history of any Martian rock could potentially be extremely important. My experience has been that fluid inclusion artifacts can be accidently introduced into extraterrestrial samples (meteorites and lunar rocks) during thin section preparation (Rudnick et al., Proc. 15th LPSC, C669-C675, 1985, attached). Evidently laboratory fluids (epoxies, saw coolants) were introduced into pre-existing vacuum or low pressure microcavities along fractures created during thin section preparation. We suggested that current procedures for preparing thin sections of meteorites and lunar samples (particularly at JSC) be modified so as to avoid creating these artifacts. I strongly recommend similar caution in preparation of Martian thin sections.

JUN 17 1987

University of Essex

Department of Physics
Wivenhoe Park
Colchester CO4 3SQ

Tel: Colchester (0206) 862286
International +44 206 862286
Telegraphic address: University Colchester
Telex: 98440 (UNILIB G)

From Professor D.J. Barber

DJB/HSD 10th June 1987

Dr. James L. Gooding,
SN2-87-L328,
NASA Johnson Space Center,
Houston,
TX 77058,
U.S.A.

Dear Dr. Gooding,

Second Call for Input to a Mars Sample-Science Document

I am afraid that I did not reply to your first call because I saw very little chance of being able to attend any of the workshops relating to future Mars sample-return missions. However, lest this be taken to indicate no interest in Mars samples, I feel that I should respond to your second letter.

Despite strong economic pressures to be involved in more down-to-earth research (!), I and my group will continue to be keen to play a part in the analysis of returned extra-terrestrial samples. As you probably know, our main expertise lies in the use of electron beam microanalytical methods and our sample requirements are therefore very modest as regards size and weight of samples. However they are very sensitive to all types of alteration and the introductin of artefacts, so it is essential that groups such as ours receive pristine material. Our methods are, in general, destructive too.

We anticipate continued activities in the analysis of chondritic meteorites, in the correlation of isotopic anomalies with particular phases and meteoritic components, in the study of IDP's etc., and the continuing development of electron microscopic methodology. We therefore hope to have an involvement in the analysis of materials returned from future return-sample missions.

At this stage, there is as much input as we can reasonably make.

Yours sincerely,

David Barber

D.J. Barber

JUN 24 1987

St. Andrews

June 13, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

Thank you very much for including my name in the list of potential contributors to a Mars sample preservation document. I rather expect that those who have remained more active in pursuing the soil reactivity puzzle than I (e.g. Amos Banin) will already have contributed what needs to be said in that area; but for what they are worth, I submit the enclosed thoughts, keyed to your first 3 questions. I don't think #4 applies in this case.

If Earth recovery and "sterilization" protocols forbid these preservation conditions, it seems to me that serious thought should be given to parking a sealed and shielded subsample in Earth orbit during Earth approach, for recovery after quarantine protocols have confirmed the sterility of the bulk of the returned sample.

Again, thanks for offering this opportunity for input. I enjoyed your summary of the SNC papers in Geotimes. With best regards,

Sincerely,

Thomas R. Blackburn

Thomas R. Blackburn
McGaw Professor of Chemistry

enc:
TRB/ma

St. Andrews Presbyterian College
Laurinburg, North Carolina 28352
(919) 276-3652

Sample preservation desiderata with regard to soil surface oxidant:

1. The Viking GEX and LR results appear to imply the presence of a surface layer of oxidizing material on Martian soil grains. Such a layer, if present, may imply a powerful mechanism for oxidative weathering reactions not present on other planets. The reactivity is labile enough that it would be desirable to examine soil particles with surface-sensitive analytical techniques, notably x-ray photoelectron spectroscopy, that will be difficult to perform in situ. In particular, the question of the identity of the oxidant species, and whether it represents an intermediate buffer of high pE initially formed in the atmosphere can only be answered by such studies.

2. 10- to 100-mg samples of soil taken at a variety of depths in a core sample would help to resolve the question of direct photochemical oxidation of grain surfaces vs. gas-borne oxidants diffusing into the soil; a gradient of decreasing oxidation state with depth would support the latter interpretation.

3. Samples for this study should not see temperatures higher than about 50°C, or humidities and total gas pressures higher than those ambient at the sample site - preferably lower, in view of the time lag between sampling and analysis. Exceeding these limits would promote the destruction of a reactive surface oxidant layer either by direct reaction or by desorptive displacement of volatile oxidants.

4. Every effort should be made to trap a sample of high-altitude atmospheric dust during return lift-off.

ORIGINAL PAGE IS
OF POOR QUALITY

MAR 1 0 1987

UNIVERSITY OF WISCONSIN–MADISON

Department of Geology and Geophysics

Lewis G. Weeks Hall for Geological Sciences
1215 W. Dayton St.
Madison, Wisconsin 53706

Telex 26-5452
Telephone 608/262-2960

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

March 6, 1987

Dear Dr. Gooding:

Your Feb. 10, 1987 memo has found its way to me and I would like to provide you with some input. My interests are in the fields of economic geology, geochemistry and metamorphic petrology. One of my most useful tools and one that could be directly applicable to Martian samples is the study of fluid inclusions. In answer to your questions:

(1) Solid rock samples recovered from the surface of Mars could contain evidence of hydrothermal activity dating to the time of a liquid hydrosphere and groundwater system. Igneous activity would mobilize such fluids and proof of such processes would be preserved in the rocks of the planet.

(2) Any solid rocks, of any size, when thin sectioned would allow the search for trapped fluid inclusions. These inclusions could record direct magmatic processes or the passage of circulating hydrothermal fluids. Of course if vein-type material could be identified that would be best of all.

(3) Pressure is not a problem. Excessive heating would be a problem. As the trapped fluid inclusions are heated up their internal pressure increases as they are essentially constant volume systems. Too much pressure and they will decrepitate and their information would be lost. It is not possible to specify how much heating is too much without specifying the composition of the inclusion and its formation conditions. If required some limits could be calculated but are certainly beyond the scope of this letter.

(4) No reasonable in situ measurements could be made.

I would be interested in getting on your mailing list as I am serious about the possibility that fluid inclusion analyses could provide direct evidence about fluid speciation and activity in the early history of Mars.

Sincerely,

Phil Brown

Dr. Philip E. Brown
Associate Professor
608-262-5954 (-8960)

WCSAR

Wisconsin Center for
Space Automation and Robotics

1357 University Avenue Madison, Wisconsin 53706 608/262-5524

June 11, 1987

Dr. James L. Gooding
NASA Johnson Space Center
Mail Code SN2
Houston, Texas 77058

Dear Dr. Gooding:

This is in response to your requested input to a Mars sample-science document sent to Dr. T. W. Tibbitts. This letter will represent his inputs as well as mine.

As plant scientists, we would recommend that samples returned from Mars missions be preserved in their *in situ* chemical and biological condition. This would require that the samples be maintained in an atmosphere that mimics the Mars atmosphere. The samples should be maintained at low temperatures to reduce or eliminate any molecular, chemical, or biological activity.

The samples would need to be collected with devices and stored in containers that are free of biological entities carried on the mission from Earth sources. Likewise, when the containers are opened for analyses in Earth-based laboratories these same precautions should be followed.

It would be desirable that these analyses be conducted as promptly as possible after return of the samples to Earth to avoid alteration of the samples and development of artifacts. Thus, the sample-science document might also contain a section that identifies in detail the types of analyses that are planned.

If you may have need for elaboration of these comments, please do not hesitate to contact me.

Sincerely,

Raymond J. Bula
Senior Scientist

RJB:rb

cc: T. W. Tibbitts

The College of Engineering
University of Wisconsin–Madison

ORIGINAL PAGE IS
OF POOR QUALITY

JUN 1 1987

UNIVERSITY AT BUFFALO
STATE UNIVERSITY OF NEW YORK

Department of Chemistry
Faculty of Natural Sciences
and Mathematics
Acheson Hall
Buffalo, New York 14214
Tel: 831-3014

May 27, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

Please find enclosed my responses to your inquires with regard to the treatment of possible Martian samples. As things stand at this time it would seem as if the Soviets will carry out a similar study, possibly in advance of one by the U.S. A sample exchange, similar to that carried out during the period of Lunar exploration should be organized. If the Soviets do preceed us then we should use the results obtained to ascertain whether there is any need to sterilize even part of the U.S. return sample.

Yours sincerely,

D. A. Cadenhead
Professor of Chemistry

DAC/bjm
Enclosure

(1) What aspects of Martian history can be uniquely (or best) addressed by direct analysis of samples returned to Earth?

My own particular answer to this question would be the past and current interactions of Martian soil with the Martian atmosphere and the high level UV irradiation present. Lunar samples exposed to the solar wind had a micron deep amorphous or microcrystalline outer surface. While the Martian atmosphere may well afford a much greater degree of protection it is not unreasonable to anticipate that the immediate outer surface will be affected. Surface irradiation studies can provide exposure as opposed to formation history. Subtle differences in surface structures could best be detected by Synchotron studies. Chemical differences by Auger, ESCA, SIMS in conjunction with (say) scanning electron microscopy studies (SEM) to distinguish between chemical and morphological differences. None of the above studies could easily be carried out in situ.

Should a site be chosen near the edge of one of the polar ice caps during a period of shrinkage, the real possibility that liquid water may be temporarily produced. The maintainance of a relatively high humidity and liquid water is possible in porous rocks with pore structure in the mesopore (20-500Å width) range. Should any primitive life form exist on Mars the existence of such conditions could be critical. The determination of gas content and composition would require precision mass spectrometry which would best be carried out following the return of carefully preserved samples (e.g. in stainless steel containers sealed with a gold seal). The existance of highly porous (volcanic) cinders is more likely on Mars than on the Moon. Other gases typical of fumerolic activity might readily be detected by controlled degassing with temperature programmed studies.

(2) What types and quantities of samples are needed to support the analyses related to (1)?

For UV and other irradiation surface damage studies samples in the 2-10 mm range would be most suitable. Alternatively surface fragments of larger rocks could be used. Similar course fines could be used for degassing studies but so could micron sized powders, indeed the latter might be better where no porosity or internal surface area was present since minimizing the particle size, maximizes the surface area. High porosity or cinder-like particles would be particularly interesting from a degassing point of view.

(3) What degrees of sample degradation can be tolerated without defeating the analysis goals? (Specify, if possible, upper limits for temperature, pressure, radiation, acceleration/shock, etc.).

Surface and/or degassing studies are likely to be among the most sensitive to any type of sterilization treatment. For this reason samples intended for such studies should be among the untreated material. To illustrate the point heat treatment to 120°C would remove any physically adsorbed water vapor, to 250°C would remove physisorbed and chemisorbed water vapor, while heating to over 400°C would bring about surface dehydroxylation producing an irreversibly altered surface composition. Thus even moderate heating would result in some informational loss.

(4) What in situ measurements should be made on Mars to supplement or replace information that might be lost from degraded samples?

There would be little that could be done to establish surface (as opposed to bulk) structure. Degassing studies could, however, be carried out in situ and probably should be. A small quadrapole mass spectrometer could be used in this regard. Information would be greatly reduced but would provide insurance against possible subsequent sample contamination. Atmospheric sampling could be carried out with the same mass spectrometer.

ORIGINAL PAGE IS
OF POOR QUALITY

MARTIN MARIETTA DENVER AEROSPACE

POST OFFICE BOX 179
DENVER, COLORADO 80201
TELEPHONE (303) 977-3000

June 29, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim,

Enclosed are my comments on sample return mission strategies. To a large extent, I simply did not remark extensively on areas that I believe will be well represented by others. Furthermore, I added some points that were not specifically solicited, but nevertheless need to be said somewhere sometime.

I liked your follow-up letter -- it should get results. Looking forward to seeing this document, and even more so to seeing samples here on Earth.

With best regards,

Benton C. Clark
Dept. Staff Scientist

P.S. Things are super-hectic, what with Mars starting to get hot again, and Martin Marietta going through a major reorganization. Sorry I couldn't be more prompt on this.

Input to **Mars Sample Science Document.**
Benton Clark, 6-87

(1) Martian history addressed by direct analysis of samples returned to Earth. As a designer of space instruments for the past 25 years, I regard the power of automated instruments to be considerable, and constantly improving due to advances in sensor technology, electronics, on-board computational capability, and development of new approachs. Nevertheless, there is a limit to what can be accomplished remotely. Some analytical techniques are extremely difficult to fully automate. The example usually given is isotope geochemical analyses used to "age date" samples. In fact, K/Ar dating might be possible, but the full range of isotopic studies are definitely not, and this only scratches the surface. There are an enormous number of analysis approaches whose methodology is very involved, requiring multiple physical and chemical manipulations of samples to accomplish a single end result. Often, a few supertechnicians in a given laboratory are absolutely essential to maintaining the skills necessary to provide these unique capabilities. Obviously, we will never be able to send all the good laboratory people and delicate, sophisticated laboratory equipment to Mars. The samples must come to us. My judgement is that we have already reached the trade-off point where it is more economical to bring samples to Earth than to attempt microminiaturization and remote operation of the analytical techniques needed for real advances in our understanding of Mars. This does not preclude certain requirements for measurements on Mars that cannot be made on Earth.

The study of the history of Mars includes not only igneous petrogenesis, but the extremely critical question of the past climatic history and the fate of volatiles at the surface of the planet. If anything, the study of weathering products and their production routes is even more challenging. It will certainly require the use of all the various microprobing instruments (Petromicroscopy, SEM/XRF, TEM, EELS, SIMS, micro-IR), and many other techniques as well (DSC/EGA, XRD, etc.).

(2) Types and quantities needed. Variety should be sought more than quantity, as more sensitive microanalytical techniques are always being developed. Milligram quantities of unique samples can be extremely illuminating and more valuable than kilogram quantities of some other material.

My opinion is that most surface soils on Mars may be part of a ubiquitous unit, "universal martian fines." *In situ* geochemical screening, following up the Viking measurements, should allow further definition of this possibility. If so, a relatively large sample of this universal material should be taken, for the following reasons: (1) most of the surface geochemical processes on the planet will be reflected in the make-up of this material, requiring an enormously broad spectrum of analyses, (2) this material is the most appropriate for biological screening (for "back-contamination"), which may require relatively large amounts, and (3) this material is also the most appropriate for studies of manufacturing processes using indigenous martian resources. This latter point is because of several reasons, including the fact that this material may be available at a wide variety of candidate landing sites for future manned bases; and the fines probably contain many salts, compounds of low-Z volatiles, high surface-area particles, clays, magnetic minerals, and ferric oxyhydroxides, many of which are quite promising starting materials for producing useful end-products. Perhaps one-fourth of the returned material should be such universal fines, if found. At least 10 g of fines should be returned, 250 g would be better, and up to 1000 g is highly desirable.

ORIGINAL PAGE IS
OF POOR QUALITY

scan the surface beneath a rover as it traverses the surface. This capability should also be provided.

Measurements of low-temperature volatile components should also be performed on Mars since it will be very difficult to assure perfect preservation of H_2O and CO_2 ices during sample handling and the return trip. Subsampling of drill cores will probably be desired to minimize the amount of returned material. Splits could be inserted into DSC, EGA, and other on-board analytical devices.

The oxygen release detected on Mars should be further investigated on-site, as the disconnection of the sample from the large atmospheric reservoir of gases and free radicals could upset the equilibrium of the oxygenic compound.

The natural rock size distribution should be measured, not only photographically, but by screening out lithic fragments from the soil. This is important to follow-up the indication from Viking that small rock populations are deficient and to investigate the consequences thereof. Likewise, it is important to obtain statistical data on the variety of rock morphologies that are present. These investigations represent a class of studies that cannot be performed on Earth because of practical limitations on the amounts of material that can be returned.

Mechanical properties of martian soils should be directly measured *in situ*, as the amounts of sample returned will not be adequate for a full evaluation of all aspects of this problem (especially when compounded by the difficulties of fully simulating the physical conditions of the environment). This should include soil bulk density, bearing strength, traction properties, angle of internal friction, pore gases, crushing strength (duricrust), rock burial per centages, etc.

The interaction of water with martian soil under ambient conditions should be investigated. The UV flux should be measured over a wide spectrum range and as a function of daily, monthly, and yearly variations.

Consideration should be given to depth sounding, including both seismic experiments and electromagnetic sounding designed to detect ice. Attempts to detect deep liquid water and the base of the megaregolith should be made. The depth of the fine-grained mantle should also be determined if feasible.

Effects of the martian environment on various materials, both of scientific interest and engineering interest, should be investigated. This would include photolysis of compounds, corrosion of engineering materials, and long-term degradation of performance of solar energy converters.

(5) General comments.

The Mars Sample Return Mission should be engineered to provide a logical basis and derivitization for follow-on missions, such as autonomous rover and manned missions. This includes not only all aspects of sampling and sample preservation, but the specific engineering choices of all phases of the mission, such as entry/landing techniques and communications. Our planning should be ambitious and forward-looking. This has not been the characteristic of past missions.

Core drilling is extremely important, to search for layering, free ice, hydrated minerals, salt-free fines, depth of the fine-grained regolith, etc.

Salt beds should be sought out. They should be cored to preserve stratigraphic relationships critical to interpretation of the mode of formation. High sulfur and chlorine content materials should be sought. Carbonates and nitrates should be diligently searched for.

Small rocks (apparently missing at both Viking lander sites) should be specifically sought.

(3) Sample degradation allowed. Ideally each sample should be preserved at the temperature and humidity conditions existing at the time of sampling. However, this is physically impossible because a variety of samples will be taken under a variety of ambient conditions, and it will be totally impractical to provide segregated thermal environments in the sample holding canister. The best solution seems to be to hold the samples at the lowest temperature of all the sampling. This is probably about 215 K for mid- and low-latitude sites. It may be much lower for polar sites. However, if maintenance temperatures of 160 K or so are difficult to guarantee, it may be preferable to conduct careful *in situ* measurements and capture of released gases (for return to Earth) during programmed warming of samples up to the planned canister temperature. Samples which may contain H_2O should be sealed individually, if possible.

Radiation exposure is in general to be avoided. However, many practicalities may interfere with this. For example, no shielding against interplanetary cosmic rays should be attempted, because the exposure will be relatively short and any shield would be dead weight that could have permitted more sample instead. Likewise, it is probably counterproductive to rule out the use of an RTG power source on Mars because alternative electrical power methods will entail severe engineering penalties which will result in lesser sampling capabilities, and the neutrons from an RTG will not compromise many, if any, experiments.

In fact, there is the possibility that it may be considered the lesser of two evils to purposely irradiate the sample. This would arise if a decision were made that the samples must be "sterilized" prior to Earth encounter. Heating would be the worst possible method of sterilization. Chemical treatments involving liquids would likewise destroy much of the desired information related to weathering and other mineralogic processes. More preferable would be a radiation treatment, such as 100 Megarad of gamma or x-ray exposure. This would provide minimum compromise of analytical objectives.

(4) *In situ* measurements to be made on Mars. A major emphasis should be placed upon obtaining a complete suite of samples. This implies wide-ranging surface exploration, with various methods of sample screening. Visual examination is appropriate, but geochemical screening is likewise of great importance. This should allow the detection of unique soils and rocks. Infrared reflectance spectroscopic mapping is also appropriate and should be provided, but surficial coatings or alterations may mask the true nature of many or most samples. It is technically feasible to not only perform x-ray fluorescence (XRF) analysis of individual specimens, but to actually continuously

LUNAR AND PLANETARY INSTITUTE
3303 NASA ROAD 1 HOUSTON TEXAS 77058-4399 CABLE ADDRESS LUNSI
TEL (713) 486-2160

MAY 7 1987

May 4, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

Enclosed are three responses from the Institute's scientific staff to your "Call for input to a Mars Sample-Science Document". The recommendations are for sample collection at the poles (Clifford), ridged plains (Barlow), and young volcanic terrains associated with Tharsis. Each recommendation includes a discussion of the issues raised by questions 1, 2, and 4, in your letter of February 10th. In response to question 3, we have identified some of our own concerns regarding sample storage that we believe are applicable to any sample obtained from the martian surface. Since these concerns are common to all three of our proposals, we have prepared the following joint response:

3) Since it is desirable to keep sample degradation to an absolute minimum in order to extract the most information regarding the materials original state, we recommend that the following storage conditions be met:

Temperature: Sample storage temperatures should be maintained as close as possible to those which characterize the collection sites, thus minimizing the possibility of volatile release or adsorption by the samples. Temperature gradients within the storage compartment should also be kept to an absolute minimumin (<0.1 K m^{-1}) in order to prevent volatile migration and redistribution within the samples. This is especially important for any samples of the polar ice, where prolonged exposure to even small gradients could result in significant alteration of the sample (e.g., by regelation of embedded dust grains and thermal metamorphism of the ice crystal structure).

Atmospheric pressure: The samples should be stored at an atmospheric pressure appropriate to the conditions under which they were first obtained. However, if this proves unfeasible, then a constant pressure of between 5-10 mb of CO_2 would be the next best alternative. Once again, the principal concern is over the possible migration and release of volatiles from the samples.

Radiation: It does not appear that the effects of radiation on the mineral or volatile components of the samples will be a major concern at the exposure levels likely in a rover mission. Rather, the upper limit to exposure appears to be set by the extent to which the science team wishes to insure the survival of any possible examples of native martian life. While estimates of the radiation tolerances of such organisms are purely speculative, exposures in excess of several hundred rads per year often result in death for complex terrestrial organisms. Terrestrial bacteria are generally more resistant and can survive exposures as much as an order of magnitude higher.

Acceleration/shock: To prevent sample compaction, particularly of low-density regolith and polar deposit samples, it is desirable to keep all accelerations to a minimum. However, of all the storage parameters, this is certainly the least sensitive.

We would be most interested in any further opportunities for participation in the planning of the Mars Rover mission. If you have any questions concerning the enclosed contributions, or if we can be of any further assistance, please don't hesitate to call (Clifford: 486-2146; Barlow: 486-2156; Zimbelman: 486-2196).

Sincerely,

Steve

Stephen M. Clifford
Staff Scientist

enc.

cc: N. Barlow
J. Zimbelman
K. Burke

RATIONALE FOR SAMPLING THE MARTIAN POLAR DEPOSITS

Stephen M. Clifford

Within the ~10^6 km^2 covered by the north and south polar deposits, there are no craters with diameters greater than 300 m. This argues for an age of the exposed surface which is less than 10^6 years. Both units are characterized by numerous, laterally extensive, horizontal layers that appear to have individual thicknesses of 10-50 m, although finer scale layering, below the resolution of the best available Viking imagery, seems likely. Observational evidence and theoretical arguments suggest that the layers are composed predominantly of water ice, with a small a stratigraphically variable component of entrained dust. VL 2 observations indicate that thin (10-100 microns thick) layers of sediment are deposited annually during the hemsipheric fall and winter. The extent of this deposition is thought to be modulated by periodic variations in insolation that result from cyclical changes in the Martian obliquity and orbital elements. Cores of the polar deposits would provide invaluable information on the composition and mechanical properties of the polar ice, the rate and interannual variability of sedimentation, and a basis for gauging the extent of climatic change as a function of each of the known time-varying astronomical parameters.

To investigate the uniformity of deposition and erosion over the surface of the polar deposits, it is important that the cores be obtained from sites as widely separated as possible. To supplement these surface cores, cores taken at several locations down the exposed wall of a polar trough (which have surface slopes of <8°) would provide a means of sampling far deeper in the stratigraphy. The diameter of the cores need not be large, but each core should sample a total depth of at least several meters. A mission returning three widely-spaced surface cores and three trough cores would improve our understanding of the evolution of the polar terrains and the martian climate enormously.

In situ measurements might include preliminary analysis of the polar stratigraphy by examination of the cores and boreholes with the aid of a high-resolution optical densitometer or neutron absorbtion/scattering device. Provisions for conducting remote photomicroscopy and detailed chemical or elemental analyses would also prove useful.

In addition to sample collection, exploration of the polar regions by a rover vehicle would provide the opportunity to deploy a variety of important stand-alone and long-term surveillance instruments, such as meteorological stations, seismometers, and long wavelength radio-echo sounding devices. The meteorological observations would clearly benefit our understanding of the current martian climate, while the seismometers and radio-echo sounding equipment could provide detailed information regarding the basal topography and internal structure of the deposits.

Samples of young volcanic materials on Mars

The Tharsis region includes some of the youngest plains units found on Mars, based on the density of superimposed impact craters. Locations near the periphery of the Tharsis plains might allow sampling of both younger volcanic plains and the older materials on which the plains have been emplaced. The volcanic plains might represent a significant trafficability problem since lava flow surfaces are often quite rough on the scale of 10s of centimeters to meters. However, most of the Tharsis volcanic plains presently are covered by aeolian products that may smooth out the immediate surface at the 10s of centimeter scale.

Responses to the specific questions:

1) Samples from the young volcanic terrains would be very useful in constraining the absolute age of major volcanism on Mars. Age determination will not be adequately addressed without direct analysis of samples. The Tharsis volcanic plains represent a distinct component of the stratigraphic column for the entire Martian crust; precise age information for virtually any mappable young volcanic unit would provide a crucial benchmark for geologic mapping of the whole planet. Compositional information from the young volcanic material would be very important for a proper assessment of possible changes in the Martian mantle source area during the history of the planet. Volatile components within the young materials would constrain the recent climatic evolution on Mars.

2) The most important type of sample would be from unweathered bedrock; this material would be of most use in addressing the issues discribed above. Samples of the weathering products would also be important for evaluating the ultimate source of the fine materials that are widely distributed about the planet through aeolian processes. Sample quantities would not need to be very large to address the issues discussed above; probably 20 - 100 grams of the appropriate material should be sufficient.

4) Measurments made in situ would not neccessarily aid in addressing the age and lava composition questions. Measurements of specific gravity or density at the time of collection might aid in evalutating
; of volatile content from the sample during the
emperatures, both at the surface and at identified
, would aid in constraining the possible weathering
e presently acting upon the bedrock materials. If
re measurements could be made at several depths the
lux of Mars could be measured, providing a crucial
ls of the compostion and distribution of materials

SOIL SAMPLES FROM MARS--PROVIDING CONSTRAINTS ON AN ABSOLUTE CHRONOLOGY

Nadine G. Barlow

Absolute ages of geologic units on Mars have been estimated assuming the intensity and time-variance of the impact flux at Mars are equal to or are small multiples of the lunar values (Soderblom, et al., 1974; Neukum and Wise, 1976; Neukum and Hiller, 1981). The return of martian soil samples would allow these rocks to be dated using established laboratory techniques, resulting in the most reliable age estimate of at least one and possibly more geologic units. Ideally, samples from very old and very young terrains should be collected for analysis so the entire temporal range of geologic activity can be estimated. Such analyses would provide (a) a more accurate absolute chronology, which would place constraints on the proposed models for the thermal evolution of Mars, and (b) information on the impact flux at Mars, which would increase our understanding of cratering rates in the inner solar system.

Barlow (1987) has recently derived a relative-age chronology based on the Relative crater size-frequency distribution curves for martian geologic units. This study showed that the ridged plains units (ie, Lunar Planum and Syrtis Major Planum) date from near the end of the period of heavy bombardment. This event occurred about 3.8 billion years ago on the moon, according to ages determined from Apollo samples. Theoretical models disagree on whether or not the end of heavy bombardment was an essentially simultaneous event within the inner solar system (Wetherill, 1975; Wetherill, 1977). Analysis of samples from a ridged plains region would provide information necessary to confirm or dismiss the hypothesis of simultaneous termination of heavy bombardment on the terrestrial planets. In addition, these units are generally believed to have a volcanic origin, so samples from these areas would allow petrologists to study a relatively old volcanic region on Mars. The ridged plains are generally located between the older southern highlands and the younger northern plains; well-planned site selection would allow a rover to obtain samples from a number of different-aged units, providing better constraints on an absolute chronology and the thermal evolution of Mars.

The amount of samples needed for accurate age determination need not be large--50 to 100 grams of material from each site should be sufficent for laboratory procedures to determine rubidium-strontium, uranium-lead, potassium-argon, and samarium-neodymium ages of volcanic rocks. In situ measurements are not practical at this point in time for age-dating purposes due to the detailed procedures necessary to insure proper preparation of the samples.

REFERENCES:

Barlow, N.G. (1987). PhD dissertation, Univ. of Arizona, Tucson, Arizona. 134 pgs.

Neukum, G. and D.U. Wise (1976). Science, 194. 1381-1387.

Neukum, G. and K. Hiller (1981). J. Geophys. Res., 86. 3097-3121.

Soderblom, L.A., C.D. Condit, R.A. West, B.M. Herman, and T.J. Kreidler (1974). Icarus, 22. 239-263.

Wetherill, G.W. (1975). Proc. Lunar Sci. Conf. 6th. 1539-1561.

Wetherill, G.W. (1977). Proc. Lunar Sci. Conf. 8th. 1-16.

ORIGINAL PAGE IS
OF POOR QUALITY

MARS SAMPLE SCIENCE DOCUMENT

(Response to letter from J.L. Gooding, dated Feb. 10, 1987)

PROPOSAL FOR STUDY OF MAGNETIC PROPERTIES OF RETURNED MARS SAMPLES

D.W. Collinson and A. Stephenson

Department of Geophysics and Planetary Physics,

University of Newcastle upon Tyne,

Newcastle upon Tyne, NE1 7RU, England,

1. Two types of investigation of the magnetic properties of returned Mars samples are potentially very profitable for advancing our knowledge of a Martian magnetic field and of Martian surface materials and processes.

a) Investigation of natural remanent magnetization (NRM) and its stability. This could provide evidence for the presence of a Martian magnetic field at the time of formation of the samples, or of their constituent magnetic minerals. Under optimum conditions of sample availability and NRM characteristics it should also be possible to estimate the strength of the field, if it existed, in which the samples acquired their remanent magnetization.

b) To fully understand the nature of any remanent magnetization that the samples possess, it would be highly

desirable to study the nature and magnetic properties of the constituent magnetic minerals(s). At the same time these investigations could provide evidence for the quantity of magnetic minerals present and, depending on the nature of the minerals, evidence for past and present conditions in which the minerals formed. Examples are the oxidation state of any titanomagnetites present and the presence and stability of maghemite (γ-Fe_2O_3). Another property of interest is anisotropy of magnetic susceptibility, the existence and nature of which might provide evidence of stress and/or shock history of the samples.

2. For satisfactory measurement of NRM and testing its stability, rock fragments each with a minimum mass of approximately 0.2g are desirable, although given sufficient intensity of magnetization useful measurements could be made on a smaller mass. The minimum useful mass would also depend in part on the grain size and homogeneity of the fragments. If rocks of distinctly different lithologies are collected, measurement of fragments of each would be highly desirable. It would also be of some interest if there was a record of the attitude of the collected samples prior to removal from the surface.

Measurement of bulk magnetic properties can be carried out on dust-sized particles, a minimum useful quantity being $\sim$0.1g. Alternatively, if samples used for NRM measurements have not been heated (i.e. during thermal demagnetization), they could be used

for other magnetic measurements after completion of the NRM tests.

3. The most likely form of sample degradation affecting magnetic measurements appears to be the heating involved in sterilization. Heating may degrade the samples in two ways:-

a) Partial demagnetization of any NRM, and, if an ambient magnetic field is present, acquisition of a partial thermoremanent magnetization on cooling.

b) If maghemite (γ-Fe_2O_3) is present, partial inversion to hematite (α-Fe_2O_3): if hydrated iron oxides such as goethite (α-FeOOH) or lepidocrocite (γ-FeOOH) are present, partial or complete dehydration to hematite and maghemite respectively may occur. For temperatures not much in excess of $\sim$ 100°C, and weak (<100μT) ambient magnetic fields, (a) could probably be tolerated. Inversion of maghemite to hematite would probably be slow at 100°C (it inverts completely at $\sim$350°C at 1 bar pressure), but dehydration of hydrated oxides could result in acquisition of chemical remanence by the products which could obscure any original NRM present. Laboratory tests on terrestrial mineral samples, both natural and synthetic, could be carried out on these processes, to supplement results already known.

Only relatively high levels of shock would affect the NRM of the samples, levels very unlikely to be reached in any procedure between collection and measurement.

4. If it can be assumed that measurements of NRM or bulk magnetic properties cannot be carried out on the Martian surface, there appear to be no useful measurements, magnetic or other, which could replace or supplement magnetic information lost from degraded samples.

If a field magnetometer is included in the lander module, and it is recording during the descent and landing phase, the magnetometer might respond to any strongly magnetized surface rocks or features, but any quantitative derivation of strength and direction of NRM would probably not be feasible. Alternatively, if a "rover" vehicle is used, magnetic field variations during vehicle motion might indicate nearby magnetized features.

General comments

a) It is worth noting that all magnetic measurements that do not involve heating the samples are non-destructive, and the material could be used for other investigations. Although for complete understanding of magnetic properties some heating tests might be desirable, much information could be obtained from room-temperature measurements only, including that relevant to an ancient Martian magnetic field.

b) Results of the Viking magnetic properties experiment (Ref. 1)

The Viking magnetic studies proved the existence of strongly magnetic material in the Martian surface at the two landing sites. Although this material was in the form of fine particles, it suggests that material capable of retaining a measurable remanent magnetization certainly exists on Mars. A likely source of the surface material at the sites and in other regions of Mars is thought to be weathered basalt, and if basalts are collected they would be expected to carry a strong remanence if magnetized in a significant magnetic field.

Maghemite (γ-Fe_2O_3) is favoured as the magnetic mineral in the Martian surface, and it is possible that some hydrated iron oxides are also present. Hence the comments in section 3(b) concerning the degradation by heat of these minerals.

c) Evidence from SNC (Martian?) meteorites (Refs. 2, 3)

Results of studies of the magnetic properties of SNC meteorites are consistent with the presence of a magnetic field on the parent body. If this body is indeed Mars, confirmatory results from Martian returned samples would be of exceptional interest, particularly if the ages of the various types of sample can be definitely established.

SUMMARY

The primary aim of the study of magnetic properties of returned Martian samples would be detection of an ancient magnetic field and estimation of its strength, through investigations of remanent magnetization of the samples and its stability. Study of bulk magnetic properties will provide information on the magnetic minerals present, their history and possibly on the shock and/or stress history of the samples. Since the most likely origin of an ancient Martian magnetic field is generation in a molten, electrically-conducting core, there may be important implications for the history and structure of the Martian interior in the results of NRM investigations.

In recent years much experience has been gained in palaeomagnetic and rock-magnetic measurements on all types of materials. Instruments and techniques have been developed for measurement of very small, weakly magnetic samples, and relevant and informative measurements could be made on almost any form of returned Martian material. Following the revolutionary results of terrestrial palaeomagnetic studies and the more recent successes of lunar palaeomagnetism, Martian palaeomagnetism could provide equally interesting and exciting results.

REFERENCES

1. Hargraves, R.B., Collinson, D.W., Arvidson, R.E. and Spitzer, C.R., 1977. The Viking magnetic properties experiment: primary mission results. J. Geophys. Res., 82, 4547-4558.

7

2. Collinson, D.W., 1986. Magnetic properties of Antarctic Shergottites EETA 79001 and ALHA 77005: possible relevance to a Martian magnetic field. Earth Plan. Sci. Lett., 77, 159-164.

3. Cisowski, S.M., 1986. Magnetic studies on Shergotty and other SNC meteorites. Geochim. Cosmochim. Acta. 50, 1043-1048.

SAN JOSE STATE UNIVERSITY FOUNDATION

November 10, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space center
Houston, TX 77058

Dear Dr. Gooding:

I am writing briefly in response to your call for input to a Mars Sample-Science Document. I trust that the information, if you do not already have it from other sources, will still be of use to you. I have not responded globally to your questions, but within the context of my own research interests having to do with exobiology, electronic energy storage in minerals and its effect on the chemistry occurring at mineral surfaces and the possible existence of clays on Mars.

1) Earth-based analyses

a. The electronic energy content of the surface minerals, unless a reflectance signature can be identified for this (and I am looking), will be difficult to detect other than by luminescence or ESR spectra. These are both difficult to obtain from an orbiting or landing probe.

b. The remotely sensed reflectance signature should be confirmed under better controlled conditions on the ground.

c. The oxidation state and ligand geometry of several transition metal constituents of Mars, which are needed to confirm the mineralogy, will require documentation by several, rather than a single spectroscopic and chemical methods. Some of these can be done remotely, but it is difficult to believe that the mineralogy can be done definitively by only remote methods.

2) Sample requirements for earth-based supporting analyses.

a. By TL, ~50 mg would be required of powdered sample. This method is destructive. By ESR, ~200-500 mg would be required, but this method is non-destructive. Three replicates would require 500 mg, one requires 150 mg.

b. By diffuse reflectance ~1.5 grams is required for one replicate run. For three replicates, 4.5-5 grams are required. This method is non-destructive.

c. The ferrous iron can, to some extent, be characterized using ESR. These determinations can be made simultaneously with the ESR measurements of stored energy. Mossbauer spectra, perhaps in conjunction with chemical analysis would be required to determine also the ferrous. Total iron, regardless of oxidation state and ligand geometry can be done by XRF or ICP. I am not knowlegeable as to how well this could be done remotely.

3) Sample treatment

Samples should be minimally heated, in no case to temperatures greatly in excess of 100° C. Heating is preferably done dry and in the absence of oxygen to minimize chemical reactions. If the stored energy content is to be measured, the samples should not be exposed to light and the exposure to ionizing radiation should be minimal and monitored.

4) In situ measurements

Diffuse reflectance of a smooth sample excited by a well-defined light beam should be done. This measurement will probably give the maximum structural information on undegraded samples. Unless a reflectance signature can be found for stored energy, this quantity may continue to remain in question, even given returned samples, unless care is taken. Much of the basic work required to define what is meant by "care" has not yet been completed.

P.S. I guess we will meet at MEVTV. Say hi to Doug for me. Hope his finger is better

Lelia N. Coyne
Mail Stop 239-12
NASA-Ames Research Center
Moffett Field CA
94035

ONE WASHINGTON SQUARE. SAN JOSE. CALIFORNIA 95192-0139 (408) 277-3191

Please address correspondence to:
Lelia M. Coyne
Mail Stop 239-4
NASA-Ames Research Center
Moffett Field CA
94035

National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
Houston Texas
77058

NASA

Reply to Attn of

M045

Dr. James L. Gooding
NASA/JSC SN/4
Houston, TX 77058

Dear Jim:

As discussed briefly in Newcastle a couple of weeks ago, I am jotting down a point you and your colleagues may wish to consider, relative to returned samples from Mars.

Should Mars have once had a significant hydrosphere, it is possible that dissolved Sr, Nd, and Pb may be of chronologic and tracer significance for the surficial evolution of Mars, similar to the use that has been made of these marine species on Earth. With this possibility in mind, it would be advantageous to collect and preserve martian samples from which these nuclides might be extracted--eg. carbonates, oxides, hydroxyoxides, and sulfates.

The terrestrial use of marine radiogenic nuclides began with the seminal observation by Wickman (1948) that Sr and Pb, substituting for Ca in marine limestones, might record systematic radiogenic growth with time, and that limestones might simply be dated by measuring the isotopic composition of Sr and Pb in these carbonates--the isotopic composition would fall on a theoretical curve constructed for the predicted growth of Sr and Pb in seawater. With the advent of more modern mass spectrometry, Gast (1955) tested the Sr hypothesis, but poor precision obscured the results. More recent work has shown that the isotopic composition of marine Sr has had very successful use as a chronometer and enormous potential as an integrated tracer of global tectonic processes (eg. Peterman, Hedge, and Tourtelot, 1966; Dasch, 1969; DePaolo and Ingram, 1985).

The use of Sr as a global indicator results from its long residence time in the oceans (about 2 My), relative to the mixing rate in the oceans (about 1000 years). The very short residence times of Pb and Nd (less than 100 years) means that their use for terrestrial problems is quite different, although some interesting observations have been made (Piepgras, Wasserburg, and Dasch, 1980).

The "oceanic" situation on Mars undoubtedly will have been markedly different from that on Earth, but the potential use of these aqueous, radiogenic chronometers and/or tracers makes their collection and study worthwhile.

References:

Dasch, E.J., 1969, Geochim. et Cosmochim. Acta, v.33, p.1521-1552.
DePaolo,D.J., and Inghram, B.L., 1985, Science, v.227, p.938-941.
Gast, P.W., 1955, Geol. Soc. Amer. Bull., v.66, p.1449-1454.
Peterman, Z.E., Hedge, C.E., and Tourtelot, H.A., 1970, Geochim. et Cosmochim. Acta, v.34, p.105-120.
Piepgras, D.P., Wasserburg, G.J., and Dasch, E.J., 1979, Earth and Planet. Sci. Letters, v.45, p.223-236.
Wickman, F.E., 1948, Jour. Geology, v.56, p.61-66.

Sincerely,

E. Julius Dasch
NRC Fellow
NASA/JSC/SN4

JUN 5 1987

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DATE May 29, 1987
IN REPLY REFER TO ESS-8:87-537
MAIL STOP MS D438
TELEPHONE (505) 667-5446
FTS 843-5446

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim,

In reply to your request for input on Mars returned-sample science, here are some preliminary thoughts on cosmogenic nuclides in returned martian surface samples and their use in studying past climates on Mars. In planning for the Gamma-Ray Spectrometer experiment that is scheduled to fly on the Mars Observer Mission, we have done a number of calculations on the nuclear reactions that occur in the martian surface, mainly as to how they relate to the production of neutrons and gamma rays. We have found that three aspects of Mars can very significantly affect the production of cosmogenic products in Mars: the martian atmosphere and the presence of water in or dry ice on the surface of Mars. (Some of the results of these calculations will be published in J. Geophys. Res. in a paper by D. Drake, W. Feldman, and B. Jakosky.) These climatic factors can greatly affect the energy and spatial distribution of neutrons, especially those with thermal or near thermal energies, in the surface of Mars. For example, hydrogen in the martian surface can rapidly thermalize neutrons and shift their energy and depth distributions in the top few tens of centimeters. Dry ice or the atmosphere can attenuate the intensity of cosmic-ray particles and also can moderate fast neutrons and build a reservoir of low-energy neutrons that will leak into the martian surface.

Most cosmogenic nuclides are produced by secondary neutrons made by galactic-cosmic-ray interactions in the martian atmosphere and surface. To unfold the cosmic-ray record in martian samples, a number of products with a variety of half-lives made by cosmic-ray particles with different energies would need to be measured. For example, ^{10}Be made by high-energy reactions, ^{26}Al made by lower-energy secondary neutrons, and ^{36}Cl made by neutron-capture reactions could be used to establish the average cosmic-ray particle environment in the martian surface over the last million years (the approximate half-lives of these three long-lived radionuclides). If the systematics of these radioactivities differ from that observed for short-lived radionuclides, such as spallogenic 2.6-year ^{22}Na and neutron-capture-produced 5.27-year ^{60}Co, then we could possibly infer that changes had occurred in the martian climate (thickness of the martian atmosphere or the hydrogen content of the martian surface) over the last million years. Stable cosmogenic nuclides, such as high-energy-produced ^{3}He, low-energy-produced ^{21}Ne, and ^{36}Ar (mainly from the decay of neutron-capture-produced ^{36}Cl) could extend this comparison to longer time periods. Such studies would complement those done now with cosmogenic nuclides in lunar samples, such as exposure ages and gardening rates of the regolith.

The analyses of these cosmogenic nuclides can now be done with sample sizes less than a gram. Both cores in the martian regolith down to depths of about a meter and surface rocks would be needed to unfold the various cosmic-ray records. Care

An Equal Opportunity Employer/Operated by University of California

would be needed to prevent the loss of certain cosmogenic products that are volatile, such as chlorine or the noble gases, from the returned samples.

Sincerely yours,

Robert C. Reedy

William C. Feldman

Darrell M. Drake

cc: ESS-8 file
CRM-4 (2)

JUL 31 1987

United States Department of the Interior

GEOLOGICAL SURVEY
BOX 25046 MS
DENVER FEDERAL CENTER
DENVER, COLORADO 80225

July 28, 1987

James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

I'm very sorry that I haven't answered your call for input to a Mars sample-science document (dated Feb. 10, 1987) sooner. I realize that is too late now to be included in the published report, but I would like to express my interest, support and enthusiasm for this unique project. If there is any way you can use a clay mineralogist/geochemist, please count me in.

Clays can tell us a great deal about the geologic history of a region (see enclosed reprint), so they should be very helpful for Martian studies. Only a small amount (200 mg total/sample) would be needed for X-ray diffraction, infrared, electron microscopy and chemical analysis. Because clay loses structural hydroxyls when heated in air to temperatures greater than about 550 C (lower temperatures in a vacuum), it should be protected from temperature extremes. Also, illitic clay loses argon at about 300 C; therefore if it is to be dated by K/Ar, heating to this temperature should be avoided. If possible, it would be useful to put a X-ray diffractometer on Mars to determine the structure of the clays on the planet.

Please keep me informed about this project.

Sincerely yours,

Dr. Dennis D. Eberl

JUN 8 1987

The University of New Mexico

DEPARTMENT OF GEOLOGY
Northrop Hall
Albuquerque, NM 87131
Telephone 505 277-4204

June 3, 1987

Dr. James L. Gooding, SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Jim:

Any suggestions I can make for a Mars sample mission have probably been made before. In response to your circular of May 27, 1987, I am sending them to you for what they are worth.

The Tharsis volcanoes have relatively uncratered caldera floors and more densely cratered flanks. On the assumption that the craters formed primarily by impact, Larry Crumpler and Jayne Aubele (Icarus, v. 34, p. 496-511, 1978) estimated that the edifices took 10^8 years to grow. If it is possible to land on the smooth caldera floor near a place where the caldera walls or flanks are accessible, collected samples should be large enough for petrogenetic-geochemical studies and radiometric dating.

Results would tell us a great deal about:

1. The actual age and time span of volcanism, with implication about the thermal regime of Mars.
2. Validity and calibration of martian time scales based on crater counts (note the wildly different time scales of Neukum and Hiller, JGR, v. 86, p. 3097-3121, 1981; Soderblom et al., Icarus, v. 22, p. 239-263, 1974; and Hartmann, Geophys. Res. Letters, v. 5, p. 450-452, 1978).
3. Magma generation and differentation over a known time span.
4. Chemistry and zoning of the mantle, especially if xenoliths are present.

With best regards,

Sincerely,

Wolfgang E. Elston
Professor of Geology

WEE/smf

ORIGINAL PAGE IS
OF POOR QUALITY

SJSU SAN JOSE STATE UNIVERSITY

MAY 11 1987

School of Science • Department of Chemistry
One Washington Square • San Jose California 95192-0101 • 408 277-2366

Peter A.J. Englert
Department of Chemistry
Nuclear Science Facility
05-07-87

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Re.: SN2-87-L084

Dear Jim,

Please find enclosed my contribution to the Mars Sample-Science Document. I concentrate on questions that could be answered by comogenic nuclide studies.

If you have any questions regarding this brief outline, please do not hesitate to call me.

Sincerely,

(Peter Englert)

SJSU SAN JOSE STATE UNIVERSITY

MAY 11 1987

School of Science • Department of Chemistry
One Washington Square • San Jose California 95192-0101 • 408 277-2366

PETER ENGLERT
DEPARTMENT OF CHEMISTRY
NUCLEAR SCIENCE FACILITY
05-07-1987

Re.: SN2-87-L084, Mars Sample-Science Document

COSMOGENIC NUCLIDE AND COSMIC RAY EFFECT STUDIES IN SAMPLES RETURNED FROM MARS

RECENT AND PAST SURFACE PROCESSES ON MARS

The outermost surfaces of planets are steadily bombarded by energetic cosmic ray particles. This radiation interacts with matter in different ways including nuclear reactions, leading to a number of stable and radioactive so-called cosmogenic nuclides. Cosmogenic nuclide and cosmic ray effect studies have proven to be exceptionally valuable tools in the deconvolution of recent and past near surface processes on the Moon, which are dominated by meteorite and micrometeorite impact. The extent and the time of regolith formation on this atmosphere free planetary body was determined by the analysis and interpretation of both solar cosmic ray and galactic cosmic ray effects on the production of cosmogenic stable and radioactive isotopes and cosmic ray tracks.

Compared to the Moon, Mars has a few properties which cause enormously interesting and comparatively complex erosional-depositional scenarios. An atmosphere of about 16 to 20 g/cm^2 minimizes solar cosmic ray effects so that galactic cosmic ray interactions dominate the production of cosmogenic nuclides. Atmosperic volatiles form seasonal and permanent frozen deposits around the polar regions. The martian atmosphere is also responsible for aeolian activities which move and create surface deposits in comparatively short time scales, literally overlaying those of many other geological processes and events. Questions that can be addressed specifically by the study of cosmic ray effects are martian dust turnover rates, the general long-term history of aeolian activity, the depth of aeolian or meteoritic 'gardening', the volatile condensation depth, and volatile and wind-related weathering, as well as erosion rates of hard surface rocks. Turnover rates, for example, can be determined by comparison of cosmic ray effects with integral and differential time memory, the latter one provided by radioactive cosmogenic nuclides with their wide range of half-lives. In addition, <u>in situ</u> produced cosmogenic radionuclides and atmospherically produced deposited cosmogenic nuclides could help to unravel the depositional history of permanent ices, provided that ice cores

can be returned into laboratories at reasonable cost.

Volatiles, especially hydrogen and carbon, can affect the depth dependent production of cosmogenic nuclides significantly. This effect can indirectly give clues on the volatile abundance and distribution in a rock or dust sampling site, if volatiles were deliberately removed from the sample by sterilization without precise records. If information on the moderator content is not lost, cosmogenic nuclide depth profiles can be used to better understand the cosmic ray interaction with the martian surface. Neutron produced isotopic abundance shifts in such elements as Gd and Re as well as other neutron capture products may be valuable to derive long term estimates on the presence and history of volatiles and their concentrations in the sampling location.

The following groups of cosmic ray effects shall be studied:

-Stable and radioactive nuclear reaction products of the primary galactic cosmic radiation and its cascade of secondaries.

-Effects of the heavy component of the galactic cosmic radiation, i.e. cosmic ray tracks.

-General radiation exposure/damage effects such as those detectable via thermoluminescence (TL) and electron spin resonance (ESR) and other methods.

-Atmospherically produced and deposited radioisotopes.

SAMPLE QUANTITIES

Sample size for a complete consortium study of cosmogenic nuclides and other radiation exposure effects is estimated to be in the few gram range or lower (if necessary) per sample for rock and dust samples. Volatile deposits require at least tens of grams. In most fields mentioned, techniques have been developed to a high degree of perfection. In the case of the cosmogenic radionuclides, Accelerator Mass Spectrometry has lowered the limits of detection by orders of magnitude during the last few years. Only ESR has not yet been applied to extraterrestrial samples extensively, though it is very similiar to TL in its range of application.

It can be anticipated that samples of every centimeter from drill cores would be requested at shallow depths and from every third to fifth centimeter from deeper locations. Similar reqirements could be established for complete surface rocks and for samples from more random finding sites.

OTHER SAMPLE REQUIREMENTS

To study cosmic ray effects on Mars samples, the geological/mineralogical composition of the samples taken is of secondary order. No matter how small the sample is that is received for cosmic ray effect studies, the first and most important requirement is the exact documentation of the sample's location within the martian surface and its direct environment; the environment is responsible for the primary and secondary particle fluxes which produce the cosmogenic nuclides. This applies to all possible modes of sampling.

The mode of collection that is most likely to preserve the geometric and stratigraphic information is coring. Several cores of up to 1.5 m depth, including those of different kinds of aeolian deposits, are therefore recommended to be taken also for cosmic ray effect studies. Cores of frozen volatiles should preferably be longer, if feasible.

DEGRADATION REQUIREMENTS

In principle, the removal of a sample from its finding site is the first step of degradation. This step changes the irradiation environment of the sample and thus affects the production of cosmogenic nuclides. However, if a maximum time span of 1.5 years between the first sample collection and the arrival in the terrestrial laboratory can be assumed, only radionuclides with half-lives in that time range will be affected seriously in their abundance and consequently their use in interpreting martian surface history.

As complete shielding from cosmic radiation after sampling is close to impossible (unless the samples are stored in a deep cave within a reasonable time after retrieval) and monitoring of these different radiation exposures is extremely questionable, (cruise phases and sampling phases produce changing radiation environments of varying duration) short-lived isotopes, in gerneral, may not prove to be very valuable for Mars surface history interpretation. Nevertheless, in order to minimize these effects retrieval of those samples which are important for short-term time studies of surface processes should occurr close to the end of the mission.

Loss of geometric or stratigraphic information affects the analysis and interpretation of cosmogenic nuclide and cosmic ray effect data significantly. Especially drill cores of aeolian deposits shall be stored in a way that prevents or at least minimizes loss of stratigraphic information by vibration, acceleration or shock.

High temperatures that may be applied for biological sterilization up to a few hundred degrees Celsius will not affect cationic and non volatile anionic species of stable and radioactive cosmogenic nuclides in rock or dust cores. Low atomic weight radioactive and noble gases, however, can be seriously affected. Those cosmic ray effects that caused radiation damage to solid martian material will definitely suffer from elevated

temperatures (tracks) or may completely disappear (TL,ESR). Here annealing and fading studies will help to determine controlled conditions of sterilization and storage in order to keep the effects minimal. Sterilization by heat may prevent the retrieval and study of frozen volatile deposits. Other methods of sterilization should be investigated.

IN SITU MEASUREMENTS

In situ measurements of contemporary neutron depth profiles during the mission in the location of the drill cores can complement the information to be obtained from later laboratory studies of cosmogenic nuclides. They would define the latest point in time to which all other results could be set into relation. These measurements could possibly be made by active neutron or gamma ray counting or spectrometry instrumentation because passive experiments (such as the Lunar Neutron Experiment equivalent) would suffer from the problem of additional and possibly unknown radiation exposures during other phases of the experiment.

In principle, gamma ray or neutron depth profile measurements have the capability to determine the volatile concentration also as a function of depth in the coring sites, information that may be lost during subsequent deliberate and/or involuntary sample degradation. The volatile element analysis may be a part of a gamma ray spectrometry/ neutron spectrometry instrument for elemental survey, which may be implemented into the rover as standard instrumentation.

Universitat Bern

Physikalisches Institut

Prof. Dr. J. Geiss
PD Dr. O. Eugster
CH-3012 Bern, Sidlerstrasse 5, Telefon 031 65 86 ...
Telex CH 912 643, Telefax 031 65 44 05

JUL 1 1987

Dr. James L. Gooding
National Aeronautics and
Space Administration
Lyndon B. Johnson Space
Center

Houston, TX 77058

- U.S.A. -

June 25, 1987/ip

Dear Dr. Gooding,

Enclosed please find our remarks concerning the field of isotopic studies of martian samples in Earth-bound laboratories. We strongly encourage your efforts to summarize the scientific requirements for a Mars sample return mission and we would be glad to be kept informed on the progress and results of the project. Presumably we shall not be able to participate in the Mars Sample Return Science Workshop in Houston next November.

Sincerely yours,

J. Geiss O. Eugster

Encl. - our recommendation
- ESF/NAS Report on the Exploration of Mars (Chairman H. Fechtig)
- Recommendation by the Space Science Committee of ESF (Chairman J. Geiss)

605 9 15 7

MARS SAMPLE RETURN MISSION

Recommendations with respect to isotope studies and dating of martian samples in Earth-bound laboratories.

Scientific objectives

From the point of view of isotopic studies the following questions can be addressed by direct analyses of martian samples returned to Earth:

1) Determination of the abundances of the chemical elements in samples from various sites for the study of the geochemical characteristics and evolution of the martian crust.

2) Precise isotopic analyses of solid and volatile elements. Comparison with the respective isotopic abundances of these elements with those in other reservoirs of the solar system (Earth, Moon, Sun, meteorites, comets).

3) Dating of the mineral formation ages using more than one and preferably all of the decay systems K-Ar (^{39}Ar-^{40}Ar method), Rb-Sr, Sm-Nd, and U/Th-Pb. Formation ages of the different geologic units on Mars and of the martian crust.

4) The martian surface is essentially unshielded from galactic cosmic rays. Surface exposure ages can be derived from the concentration of stable cosmogenic nuclei, or by using the ^{81}Kr-Kr dating method.

Masses and types of samples

In the case of a Mars sample return individual rock samples and the total amounts of material will probably have to be much smaller than in the case of Apollo. Thus, prior to the mission a special effort has to be made to improve the sensitivities of methods and equipment. With this assumption we estimate that depending on the concentrations of the elements to be studied 1-5 g of material has to be processed to achieve the scientific goals mentioned above. Usually, mineral or structural phases have to be separated in order to enrich the respective elements in the studied samples.

The largest possible variety of samples from different geological sites on Mars is desired: single rocks, rock specimen from large boulders, rock fragments as parts of rake samples, soil samples, and core samples if possible from the full depth of the martian regolith.

Sample storage

Storage of the samples in closed containers without contamination by non martian volatiles is essential. Contamination by rocket fuel gases and by terrestrial atmospheric gases after return on Earth may seriously hamper the study of indigenous martian volatiles. Samples should be stored in vacuum or in a controlled atmosphere. Storage in an environment without contact to the terrestrial atmosphere should be guaranteed until scientific investigation in Earth-bound laboratories. The receiving facilities should be equipped to provide this type of storage for several years.

In-situ measurements

A valuable supplement to the Earth-bound laboratory analyses are the in-situ analyses of the chemical and isotopic composition for some elements of the martian surface and atmosphere. Remote rock characterization is essential for selecting the samples for return.

General remarks

In addition to these specific remarks we refer to the enclosed "Report on the exploration of Mars" composed by a sub-group of the former European Science Foundation/National Academy of Science working group.

J. Geiss O. Eugster

JUL 1 1987

EUROPEAN SCIENCE FOUNDATION

1, quai Lezay-Marnésia F 67000 STRASBOURG Tel. (88) 35.30.63 Telex 890440

4. Recommendation on an International Mars Mission including Sample Return
(issued September 1986)

The Space Science Committee recognizes the immense scientific, political and technological potential of an unmanned mission to the surface of Mars, to include sample return. It acknowledges the report of the subgroup of the former ESF/NAS Joint Working Group on this subject. Because of the importance of such a programme its ultimate realization is inevitable, and indeed informal discussions have already taken place between members of the space science community in the USA and the USSR about possible international cooperation on such a venture. The SSC recommends that, if such discussions proceed further, Europe should be involved, with a view to a three-way partnership. Europe has much to gain and to contribute from a full technological and scientific involvement in the mission, and has a strong and experienced community interested in the analysis of returned samples. This recommendation is consistent with the Long-term plans of ESA, as expressed in the document Horizon 2000.

J. Geiss
Chairman, Space Science Committee

APR 7 1987

References

Dorn, R. I., 1983, Cation-ratio dating: A new rock varnish age-determination technique, Quaternary Research, v. 20, p. 49-73.

Dorn, R. I., M. J. DeNiro, H. O. Ajie, 1987, Isotopic evidence for climatic influence on alluvial-fan development in Death Valley, California, Geology, v. 15, p. 108-110.

Dorn, R. I., and T. M. Oberlander, 1982, Rock varnish, Prog. Phys. Geog., v. 6, p. 317-367.

Farr, T. G. and J. B. Adams, 1984, Rock coatings in Hawaii, Geological Society of America Bulletin, vol. 95, p. 1077-1083.

McCord, T. B., R. B. Singer, B. R. Hawke, J. B. Adams, D. L. Evans, J. W. Head, P. J. Mouginis-Mark, C. M. Pieters, R. L. Huguenin, S. H. Zisk, 1982, Mars: Definition and characterization of global surface units with emphasis on composition, Jour. Geophys. Res., v. 87, p. 10,129-10,148.

JUN 5 1987

Los Alamos
Los Alamos National Laboratory
Los Alamos,New Mexico 87545

DATE May 29, 1987
IN REPLY REFER TO ESS-8:87-537
MAIL STOP MS D438
TELEPHONE (505) 667-5446
FTS 843-5446

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim,

In reply to your request for input on Mars returned-sample science, here are some preliminary thoughts on cosmogenic nuclides in returned martian surface samples and their use in studying past climates on Mars. In planning for the Gamma-Ray Spectrometer experiment that is scheduled to fly on the Mars Observer Mission, we have done a number of calculations on the nuclear reactions that occur in the martian surface, mainly as to how they relate to the production of neutrons and gamma rays. We have found that three aspects of Mars can very significantly affect the production of cosmogenic products in Mars: the martian atmosphere and the presence of water in or dry ice on the surface of Mars. (Some of the results of these calculations will be published in J. Geophys. Res. in a paper by D. Drake, W. Feldman, and B. Jakosky.) These climatic factors can greatly affect the energy and spatial distribution of neutrons, especially those with thermal or near thermal energies, in the surface of Mars. For example, hydrogen in the martian surface can rapidly thermalize neutrons and shift their energy and depth distributions in the top few tens of centimeters. Dry ice or the atmosphere can attenuate the intensity of cosmic-ray particles and also can moderate fast neutrons and build a reservoir of low-energy neutrons that will leak into the martian surface.

Most cosmogenic nuclides are produced by secondary neutrons made by galactic-cosmic-ray interactions in the martian atmosphere and surface. To unfold the cosmic-ray record in martian samples, a number of products with a variety of half-lives made by cosmic-ray particles with different energies would need to be measured. For example, ^{10}Be made by high-energy reactions, ^{26}Al made by lower-energy secondary neutrons, and ^{36}Cl made by neutron-capture reactions could be used to establish the average cosmic-ray particle environment in the martian surface over the last million years (the approximate half-lives of these three long-lived radionuclides). If the systematics of these radioactivities differ from that observed for short-lived radionuclides, such as spallogenic 2.6-year ^{22}Na and neutron-capture-produced 5.27-year ^{60}Co, then we could possibly infer that changes had occurred in the martian climate (thickness of the martian atmosphere or the hydrogen content of the martian surface) over the last million years. Stable cosmogenic nuclides, such as high-energy-produced ^{3}He, low-energy-produced ^{21}Ne, and ^{36}Ar (mainly from the decay of neutron-capture-produced ^{36}Cl) could extend this comparison to longer time periods. Such studies would complement those done now with cosmogenic nuclides in lunar samples, such as exposure ages and gardening rates of the regolith.

The analyses of these cosmogenic nuclides can now be done with sample sizes less than a gram. Both cores in the martian regolith down to depths of about a meter and surface rocks would be needed to unfold the various cosmic-ray records. Care

An Equal Opportunity Employer/Operated by University of California

would be needed to prevent the loss of certain cosmogenic products that are volatile, such as chlorine or the noble gases, from the returned samples.

Sincerely yours,

Robert C. Reedy

William C. Feldman

Darrell M. Drake

cc: ESS-8 file
CRM-4 (2)

ORIGINAL PAGE IS
OF POOR QUALITY

JUL 31 1987

United States Department of the Interior

GEOLOGICAL SURVEY
BOX 25046 MS
DENVER FEDERAL CENTER
DENVER, COLORADO 80225

July 28, 1987

James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

I'm very sorry that I haven't answered your call for input to a Mars sample-science document (dated Feb. 10, 1987) sooner. I realize that is too late now to be included in the published report, but I would like to express my interest, support and enthusiasm for this unique project. If there is any way you can use a clay mineralogist/geochemist, please count me in.

Clays can tell us a great deal about the geologic history of a region (see enclosed reprint), so they should be very helpful for Martian studies. Only a small amount (200 mg total/sample) would be needed for X-ray diffraction, infrared, electron microscopy and chemical analysis. Because clay loses structural hydroxyls when heated in air to temperatures greater than about 550 C (higher temperatures in a vacuum), it should be protected from temperature extremes. Also, illitic clay loses argon at about 300 C; therefore if it is to be dated by K/Ar, heating to this temperature should be avoided. If possible, it would be useful to put a X-ray diffractometer on Mars to determine the structure of the clays on the planet.

Please keep me informed about this project.

Sincerely yours,

Dr. Dennis D. Eberl

JUN 8 1987

The UNM
University of New Mexico

DEPARTMENT OF GEOLOGY
Northrop Hall
Albuquerque, NM 87131
Telephone 505 277-4204

June 3, 1987

Dr. James L. Gooding, SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Jim:

Any suggestions I can make for a Mars sample mission have probably been made before. In response to your circular of May 27, 1987, I am sending them to you for what they are worth.

The Tharsis volcanoes have relatively uncratered caldera floors and more densely cratered flanks. On the assumption that the craters formed primarily by impact, Larry Crumpler and Jayne Aubele (Icarus, v. 34, p. 496-511, 1978) estimated that the edifices took 10^8 years to grow. If it is possible to land on the smooth caldera floor near a place where the caldera walls or flanks are accessible, collected samples should be large enough for petrogenetic-geochemical studies and radiometric dating.

Results would tell us a great deal about:

1. The actual age and time span of volcanism, with implication about the thermal regime of Mars.
2. Validity and calibration of martian time scales based on crater counts (note the wildly different time scales of Neukum and Hiller, JGR, v. 86, p. 3097-3121, 1981; Soderblom et al., Icarus, v. 22, p. 239-263, 1974; and Hartmann, Geophys. Res. Letters, v. 5, p. 450-452, 1978).
3. Magma generation and differentation over a known time span.
4. Chemistry and zoning of the mantle, especially if xenoliths are present.

With best regards,

Sincerely,

Wolfgang E. Elston
Professor of Geology

WEE/smf

SJSU SAN JOSE STATE UNIVERSITY

School of Science • Department of Chemistry
One Washington Square • San Jose California 95192-0101 • 408 277-2366

MAY 11 1987

Peter A.J. Englert
Department of Chemistry
Nuclear Science Facility
05-07-87

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Re.: SN2-87-L084

Dear Jim,

Please find enclosed my contribution to the Mars Sample-Science Document. I concentrate on questions that could be answered by comogenic nuclide studies.

If you have any questions regarding this brief outline, please do not hesitate to call me.

Sincerely,

(Peter Englert)

SJSU SAN JOSE STATE UNIVERSITY

School of Science • Department of Chemistry
One Washington Square • San Jose California 95192-0101 • 408 277-2366

MAY 11 1987

PETER ENGLERT
DEPARTMENT OF CHEMISTRY
NUCLEAR SCIENCE FACILITY
05-07-1987

Re.: SN2-87-L084, Mars Sample-Science Document

COSMOGENIC NUCLIDE AND COSMIC RAY EFFECT STUDIES IN SAMPLES RETURNED FROM MARS

RECENT AND PAST SURFACE PROCESSES ON MARS

The outermost surfaces of planets are steadily bombarded by energetic cosmic ray particles. This radiation interacts with matter in different ways including nuclear reactions, leading to a number of stable and radioactive so-called cosmogenic nuclides. Cosmogenic nuclide and cosmic ray effect studies have proven to be exceptionally valuable tools in the deconvolution of recent and past near surface processes on the Moon, which are dominated by meteorite and micrometeorite impact. The extent and the time of regolith formation on this atmosphere free planetary body was determined by the analysis and interpretation of both solar cosmic ray and galactic cosmic ray effects on the production of cosmogenic stable and radioactive isotopes and cosmic ray tracks.

Compared to the Moon, Mars has a few properties which cause enormously interesting and comparatively complex erosional-depositional scenarios. An atmosphere of about 16 to 20 g/cm^2 minimizes solar cosmic ray effects so that galactic cosmic ray interactions dominate the production of cosmogenic nuclides. Atmosperic volatiles form seasonal and permanent frozen deposits around the polar regions. The martian atmosphere is also responsible for aeolian activities which move and create surface deposits in comparatively short time scales, literally overlaying those of many other geological processes and events. Questions that can be addressed specifically by the study of cosmic ray effects are martian dust turnover rates, the general long-term history of aeolian activity, the depth of aeolian or meteoritic 'gardening', the volatile condensation depth, and volatile and wind-related weathering, as well as erosion rates of hard surface rocks. Turnover rates, for example, can be determined by comparison of cosmic ray effects with integral and differential time memory, the latter one provided by radioactive cosmogenic nuclides with their wide range of half-lives. In addition, in situ produced cosmogenic radionuclides and atmospherically produced deposited cosmogenic nuclides could help to unravel the depositional history of permanent ices, provided that ice cores

can be returned into laboratories at reasonable cost.

Volatiles, especially hydrogen and carbon, can affect the depth dependent production of cosmogenic nuclides significantly. This effect can indirectly give clues on the volatile abundance and distribution in a rock or dust sampling site, if volatiles were deliberately removed from the sample by sterilization without precise records. If information on the moderator content is not lost, cosmogenic nuclide depth profiles can be used to better understand the cosmic ray interaction with the martian surface. Neutron produced isotopic abundance shifts in such elements as Gd and Re as well as other neutron capture products may be valuable to derive long term estimates on the presence and history of volatiles and their concentrations in the sampling location.

The following groups of cosmic ray effects shall be studied:

-Stable and radioactive nuclear reaction products of the primary galactic cosmic radiation and its cascade of secondaries.

-Effects of the heavy component of the galactic cosmic radiation, i.e. cosmic ray tracks.

-General radiation exposure/damage effects such as those detectable via thermoluminescence (TL) and electron spin resonance (ESR) and other methods.

-Atmospherically produced and deposited radioisotopes.

SAMPLE QUANTITIES

Sample size for a complete consortium study of cosmogenic nuclides and other radiation exposure effects is estimated to be in the few gram range or lower (if necessary) per sample for rock and dust samples. Volatile deposits require at least tens of grams. In most fields mentioned, techniques have been developed to a high degree of perfection. In the case of the cosmogenic radionuclides, Accelerator Mass Spectrometry has lowered the limits of detection by orders of magnitude during the last few years. Only ESR has not yet been applied to extraterrestrial samples extensively, though it is very similiar to TL in its range of application.

It can be anticipated that samples of every centimeter from drill cores would be requested at shallow depths and from every third to fifth centimeter from deeper locations. Similar reqirements could be established for complete surface rocks and for samples from more random finding sites.

OTHER SAMPLE REQUIREMENTS

To study cosmic ray effects on Mars samples, the geological/mineralogical composition of the samples taken is of secondary order. No matter how small the sample is that is received for cosmic ray effect studies, the first and most important requirement is the exact documentation of the sample's location within the martian surface and its direct environment; the environment is responsible for the primary and secondary particle fluxes which produce the cosmogenic nuclides. This applies to all possible modes of sampling.

The mode of collection that is most likely to preserve the geometric and stratigraphic information is coring. Several cores of up to 1.5 m depth, including those of different kinds of aeolian deposits, are therefore recommended to be taken also for cosmic ray effect studies. Cores of frozen volatiles should preferably be longer, if feasible.

DEGRADATION REQUIREMENTS

In principle, the removal of a sample from its finding site is the first step of degradation. This step changes the irradiation environment of the sample and thus affects the production of cosmogenic nuclides. However, if a maximum time span of 1.5 years between the first sample collection and the arrival in the terrestrial laboratory can be assumed, only radionuclides with half-lives in that time range will be affected seriously in their abundance and consequently their use in interpreting martian surface history.

As complete shielding from cosmic radiation after sampling is close to impossible (unless the samples are stored in a deep cave within a reasonable time after retrieval) and monitoring of these different radiation exposures is extremely questionable, (cruise phases and sampling phases produce changing radiation environments of varying duration) short-lived isotopes, in gerneral, may not prove to be very valuable for Mars surface history interpretation. Nevertheless, in order to minimize these effects retrieval of those samples which are important for short-term time studies of surface processes should occurr close to the end of the mission.

Loss of geometric or stratigraphic information affects the analysis and interpretation of cosmogenic nuclide and cosmic ray effect data significantly. Especially drill cores of aeolian deposits shall be stored in a way that prevents or at least minimizes loss of stratigraphic information by vibration, acceleration or shock.

High temperatures that may be applied for biological sterilization up to a few hundred degrees Celsius will not affect cationic and non volatile anionic species of stable and radioactive cosmogenic nuclides in rock or dust cores. Low atomic weight radioactive and noble gases, however, can be seriously affected. Those cosmic ray effects that caused radiation damage to solid martian material will definitely suffer from elevated

temperatures (tracks) or may completely disappear (TL,ESR). Here annealing and fading studies will help to determine controlled conditions of sterilization and storage in order to keep the effects minimal. Sterilization by heat may prevent the retrieval and study of frozen volatile deposits. Other methods of sterilization should be investigated.

IN SITU MEASUREMENTS

In situ measurements of contemporary neutron depth profiles during the mission in the location of the drill cores can complement the information to be obtained from later laboratory studies of cosmogenic nuclides. They would define the latest point in time to which all other results could be set into relation. These measurements could possibly be made by active neutron or gamma ray counting or spectrometry instrumentation because passive experiments (such as the Lunar Neutron Experiment equivalent) would suffer from the problem of additional and possibly unknown radiation exposures during other phases of the experiment.

In principle, gamma ray or neutron depth profile measurements have the capability to determine the volatile concentration also as a function of depth in the coring sites, information that may be lost during subsequent deliberate and/or involuntary sample degradation. The volatile element analysis may be a part of a gamma ray spectrometry/ neutron spectrometry instrument for elemental survey, which may be implemented into the rover as standard instrumentation.

Universitat Bern

Physikalisches Institut

Prof. Dr. J. Geiss
PD Dr. O. Eugster

CH-3012 Bern, Sidlerstrasse 5, Telefon 031 65 86
Telex CH 912 643, Telefax 031 65 44 05

JUL 1 1987

Dr. James L. Gooding
National Aeronautics and
Space Administration
Lyndon B. Johnson Space
Center

Houston, TX 77058

- U.S.A. -

June 25, 1987/ip

Dear Dr. Gooding,

Enclosed please find our remarks concerning the field of isotopic studies of martian samples in Earth-bound laboratories. We strongly encourage your efforts to summarize the scientific requirements for a Mars sample return mission and we would be glad to be kept informed on the progress and results of the project. Presumably we shall not be able to participate in the Mars Sample Return Science Workshop in Houston next November.

Sincerely yours,

J. Geiss O. Eugster

Encl. - our recommendation
- ESF/NAS Report on the Exploration of Mars (Chairman H. Fechtig)
- Recommendation by the Space Science Committee of ESF (Chairman J. Geiss)

805 9 15 7

MARS SAMPLE RETURN MISSION

Recommendations with respect to isotope studies and dating of martian samples in Earth-bound laboratories.

Scientific objectives

From the point of view of isotopic studies the following questions can be addressed by direct analyses of martian samples returned to Earth:

1) Determination of the abundances of the chemical elements in samples from various sites for the study of the geochemical characteristics and evolution of the martian crust.

2) Precise isotopic analyses of solid and volatile elements. Comparison with the respective isotopic abundances of these elements with those in other reservoirs of the solar system (Earth, Moon, Sun, meteorites, comets).

3) Dating of the mineral formation ages using more than one and preferably all of the decay systems K-Ar (^{39}Ar-^{40}Ar method), Rb-Sr, Sm-Nd, and U/Th-Pb. Formation ages of the different geologic units on Mars and of the martian crust.

4) The martian surface is essentially unshielded from galactic cosmic rays. Surface exposure ages can be derived from the concentration of stable cosmogenic nuclei, or by using the ^{81}Kr-Kr dating method.

Masses and types of samples

In the case of a Mars sample return individual rock samples and the total amounts of material will probably have to be much smaller than in the case of Apollo. Thus, prior to the mission a special effort has to be made to improve the sensitivities of methods and equipment. With this assumption we estimate that depending on the concentrations of the elements to be studied 1-5 g of material has to be processed to achieve the scientific goals mentioned above. Usually, mineral or structural phases have to be separated in order to enrich the respective elements in the studied samples.

The largest possible variety of samples from different geological sites on Mars is desired: single rocks, rock specimen from large boulders, rock fragments as parts of rake samples, soil samples, and core samples if possible from the full depth of the martian regolith.

Sample storage

Storage of the samples in closed containers without contamination by non martian volatiles is essential. Contamination by rocket fuel gases and by terrestrial atmospheric gases after return on Earth may seriously hamper the study of indigenous martian volatiles. Samples should be stored in vacuum or in a controlled atmosphere. Storage in an environment without contact to the terrestrial atmosphere should be guaranteed until scientific investigation in Earth-bound laboratories. The receiving facilities should be equipped to provide this type of storage for several years.

In-situ measurements

A valuable supplement to the Earth-bound laboratory analyses are the in-situ analyses of the chemical and isotopic composition for some elements of the martian surface and atmosphere. Remote rock characterization is essential for selecting the samples for return.

General remarks

In addition to these specific remarks we refer to the enclosed "Report on the exploration of Mars" composed by a sub-group of the former European Science Foundation/National Academy of Science working group.

J. Geiss O. Eugster

JUL 1 1987

EUROPEAN SCIENCE FOUNDATION

1, quai Lezay-Marnésia · F 67000 STRASBOURG · Tel. (88) 35.30.63 · Telex 890440

4. Recommendation on an International Mars Mission including Sample Return
(issued September 1986)

The Space Science Committee recognizes the immense scientific, political and technological potential of an unmanned mission to the surface of Mars, to include sample return. It acknowledges the report of the subgroup of the former ESF/NAS Joint Working Group on this subject. Because of the importance of such a programme its ultimate realization is inevitable, and indeed informal discussions have already taken place between members of the space science community in the USA and the USSR about possible international cooperation on such a venture. The SSC recommends that, if such discussions proceed further, Europe should be involved, with a view to a three-way partnership. Europe has much to gain and to contribute from a full technological and scientific involvement in the mission, and has a strong and experienced community interested in the analysis of returned samples. This recommendation is consistent with the Long-term plans of ESA, as expressed in the document Horizon 2000.

J. Geiss
Chairman, Space Science Committee

Universität Bern

Physikalisches Institut

PD Dr. O. Eugster

CH-3012 Bern, Sidlerstrasse 5, Telefon 031 65 86
Telex CH 912 643, Telefax 031 65 44 05

MAR 05 1987

Dr. James L. Gooding
National Aeronautics and
Space Administration
Lyndon B. Johnson Space
Center

Houston, TX 77058

- USA -

February 26, 1987/ip

Dear Dr. Gooding,

In response to your call for input to a Mars sample-science document I send you a paper written in 1979. It has never been published but some parts in it may now be useful for the above mentioned subject. Please refer to pages 56-61. In my opinion, a Mars sample return is highly desirable for all scientists engaged in the planetary materials program.

Thank you for your efforts in this matter.

Sincerely yours,

Otto Eugster

Otto Eugster

PS. I hope to see you at the 18th Lunar and Planetary Science Conference.

605 9 15 7

Jet Propulsion Laboratory
[illegible]
4800 Oak Grove Drive
Pasadena, California 91109
(818) 354-4321

JPL

Refer to: 326/RSG:105:87/TGF:kjb
March 31, 1987

APR 7 1987

Dr. James Gooding
Johnson Space Center
Code SN2
Houston, TX 77058

Dear Dr. Gooding:

Attached is my input to the Mars Sample Science Document. The potential information content of rock coatings is great and, if present on Mars, are well worth collecting. Please let me know if I can provide any additional information.

Sincerely,

Tom Farr

Attachment

12 Mar 87

Mars Sample Return:
Rock Coatings on Mars

APR 7 1987

Tom G. Farr
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

1) Martian history from returned samples.

Rock coatings have proven to be ubiquitous in the arid regions of earth (Farr and Adams, 1984) and useful for inference of paleoclimates (Dorn et al. 1987) and rock exposure age (Dorn, 1983). They also appear to be at least partly formed by algal organisms that become sealed into the coating (Dorn and Oberlander, 1982). Telescopic reflectance spectra indicate that rock coatings may also be present on Mars (McCord, et al. 1982). If sampled, they could prove extremely valuable for piecing together the surface ages and past climates of Mars, as well as being a good location for prospecting for organisms. Knowledge of the composition and thickness of Martian rock coatings would also allow more quantitative interpretation of visible-near infrared spectral reflectance measurements of Mars.

2) Quantities of samples.

Several 1 to 2 cm rock fragments that have been subaerially exposed in a nearly horizontal attitude for long periods of time should be collected as gently as possible. These amounts are necessary to assess the nature (both physical and chemical), thickness, and hetereogeneity of the coatings.

3) Sample degradation.

Temperature and shock will cause the most damage to rock coatings. Thermal effects include dehydration and crystallization of hydrated, poorly crystalline substances. Both the hydration state and the degree of crystallinity are important characteristics to the inference of paleoclimates from the samples. Shock will degrade the sample by causing loss of the coating material. However, it would probably require rather high g-forces to dislodge most terrestrial coatings.

4) Ancillary In-situ measurements.

The most important measurement would be high spectral and spatial resolution visible-near infrared reflectance spectra of subaerially exposed rock surfaces. These measurements should be made at about 10 nm spacings from about 0.4 - 3.0 μm. Alternatively, approximately 10 10 nm bands could be chosen to provide most of the information desired. Results would include determination of the oxidation state of Fe, crystallinity, and coating thickness.

APR 7 1987

References

Dorn, R. I., 1983, Cation-ratio dating: A new rock varnish age-determination technique, Quaternary Research, v. 20, p. 49-73.

Dorn, R. I., M. J. DeNiro, H. O. Ajie, 1987, Isotopic evidence for climatic influence on alluvial-fan development in Death Valley, California, Geology, v. 15, p. 108-110.

Dorn, R. I., and T. M. Oberlander, 1982, Rock varnish, Prog. Phys. Geog., v. 6, p. 317-367.

Farr, T. G. and J. B. Adams, 1984, Rock coatings in Hawaii, Geological Society of America Bulletin, vol. 95, p. 1077-1083.

McCord, T. B., R. B. Singer, B. R. Hawke, J. B. Adams, D. L. Evans, J. W. Head, P. J. Mouginis-Mark, C. M. Pieters, R. L. Huguenin, S. H. Zisk, 1982, Mars: Definition and characterization of global surface units with emphasis on composition, Jour. Geophys. Res., v. 87, p. 10,129-10,148.

APR 13 1987

MAX-PLANCK-INSTITUT FÜR KERNPHYSIK
Prof. H. Fechtig, Tel.: (O)6221-516-211

D-6900 HEIDELBERG 1
Postfach 10 39 80
Saupterchenweg 1 (beim Bierhelder Hof)
Telefon Sammel-Nr. (06221) 5161
Durchwahl (06221) 516
Telex 461666
Telefax (06221) 516540

Dr. James L. Gooding
SN 2
NASA Johnson Space Center

Houston, TX. 77058

USA

7 April 1987/fe

Subject: Call for Input to a Mars Sample Science Document

Reference: Your letter SN2-87-LO84 dtd. Feb. 10, 1987

Dear Dr. Gooding,

In reply to your letter dated February 10th, 1987, concerning the input to a Mars Sample Science document, I would like to inform you of our strong interest in Mars-samples as well as other extraterrestrial samples. In the past we have worked quite a lot on meteorites and we were - and partly still are - involved in the investigation of lunar samples. Interplanetary dust particles are currently analyzed with modern techniques (like PIXE and SIMS, etc.). Furthermore, our institute was heavily involved in the cometary missions to Comet Halley. On Giotto and VeGa we have flown the gas-mass-spectrometer NMS and the dust-mass-spectrometer PIA and PUMA.

I do not intend to respond to your 4 questions. However, let me rather draw your attention to two documents which you did not refer to in your letter:

The first document is from the Solar System Exploration Committee of the NASA Advisory Council, entitled "Planetary Exploration through Year 2000. An Augmented Program". From pages 58 through 101 there are all aspects for a Mars Sample Return described in some detail.

The second document is a European one (copy attached). The former chairman of the Standing Committee for Space Physics of the European Science Foundation, Prof. J. Geiss, has asked me in 1986 to chair a small subcommittee in order to address a European participation in a Mars Sample Return Mission. The subcommittee has produced the enclosed document and discussed it with the Geiss Committee in September 1986. After minor revisions the document has been accepted.

These two documents demonstrate our strong interest in sample return missions in general and in Mars samples in particular.

Sincerely yours,

H. Fechtig

AUG 25 1987

10.08.1987
Moscow

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058 USA.

Dear Dr. Gooding.

Thank you very much for your letters from February 10 and May 27, 1987. I regret that I could not reply because of my long-term trip to Australia.

I am paleontologist. My main scientific interest - early evolution of ecosystems, the most primitive forms of life which dominated on our planet in Precambrian time (before 600 m.y.). Earth in the Precambrian was dissimilar to recent Earth in many aspects. That is why I am interesting by possibility to discover the life on Mars.

In order to determine any forms or traces of life on Mars I would prefer direct methods. I suggest:
1) to take samples of atmosphere at different levels trying simultaneously to concentrate dust particles by rapid pumping the martian air through fine filters or by fixation the particles onto special surfaces covered by glue-like compound. Probably among those

August 10, 1987
Moscow

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058 USA

Dear Dr. Gooding,

Thank you very much for your letters from February 10 and May 27, 1987. I regret that I could not reply because of my long-term trip to Australia.

I am paleontologist. My main scientific interest - early evolution of ecosystems, the most primitive forms of life which dominated on our planet in Precambrian time (before 600 m.y.). Earth in the precambrian was dissimilar to recent Earth in many aspects. That is why I am interested by the possibility to discover the life on Mars.

In order to determine any forms or traces of life on Mars I would prefer direct methods. I suggest:

(1) To take samples of atmosphere at different levels trying simultaneously to concentrate dust particles by rapid pumping the martian air through fine filters or by fixation the particles onto special surfaces covered by glue-like compound. Probably among those

particles we shall find something like bacteria or spore

2) The samples of atmosphere and the dust from different altitude should be preserved hermetically at the same temperature, pressure and light up to the end of mission untill the spacecraft return to the Earth. To prevent "martian infection" of our planet, life-specimens could be studied by specialists on orbital station

3) The specimens of rocks and ice should be transported to the Earth by similar manner, e.g. under conditions they have been collected. The most promising area to collect life-specimens on the surface of Mars is place where liquid water can exist, even temporarily. Important, probably triggering role for primitive martian life can belong to regular day-night change of light. Taking into account harmful influence of UV radiation we should collect samples from the place which is in the shadow, or under surface of dust, sand or ice

4) To detect the presence of life it is not necessarily to collect rock or ice but we can extract microorganisms or any organic compounds by different kinds of liquids (water, alcohol etc). It is possible to use one volume of liquid to wash out microscopic particles or organic

particles we shall find something like bacteria or spore.

(2) The samples of atmosphere and the dust from different altitude should be preserved hermetically at the same temperature, pressure and light up to the end of mission until the spacecraft return to the Earth. To prevent "martian infection" of our planet, life-specimens could be studied by specialists on orbital station.

(3) The specimens of rocks and ice should be transported to the Earth by similar manner, e.g. under conditions they have been collected. The most promising area to collect life-specimens on the surface of Mars is place where liquid water can exist, even temporarily. Important, probable triggering role for primitive martian life can belong to regular day-night change of light. Taking into account harmful influence of UV radiation we should collect samples from the place which is in the shadow, or under surface of dust, sand or ice.

(4) To detect the presence of life it is not necessary to collect rock or ice but we can extract microorganisms or any organic compounds by different kinds of liquids (water, alcohol, etc.). It is possible to use one volume of liquid to wash out microscopic particles or organic

compounds from many volumes of rocks separating particles or organic molecules after each operation.
(5) It is possible to melt ice and to filter liquid to accumulate particles or any molecules in special mechanical or chemical traps.

There are a lot of other ideas but I am afraid all my suggestions looks very naive if not dilettante for those who carry out this martian program professionally. But if you will find something of interest in my letter, please, contact me by mail or directly. From the end of November, 1987 I plan to work at the Center of study of evolution and origin of life (CSEOL) at the University of California, Los Angeles. I am a member of Precambrian Paleobiology Research Group leading by Prof. J. W. Schopf. My mailing address during November 1987 - February 1988: CSEOL-PPRG, Geology Building, University of California, Los Angeles; Los Angeles, CA 90024. Lab. phone: (213) 825-1170.

Kind regards,

Sincerely

Mikhail A. Fedonkin

plattsburgh
STATE UNIVERSITY OF NEW YORK

DEPARTMENT OF PHYSICS
(518) 564-3156
PLATTSBURGH, NEW YORK 12901

August 24, 1987

Dear Jim:

Attached are my estimates for the survival of Cosmic Dust on Mars. As expected, much larger particles are expected to survive unaltered on Mars entry than on earth. This is mostly due to the lower Martian escape velocity permitting particles to enter with a lower minimum velocity. Generally it appears that particles 20 times larger in diameter will be heated to the same temperature as their earth counterparts. From the point of recovery of cosmic dust this may be significant since both Herb Zook and I have suggested that asteroidal particles are likely to contribute a large fraction of the particles below 100 um in diameter (essentially the largest to survive earth entry unmelted), but that larger asteroidal particles are likely to be fragmented by collisions before Poynting-Robertson drag perturbs them out of the belt. Thus particles larger than 100 um are likely to sample a different source than the smaller particles recovered on earth, most likely a cometary source.

Cosmic dust on Mars can also serve as a direct measurement of the planetary erosion rate. For this the bulk concentration of dust in the soil samples could be established (presumably by trace elements, as Anders et.al. did for the Lunar soils), and the dust infall rate independently calibrated from micrometeorite detectors (presumably on the orbiter).

I haven't had a chance to put these comments in as good a format as I had hoped, but I think the assumptions and methods have been clearly defined in the attached document. If you have any comments or questions, I'll be here through this Friday. I'll try to organize my comments more clearly once I return to Plattsburgh.

Sincerely,

George Flynn

An Equal Opportunity/Affirmative Action Employer

COSMIC DUST ON MARS

George J. Flynn

DIRECT COLLECTION

Cosmic dust particles collected from the stratosphere of the earth consist of relatively unmetamorphosed materials, suggesting they are more primitive than any known meteorites (Brownlee, 1985; Fraundorf, P. et.al, 1982). Clayton (1987) has even suggested these particles may contain remnant interstellar material. Despite their small size and the difficulties associated with their collection and analysis these particles are being collected and studied because they serve as our best probes of early solar system processes, and possibly pre-solar processes. They will continue to do so until their source(s) are identified, and samples are returned to earth from those sources.

Only the smallest particles collected from the earth's stratosphere are likely to preserve their original mineralogy and texture. Standford (1986) has shown the layer-lattice silicate class of particles undergo alterations to their mineralogy in the temperature range of 500 to 700°C. In meteorites, loss of zinc is known to occur at 600°C (Ref...). Models of atmospheric entry heating suggest that a majority of particles larger than 10 um diameter are likely to experience temperatures higher than 600°C on entry to earth's atmosphere (Fraundorf, 1980). The average heating for an isotropic flux of micrometeorites of a given size, shape and density depends on two factors: the scale height of the atmosphere in the stopping region, and the atmospheric entry velocity. This latter factor depends not only on the space distribution of velocity but also on the gravitational acceleration near the planet. The ideal collection site would be a moon or planet with low mass, to provide minimal gravitational acceleration, and sufficient atmosphere to decelerate the particles. Mars, with a mass of only 10% that of earth and sufficient atmospheric density for particle deceleration, appears to be the most favorable site in the solar system for collection of this primitive material in unaltered form (except, of course, for direct sampling on the surfaces of the cosmic dust parent bodies).

Three types of meteoritic material should be found on Mars:

1) micrometeorites, which survive atmospheric entry unmelted and should initially fall more or less uniformly of the planet's surface,

2) debris from crater forming bodies, which by analogy to terrestrial and lunar craters would be expected to be concentrated in the crater ejecta blankets except for the biggest cratering events, which by analogy to the C-T event on earth may produce planet-wide fallout),

3) debris from an early intense bombardment, which in many areas of the planet may now be incorporated into rocks due to planetary geological activity.

Flux determinations at the earth and the moon indicate that most of the meteoritic mass is concentrated in a very narrow mass range. Seventy-five percent of the total incident mass is in particles from 10^{-6} to 10^{-2} gram mass range (Hughes, 197? in Cosmic Dust). Density estimates based on meteor deceleration in the earth's atmosphere suggest a mean density of 0.8 gm/cm^3 for particles in this mass range (Hughes cites Viraini). With this density estimate, the 10^{-6} to 10^{-2} gram mass range corresponds to particle sizes from 67 um to 1440 um in radius. Fraundorf's (198?) calculations suggest that virtually none of this material will survive earth atmospheric entry unaltered. This is consistent with the discovery of an abundance of melted spheres of extraterrestrial origin but few unmelted particles in this size range in the Greenland samples.

Thus on earth we have no way to sample, unaltered, those particles which make up the bulk of the mass flux. There is good reason to believe these particles may come from different sources, and thus might be different in composition, from the smaller micrometeorites recovered from the stratosphere. The main asteroid belt is a plasuable source for many micrometeorites smaller than about 100 um in diameter. Infrared Astronomy Satellite detection of major dust bands associated with the main belt confirm an abundance of dust in that region (low, et,al., 198?). Poynting-Robertson drag will remove small particles from the belt, causing them to spiral towards the sun, and making earth collection possible. The catastrophic collision lifetimes of particles larger than about 100 um in the main belt appear to be shorter than the PR lifetimes. Thus dust larger than 100 um is likely to be fragmented by collision before it can leave the belt. See Flynn, 1987 or Zook and McKay, 1986 for a discussion of this point. This dust larger than about 100 um collected at earth or mars is less likely to include a significant asteroidal component than is dust in the smaller size range. Because of the earth collection efficiency for dust with low relative velocity, even a small interplanetary component of asteroidal dust will be enhanced relative to higher velocity cometary dust, producing near-earth collections dominated by the asteroidal component. (See, Flynn, Near Earth Enhancement of Asteroidal over Cometary Dust).

Assuming the meteorite mass-frequency distribution is similar at Mars, the Martial mass flux would also be dominated by particles in the 10^{-6} to 10^{-2} gram range. (These particles are large enough that calculations for asteroid belt survival indicate they would be destroyed by catastrophic collisions before being removed from the belt by PR drag. Thus, although asteroids are a very likely source for the stratospheric cosmic dust below 50 um in radius (Flynn, 1987, Zook and McKay, 1986) these larger particles are very likely from comets. If they survive Martian atmospheric entry, then Mars collection would be a source of a NEW type of extraterrestrial material -- comet dust -- which is unlikely to survive earth entry unaltered.)

We can assess the likelihood of Mars survival if we have an estimate of the entry velocity. On earth, particles in this mass range are detected on atmospheric entry as radar meteors. A velocity distribution for their entry was derived, after correction for instrumental bias, by Southworth and Sekenina (19??). Their distribution shows a considerable fraction of the radar meteors entering the atmosphere with velocities within a few km/sec of earth escape velocity (the minimum direct entry velocity). This indicates that a substantial fraction of the interplanetary dust has rather low relative velocity prior to the collection process. Essentially nothing is known about the velocity distribution of micrometeorites near Mars. In the absence of any other data, the S&S distribution corrected back to interplanetary space by removing earth gravitational acceleration will be assumed for Mars. This velocity distribution then must be corrected to Mars atmospheric entry by adding in the Mars gravitational acceleration. The minimum entry velocity would then be Mars escape velocity (5 km/s), with a significant fraction of the particles within a few km/s of this value.

In Table 1 the peak temperature reached on normal entry (the most unfavorable entry condition) is shown for particles at earth and at Mars, each entering with the escape velocity appropriate for that planet. For any given particle entering at planetary escape velocity, the peak temperature reached on Mars for normal incidence will be 0.55 times that for Earth because of the difference in the escape velocity as well as a small difference in the scale height. Where on earth only particles up to about 25 um radius can survive normal incidence entry unaltered the corresponding figure for Mars is almost 500 um. Particles much large can, of course, survive entry under gazing incidence. Thus a large fraction (estimate how much of the total meteoritic mass (dominated by particles from 67 to 1440 um radius) arriving at Mars will enter the atmosphere essentially unaltered.

The actual Martian mass flux will, most likely, be different from that at earth. Hughes (197? in Cosmic Dust) estimates the total mass flux at earth at 16,000 tons/year, in the 10^{-6} to 10^{-2} gram range. Again, measurements of the flux in this size range at Mars are not available. We might, however, obtain an estimate of the flux at Mars by correcting the earth flux for the ratio of

gravitational enhancements at the two planets and the roughly 1/r dependence of PR drag orbital concentrations.

Doing this the flux at Mars in the 10^{-6} to 10^{-2} gram range would be about 0.09 that at earth (REASONING BELOW)

---

grav. corr. at earth enhancement is measured as 2.6 this corresponds, for a single velocity source a velocity of 8.8 km/sec would be required to produce this enhancement. On mars an 8.8 km/s particle would experience an enhancement of 1.3. Thus the enhancement factor would reduce the Mars flux to 0.5 that of earth. But PR drag also concentrates particles as they spiral inward. Mars at 1.5 AU would thus be expected to experience a flux of 1/1.5 = .67 that at earth. Combining this with the smaller gravitational enhancement at mars leads to an estimated flux of .33 times the earth flux. This must then be corrected for the smaller planetary cross section Rmars = 0.53 Rearth giving a cross section 0.28 x earth. Overall then the martial infalling mass would be 0.09 that of earth.

Thus we expect a martial flux in the micrometeorite size range of 1100 tons/year. For a Martian surface area of 1.4×10^{14} m^2, this is sufficient to provide a covering of 7.9×10^{-10} grams/cm^2-year. If the material is density 1 gm/cc this corresponds to a coating of 8×10^{-10} cm/year. Over the age of the planet this would correspond to a planet wide layer 3 to 4 cm thick. This material would be diluted by the planetary regolith production.

This estimate for the influx of meteoritic material on Mars is considerably lower than suggested by others for the influx of much larger, crater producing objects. Anders and Arnold (1965) suggest that the meteoritic input on Mars is 25 times higher than that on the moon. If the micrometeorites are similarly enhanced at Mars, rather than depleted relative to earth as I have suggested, the thickness of the meteoritic dust layer as well as the concentration of the meteoritic component for any particular regolith thickness would be increased.

On the moon the micrometeorite impact process provides an automatic dilution mechanism.....

On mars the majority of the mass influx arrives at the surface so gently that microcraters are not produced. However there are other surface processes that can produce regolith. Estimates of the thickness of the Martian regolith vary from only twice as great as the lunar regolith (Soderbloom et.al., 1974) to as deep as 2 km (Fanale, 1976). Since the lunar regolith is estimated as 5 m deep (REF ?). If we dilute the meteoritic material into a Martial regolith only 10 m deep, approximately 0.4% of the Martian soil will be meteoritic (very comparable to the 1 to 2% seen on the moon by Anders, 19??). If, however, the Martial regolith is 2 km deep, then only 5×10^{-5} of the regolith would be meteoritic.

We can then assess the likelihood of recovery of micrometeorites from the martial soil. Since the mass flux (at earth) is roughly flat over the 10^{-6} to 10^{-2} gram range (Hughes, 197?), about 25% of the total flux in that range will occur within each decade of mass. Thus we can estimate the number of micrometeorites of a given size (where I assume all the meteorites within a given mass decade have a mass corresponding to 2x(smallest mass in the decade)) by:

$$\text{Number} = \frac{0.25\ (\text{Concentration of Meteorite Material in Soil})}{2x(\text{smallest mass in the decade})}$$

For the most favorable case, a 0.4% meteoritic content, we would then expect 50,000 micrometeorites of 90 um radius in a 100 gram soil sample. Even in the least favorable case of 0.5×10^{-5} dilution, 100 grams of soil would contain 60 such micrometeorites. The expected numbers decrease with increasing size, however, in the favorable cases, recovery of particles as large as 600 um in radius should be possible. The expected particle abundances for meteoritic concentrations covering the range calculated from the regolith thicknesses is given in Table II.

Within the limits of present technology, except for the case of the most extreme enrichment such a search would be extremely tedious. However, by the time of the sample return mission, it is not difficult to imagine an automated EDX system which would analyze numerous dispersed particles and record the locations of those giving certain characteristic spectra (say "chondritic"). Assuming an entire 3 gram sample could be completed in 20 seconds, the entire sample could be catalogued in 1 machine year. With the possibility of recovering large micrometeorites, possibly from different sources than in the earth stratospheric collection, such an allocation of instrument time seems not to be unreasonable.

MARTIAN SOIL CONTAMINATION

If the soil is enriched in meteoritic material at a level anywhere near the lunar enrichment, which is consistent with the thinner regolith estimates, then any bulk soil analyses are likely to be contaminated. In the major elements, the most likely contaminations would be S and C. However both of these appear to be highly enriched on the Martian surface. If we reject the hypothesis that almost all the regolith is meteoritic (which would be a hypothesis consistent with the high S and C) then only minor and trace

element concentrations are likely to be significantly altered. Unfortunately, due to the existence of global dust transport mechanisms, it seems unlikely that sufficiently diverse rock samples will be obtained on the first Martial sample return mission to derive an expected soil composition from mixtures of the surface rocks. Even on the moon, where dust transport is more localized and the Apollo sites were well sampled, the derivation of a meteoritic component by subtraction of the mean composition of the local rock from the mean soil still required the postulation of an "exotic" unsampled rock at the Apollo ?? site (Anders, ????).

Actually little is known about either the chemical composition or mineralogy of the micrometeorites in the 10^{-6} to 10^{-2} gram range, which make up most of the meteoritic mass arriving at the earth and presumably at mars as well. These particles are too large to be included in the stratospheric collections on earth (though perhaps with large area collectors and long collection durations some, at the lowest end of the mass range may be recovered) but they are too small to be included in the meteorite collections. Perhaps the most direct measurement of their chemistry comes from the meteoritic contamination of the lunar soil, however that analysis provided data on only a few trace elements (Anders, ????). The assumption they are like CI carbonaceous chondrites is plausible, but unproven. Since these particles constitute the bulk of the extraterrestrial material arriving at earth, an actual analysis (see Direct Collection) would be of importance.

However on the assumption they are like the CI meteorites in the concentration and type of their organic compounds, the Viking Lander gas chromatograph-mass spectrometer placed some limits on the CI type meteoritic material on Mars. Perhaps the most relevant limits come from aromatic hydrocarbons such as naphthalene which have now been detected in both the cosmic dust particles (Allamandola, L. J., et.al, 1987) and in CI meteorites (REF.). The detection limit for naphthalene in the Viking soil analyses are reported as < 0.5 ppb at the Viking I lander site and < 0.015 ppb at the Viking II lander site (Biemann, et.al., 1977). The laboratory version of the Viking gas chromatograph - mass spectrometer detected napthalene at the 1 ppm level in carbonaceous chondrites (Biemann et.al., 1977). Combining this result with the upper limit at the Viking II lander site gives an upper limit of the meteoritic component at that site of 1.5×10^{-5}, consistent with the thickest regolith suggestions. However site to site variations might be expected due to non-uniform distribution of planetary dust. Also the destruction of organic compounds in the harsh, ultraviolet rich martian surface cannot be excluded. Thus organic content may not be an appropriate way to determine meteoritic influx.

Measurement of the Planetary Erosion Rate

If the micrometeorite flux at Mars is established, presumably by a micrometeorite detector on an orbiter, than the concentration of meteoritic material in the regolith can be used to infer a planetary dust production (or erosion) rate. Analysis of several, preferably widely spaced samples, would be desirable to establish a mean meteoritic concentration. Sufficient surface rock analyses would be required so that an expected planetary dust composition can be established. Provided the planetary composition is sufficiently distinct from the meteoritic composition, the meteoritic concentration can then be derived using the subtraction technique which Anders et.al. (1973) employed in their lunar analysis. It seems, with care in selecting the rock and soil samples to be returned, this part of the analysis could be accomplished within the planned sample return constraints. The analysis techniques would likely be non-destructive, since many of the elements used by Anders et.al. (1973) in their lunar analyses can now be determined by Synchrotron X-ray Fluorescence, preserving the samples for other investigations. However, key to the derivation of an erosion rate by this technique is the requirement for a determination of the micrometeorite flux at Mars. Thus the inclusion of a micrometeorite detector on a Mars orbiter seems to be required. The required size (and mass) of the instrument would depend on the total operational lifetime of the orbiter and the desired mass limit of the determination.

REFERENCES

Anders, E., Ganapathy, R., Krahenbuhl, U, and Morgan, J.W. (1973) Meteoritic Material on the Moon. Moon, 8, 3-24. Biemann, K., Oro, J., Toulmin, P. III, Orgel, L.E., Nier, A.O, Anderson, D.M., Simmonds, P.G., Flory, D., Diaz, A.V., Rushneck, D.R., Biller, J.E., and Lafleur, A.L. (1977) The Search for Organic Substances and Inorganic Volatile Compounds in the Surface of Mars. .J. Geophys. Res., 82, 4641-4658.

Brownlee, D.E., Cosmic Dust: Collection and Research, Ann. Rev. Earth Planet. Sci., 13, 147-173.

Clayton, D.E. (1987)

Fraundorf, P., Brownlee, D.E., and Walker, R.M., (1982), Laboratory Studies of Interplanetary Dust, in Comets, ed. L. Wilkening, U. of Arizona Press, Tuscon, 383-409.

Sandford, S.A. (1986) LPSC heating abstract

Table I

Peak Temperature Reached on Atmospheric Entry

For Particles Entering With Planetary Escape Velocity

At Normal Incidence on Mars and Earth

(Particle density = 1 gm/cm^3)

Particle Radius	T_{max} Earth	T_{max} Mars
10 um	955 K	492 K
25 um		
50 um	1428 K	736 K
100 um	1698 K	876 K
250 um	2136 K	1101 K
500 um	2540 K	1309 K
750 um	2811 K	1449 K
1000 um	3020 K	1557 K

Table II

Number of Micrometeorites Per 100 gram Martian Soil Sample

Meteoritic Concentration	N > 10^{-6}g (90 um)	N > 10^{-5}g (200 um)	N 10^{-4}g (400 um)	N > 10^{-3}g (800 um)
0.01	125,000	12,500	1,250	125
0.001	12,500	1,250	125	12
0.0001	1,250	125	12	1
0.00001	125	12	1	0

Mars Sample Science

Kinds of sample

From the geological view point, samples returned from the surface of Mars can provide two fundamentally different kinds of data: compositional and textural. Each requires a different kind of sampling strategy

Compositional data allow one to address some fairly obvious but still fundamental questions. By measuring appropriate isotopic ratios etc. etc., one can determine the magmatic evolution of samples, place constraints on the source regions of magmas, and investigate problems such as the extent of interaction between magmas and putative Martian crustal rocks. Compositional data would also provide important data on the Mars surface environment: weathering processes, etc. The samples required to provide such compositional data are relatively simple to collect: small clasts or soil samples collected by a Viking - like sampling arm could be used. Individual clasts picked off the surface after imaging studies could be used to extend the range of rock compositions studied. Valuable data can be obtained from very small samples, even a few grams.

Textural data provide information about the physical processes of emplacement of deposits, and are therefore potentially rich sources of information about the Mars environment. They enable, for example, identification of impact ejecta and different kinds of aeolian deposit, differentiation between pyroclastic flow and fall deposits, and they can provide constraints on the different kinds of mass wasting and erosional processes taking place.

Data of this kind, however, require that samples be preserved in context and large samples are therefore required. Minimum requirements would probably be comparable with the drill cores recovered from the lunar surface; two of three centimetres in diameter and of the order of 1 metre in length. Such samples clearly present sampling problems of much greater complexity that those collected for purely compositional studies.

Scientific goals

Samples collected from the surface of Mars should be aimed at providing "ground truth" for remote sensing studies.

The geology of Mars as we know it today consists of small areas whose nature is obvious, and much larger areas whose nature is conjectural or speculative. These require different sampling strategies.

In known areas, such as young volcanic terrains, very specific questions can be addressed, such as the age and composition of the youngest materials erupted, the age and compositions of the predominant lava types at Tera. This requires identification from images of carefully selected small sites, perhaps as small as individual lava flows, or sites high on the slopes of volcanic edifices.

In unknown areas, problematic deposits are generally extremely extensive, covering large areas of surface uniformally, for example the extensive deposits of Amazonis Planitia, which have been variously mapped as ignimbrites or as polar deposits. In such cases, precise site selection is relatively unimportant, as innumerable sites may be capable of supplying the same formation.

In any case, it will be essential to ensure that the sample returned is genuinely representative of the unit studied, and is not a surface deposit of ejecta or aeolian accumulation. To eliminate such ambiguities, samples should preferably be obtained from steep sections, or sites undergoing active erosion, but these present formidable difficulties to sampling probes. A satisfactory strategy might be to sample fans derived from mass wasting of deposits studied, but this will provide compositional data only.

Any Mars surface sampling robot will be restricted to sampling horizontal surfaces, vertical sections such as are routinely sought by earth geologists are likely to be inaccessible to surface roving vehicles. Sampling of flat or gently sloping surfaces means that the surfaces may be covered with materials derived from elsewhere, by impact ejection, fluvial or aeolian transportation, and the surface itself is likely to be a regolith surface rather than in situ rock. A further complicating factor is that in areas of aeolian erosion mechanical fraction processes will have been operating over long periods, concentrating dense, resistant particles on the surface, and winnowing away lighter, finer grained materials. Studies of some terrestrial samples (e.g.

ORIGINAL PAGE IS
OF POOR QUALITY

ignimbrites in arid areas subjected to aeolian erosion) show that the tens of metres of friable materials may be blown away, leaving surface concentrations of dense fragments which are entirely unrepresentative of the original unit.

Some of these problems can be helped by targeting sampling areas on Ealus cones or alluvial fans immediately downslope from topographically higher areas (preferably cliffs or scarps) which are undergoing active or recent weathering. In these circumstances, some of the uncertainties concerning the provence of analysed materials can be minimised. Studies of terrestrial counterparts should be undertaken to determine the best sampling strategies for alluvial fans which themselves sample large elevated masses. Some interesting work along these lines has already been carried out using Landsat Thematic Mapper data, for example, a long prominent faults scarps in California and Nevada.

JUN 9 1987

Department of Earth Sciences
The Open University
Walton Hall, Milton Keynes, MK7 6AA
England

Telephone Milton Keynes (0908) 653012

THE OPEN UNIVERSITY

With the compliments of Department of Earth Sciences
From P. W. FRANCIS

JUN 22 1987

Ktech CORP.
901 PENNSYLVANIA AVENUE, N.E. / ALBUQUERQUE, NEW MEXICO 87110 / (505) 268-3379

18 June 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding

In response to your request for input to the Mars sample-science document, I submit the following thoughts related to the microstructure of Martian soils.

The microstructure of soils has received considerable study relative to terrestrial engineering problems. In particular, it is possible to make deductions about the load-bearing capabilities of soils by knowing details of the structure. It is also possible to infer some things about the environment in which the soil has formed or been modified. Examples of this latter type of information include identification of freeze-thaw cycles and interpretation of the sequence of events involving changes of water content and deformation. Therefore, it could be extremely useful to have samples returned from Mars which have not been subjected to accelerations and stresses great enough to cause serious damage to microstructural features. Maximum stresses at such limits might be well below 1 KPa, especially in "loose" material.

Another possible application of soil microstructure studies on returned Martian soil may be illustrated by a sample recovered recently from the vicinity of an underground nuclear test. This sample consisted of unconsolidated sand (75%) and bentonite (25%) and was loaded to about 250 MPa for tens of microseconds. In view of the suggestions by yourself and others that montronite may be a constituent of the Martian regolith, the inclusion of bentonite in this sample is particularly significant. This is a loading regime which should be representative of much of the ejecta from impact craters of about 100 m diameter. The recovered material was quite competent, requiring chiseling to remove a container from the center of a 0.5 m sample. This will be a very well documented piece of "instant rock". Polished thin sections are now being prepared, and they will be analysed soon. In particular, we will look for microstructural features which might be used to provide estimates of in situ stresses from impact events in comparable material. If such features are found, care should be taken that samples recovered from Mars are done in such a way as to preserve similar features should they be there. At this writing, I can not say what conditions those might be.

Ktech CORP.

A third item to be mentioned is that there is a considerable body of literature (much of it from the soil mechanics community in Great Britain) on methods of impregnating samples bearing large fractions of smectites. The difficulties relate to changes in the structure of the soil during drying and subsequent rewetting. These problems are worst with water but also exist to some extent even with epoxies. Of interest to a Mars sample return mission is the question, "Can ways be found to impregnate unconsolidated martian soils in situ which will preserve the essential details of their microstructure?" I sent your original letter to Drs. Peter Smart, Ken Collins and Kieth Tovey for comment suggesting that they contact you directly. They are quite knowledgable on subjects relating to studies of the microstructure of fine-grained soils.

I realize these issues are rather far removed from the sorts usually addressed by the planetary community, but I feel that they should perhaps get some consideration in design of a Mars sample return mission to assure that useful information is not heedlessly thrown away. If man is ever to set foot on Mars, the engineering characteristics of the surface will be literally vital.

I hope these comments are helpful to you. If you have any questions please feel free to call me.

Sincerely yours,

Edward S. Gaffney,
Senior Scientist

JUN 2 1987

MEMORANDUM

June 1, 1987

To: James L. Gooding, SN2

From: Everett K. Gibson, SN4

Subject: Imputs for Mars Sample-Science Document

As one of the principle authors of the 1974 NASA/JSC report I am happy to say that most of the opinions expressed in that document are still valid in 1987.

Response to your specific questions follows:

(1) Aspects of Martian history addressable by analysis of returned sample: In addition to the information given in the 1974 report, specific comparisons with possible Martian meteorites can be made (i.e. SNC meteorites). The unusual response of the Martian surface materials to the experiments carried out in association with the Viking Life Sciences Experiments. Returned samples can address the question of whether the Martian surface at the V1 and/or V2 sites are evaporites.

(2) Types of samples to be returned: Bulk soils (fines and pebbles) from multiple sites, rock chips (with surface alterations and fresh surfaces to see weathering processes), core samples from multiple sites, atmosphere sample, separate sample for the Life Sciences Experiments (give them one sample and "make-do with it"-Based upon the Apollo Lunar Receiving Laboratory experience, they cannot get enough material to "Do their thing with it". Quantities depend upon mission constraints. However, a suitable breakout might be the following: FOR A 5 KG Sample. Soils and associated pebbles 40%, cores 35%, rocklets and chips 25%.
Information given in the 1974 report is still valid as to how to collect and store the sample (i.e. material, canisters, seals, etc.) prior to return to Earth.

(3) Degree of degration: No greater than the harsh conditions given in the 1974 report. For delicate evaporite samples with their secondary minerals care should be made to not shake-up the sample too badly. Do not mix anything with the sample.

(4) <u>In situ</u> measurements in association with collected samples: Excellent photo-documentation of collected samples-both pre- and post-documentation of sampling site in relation to local terrain. Bulk chemical composition measurements via EDX type measurement (assists in characterization of returned material). I personally feel that on-board analysis instrumentation should be minimized and the corresponding weight made up with increased returned samples.

Everett K. Gibson

Everett K. Gibson, Jr.

University of Delaware

COLLEGE OF ARTS & SCIENCE
DEPARTMENT OF GEOLOGY
101 PENNY HALL
NEWARK, DELAWARE 19716

(302) 451-2569

March 25, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

In response to your letter of Feb. 10, 1987, I have the following responses to your questions regarding my special interest and expertise in reference to a possible Mars sample return:

1) Analysis of glass particles in the Martian soil can be used to determine the relative abundance of impact vs. volcanism, the average composition of the Martian soil, the kind(s) of Martian volcanism, and weathering effects. Studies of Martian surface features have indicated that impact and volcanism have played an important role in shaping the surface of the planet. Age dating of the glass particles would help determine the timing of these events. In addition, the age of the oldest unweathered glass particles might indicate when the Martian surface became "dry"--i.e., free of liquid water.

2) One gram samples taken at as many different sites as possible would be most useful for such a study. A core sample would be useful for working out the geologic history of an area--i.e., rate of volcanism and impact cratering versus time.

3) The samples should not be heated to above 100°C for any length of time and should not be subjected to shock pressures above 20 kbar.

4) It would be useful to have photographs of the sampling site before and after sampling.

If you need additional information, please feel free to call or write.

Sincerely yours,

Billy P. Glass

bd

तार Gram TECHNOLOGY टेलेक्स Telex 0325-288 दूरभाष Phone 243153

भारतीय प्रौद्योगिकी संस्थान कानपुर
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
रसायन विभाग
DEPARTMENT OF CHEMISTRY

Prof. P.S. Goel

डाकघर आई० आई० टी० कानपुर-208 016
P O I I T Kanpur 208 016 India.

Dr. James L. Gooding
SN2
NASA Johnson Space Centre
Houston TX 77058
U.S.A.

Chem/PSG/ ~~1987~~ 1988
April 9, 1987

Dear Dr. Gooding:

This is a short response to your Circular No. SN2-87-L084 dt. Feb. 10, 1987 regarding the analysis of geologic samples collected from Mars.

In my laboratory at this Institute we have been actively and extensively carrying out investigations on the isotopic compositions of Hg & Os in meteorites. We have used neutron activation analysis method to measure ratios of two isotopes of these elements in many samples. We have found, to our surprise, that sometime huge isotopic anomalies are seen. The method is far more sensitive then the mass spectrometric techniques that are available today. We can measure isotopic ratios in 100 mg samples containing the elements of interest in the ppb range.

I would very strongly suggest that the valuable samples from Mars should be made available for these investigations. Undegraded samples would be needed for Hg work because this element is highly volatile. One can combine the proposed studies with some other experiments so that the non-volatiles in the heated residues, can be concurrently measured.

Should this brief preliminary proposal interest NASA I shall be happy to write a detailed proposal with supporting documents.

With best regards,

Yours sincerely,

PSGoel
(P.S. Goel)
Professor and Head

Copy to:
Dr. M.K. Tiwari
Department of Space
ISRO Headquarters,
Cauvery Bhavan
Kempegowda Road
Bangalore-560009

ORIGINAL PAGE IS
OF POOR QUALITY

Andrew M. Gombos, Jr.
Exxon Production Research Co.
P.O. Box 2189
Houston, TX 77001

June 8, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

In response to your request about Mars sample analysis, I can only suggest, as a micropaleontologist, that a portion of the sample(s) be reserved for analysis by standard micropaleontological techniques for possible traces of fossil life. The standard proceedures would involve examination for siliceous and calcareous microfossils and for organic walled microfossils.

If, and when, the time comes for such studies to be made, I suggest you contact the biostratigraphy group leader here at Exxon Production Research Co. for guidelines as to how the samples could be examined. We might as well look for fossils in the samples, because they may very possibly be the only evidence of life left on Mars. It is important that experienced micropaleontologists do the looking, because important fossils or traces of fossils can be overlooked by the untrained eye. Thank you for your consideration.

Sincerely,

Dr. Andrew M. Gombos, Jr.

ARIZONA STATE
UNIVERSITY — TEMPE, ARIZONA 85287-1404

DEPARTMENT OF GEOLOGY
PLANETARY GEOLOGY GROUP (602) 965-7029

June 24, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

In response to your memo of February 10, here are my thoughts. Sorry to have taken so long.

1. What aspects of martian history can be uniquely (or best) addressed by direct analysis of samples returned to Earth?

   To provide age-dates which, in turn, provide calibrations for impact crater frequencies. Photogeologically, this enables other surfaces on Mars to be "dated".

2. What types and quantities of samples are needed to support the analyses related to (1)?

   Samples for as wide a range of surfaces as possible--at least for the **oldest** crustal materials and the youngest volcanic rocks.

3. General.

   Must ensure that, first, sites be selected to provide a wide variety of materials addressing a wide variety of questions (e.g., magmatic history), but second, in which the samples are unambiguous in their origin. These two considerations are in conflict to some degree, and can be satisfied only by very careful selection of the sampling site.

Very truly yours,

Ronald Greeley
Chairman and Professor

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

DEPARTMENT OF EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES
Telex 92 1473

2 July 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear James,

I've taken a moment to give you some responses to your questions:

1) First order questions of great importance in studying a new planetary body concern the evolution and development of the crust/mantle system. These questions are best answered by coordinated geochemical, petrologic and isotopic studies on a suite of hand specimens. There should be samples of Martian mantle-derived basalt, and samples of crustal igneous rocks. Based on our lunar sample experience an incredible amount of first order information can be obtained from a limited data base built around detailed geochemical studies of samples from the crust/mantle reservoirs. Also, based on the lunar experience there is no substitute for a couple of rocks as the goal of any sample return mission. If some soil comes along as well, that's fine. It (soil) brings information on surface processes, and there is much to be learned from soil that will be of importance and of scientific interest.

2) The goal of a sample return mission would be to return several 0.25 to 0.5 kg-sized rocks. Several separate locations on the crustal and flood basalt terrains should be chosen, a minimum of 2 or 3 missions to each terrain.

3) Are you talking about degradation produced during sampling? If so, the samples should be returned in as close to the as-sampled condition as possible.

4) In-situ geophysical measurements are our absolute necessity. Probably some measurements that relate to the types and physical state of volatiles in the soil would be desirable.

My own interest in geochemical studies of planetary bodies shows through in the brief responses that I've made above. I'm not a soils/surface

process person, and I've no axe to grind with science related to the study of these materials. The soils will provide a rich source of information on surface processes, evolution of the martian atmosphere, etc.

However, one can't do effective first order studies on the origin of a planetary body using soils. Rock samples are required, and these rocks should be returned from several locations on the planet's surface. This limited ground truth from sample return should be supplemented with remote-sensing data obtained by an orbiting spacecraft.

Sincerely,

Tim Grove

Timothy L. Grove
Assoc. Professor of Petrology

TG/sl

WASHINGTON UNIVERSITY IN ST LOUIS

Department of Earth and Planetary Sciences

April 20, 1987

Dr. James L. Gooding
Code SN-2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

This note is in response to your interesting "Dear Colleague" letter of February 20. I wish to confirm the interest and support of my research group for the acquisition of samples from Mars for study in terrestrial laboratories. I have now found time to review the 1974 JSC document on characterization of acquired Martian samples and effects of biological sterilization; on the whole, that document remains a reasonable, albeit incomplete, summary of both the geoscientific reasons for obtaining Martian samples and the geoscientific reasons why it would be far better not to sterilize them. Of course, there are equally compelling biological reasons not to sterilize the samples. Techniques have developed beyond those available at the time of the 1974 study, and our knowledge of Mars has improved somewhat from the Viking missions, although disappointingly little from the point of view of igneous and sedimentary geochemistry.

Rather than provide a rehash of old information, we state some points of emphasis in this letter. Should the expertise or analytical capabilities that we have in our laboratory be of further use in your considerations or in determining some effect of sterilization or some capability to make measurements, please let us know. We would like to involve ourselves in developing new measurement techniques for sedimentary materials we can expect on Mars but not on the Moon. Several of my young faculty colleagues here are also interested in this possibility.

1. My research group and I have two major interests in studying Martian samples; these are as follows: a) Determining the nature of the planet's igneous differentiation and its weathering and sedimentation, in the context of comparative planetology of silicate bodies, and b) understanding the detailed nature of the Martian surface as a place on which to live and find resources.

2. The importance of acquired samples for geoscientific study has not lessened since the 1974 study, despite some further information about Mars and despite the strong arguments by some of our colleagues that everything should be done by remote analysis. (Use of the term "returned samples" has always bothered me, since the samples are being acquired, not returned.) In my opinion, the Viking missions, while

Washington University
Campus Box 1169
St. Louis, Missouri 63130
(314) 889-5610

WASHINGTON UNIVERSITY IN ST LOUIS

Department of Earth and Planetary Sciences

technologically impressive, were a first order demonstration of how difficult and expensive it is to carry out remotely experiments that would have been trivial in a terrestrial laboratory and that were exceedingly limited in their scope and in their abilities to adjust to unexpected conditions of materials, or to make changes in response to results from initial measurements, or to carry out newly designed, second generation experiments. Partly because of their emphasis on biological information, they left use with very little characterization of the basic material of the local Martian regolith, surely an error even from the point of view of good biology.

Acquisition of Martian samples should be aided and accompanied by in situ measurements. However, the ability to apply a wide variety of measurement techniques, to respond to the actual nature of the materials being analyzed as the first information about them develops, the ability to call on techniques whose value was unanticipated, and the ability to devise and carry out second and subsequent generation experiments cannot be matched by remote techniques. No planning for exploration of Mars should be allowed to assume that remote sensing or in situ experimentation or measurement are sufficient to provide accurate characterization of the Martian regolith and geoscientific history.

3. Certain measurements are better made in situ than on acquired material. The composition of the Martian atmosphere is one example. The atmosphere is probably in steady state equilibrium with the regolith on the one hand and with the radiation environment on the other, and thus it may not be possible to preserve a representative sample of it. It will, of course, have different compositions at higher altitudes, etc., but here we are concerned with the near-surface atmosphere. Important information about the atmosphere should be and readily can be determined by in situ measurement, both at ground level and during spacecraft descent. Longer-term monitoring for changes in minor and trace components is important if reactions with the regolith and perhaps with the radiation environment are to be discovered and understood. Important changes in the nature of the gas phase may occur during dust storms.

In addition, one or more isolated (regolith-free) atmospheric samples should be acquired for detailed laboratory study of trace constituents, partly for comparison with in situ measurements, both as a check on in situ measurements and to determine what has been lost or changed by chemical reaction, and partly for precision of isotopic measurement. There should be an unsolved regolith sample taken in conjunction with the atmospheric sample; this sample ought to have a substantial amount of atmosphere contained with it. Perhaps the best way to handle this sample is to get it as cold as possible, to slow down any chemical reactions, then maintain the sample at a temperature at least as low as the temperature at which it was collected, even after the samples have been brought to the receiving laboratory and to storage areas. It seems important to understand the atmosphere-regolith interaction in detail with respect to resources and settlements.

Washington University
Campus Box 1169
St. Louis, Missouri 63130
(314) 889-5610

WASHINGTON UNIVERSITY IN ST LOUIS

Department of Earth and Planetary Sciences

Washington University
Campus Box 1169
St Louis Missouri 63130
(314) 889-5810

4. The comments on size range of materials for study in the 1974 document are still appropriate. Obtaining large enough rocks to be representative of major rock types of rock formations is not really feasible. (It was not accomplished in our lunar sampling.) The best we can do is to collect a very large number of cm-sized objects, especially from larger objects we can observe remotely, and try to construct the nature of the rocks and their formations from those samples. There should also be samples of finer material, of course.

5. Effects of cosmic-ray bombardment on acquired samples during the trip to Earth need more consideration than what I have seen so far. We cannot take time to consider this in detail right now, or, even to look at what had been done since the 1974 study, but there is the possibility for some chemical degradation of atmospheric materials, changes in characteristics that might affect measurements by spin resonance techniques, etc.

Best of luck to all of us with respect to our obtaining samples from Mars!

Sincerely yours,

Larry A. Haskin

Randy L. Korotev

ABTEILUNG NUKLEARCHEMIE
am Institut fur Biochemie
der Universitat zu Koln
im Gebaude der ehemaligen Kernchemie)

5000 Koln den June 10, 1987
Zulpicher Straße 47
Ruf 470-3209

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058
USA

Attn. of: SN2-87-L328

Dear Dr. Gooding,

Thank you very much for your friendly letter dated May 27, 1987, which reminds of an input to a Mars-sample-science document. Unfortunately, I have never received a first call. The only message with this respect was a call for a letter of intent to participate in the Mars sample return science workshop. It was possibly a misunderstanding on my side; I beg your pardon.
To overcome time-problems I "changed" the letter of intent mentioned above to an input to a Mars-sample-science document. Please, find enclosed the brief description of the anticipated contribution.
I hope that this procedure will find your consent.

Do you participate in the Meteoritical Society Meeting at Newcastle upon Tyne? If you can not come, please, give me the name of a person to whom I can handle over Antarctic meteorite samples.

Hoping to see you at Newcastle I remain

sincerely

(U. Herpers)

MARS SAMPLE — SCIENCE

name: Dr. Ulrich Herpers

address: ABTEILUNG NUKLEARCHEMIE
am Institut fur Biochemie
der Universitat zu Koln
Zulpicher Straße 47
D – 5000 Koln 1

telephone number: Cologne / 4703219 or 4703209

area of scientific interest: cosmogenic radionuclides and cosmophysics

Brief Description of Anticipated Contribution

Stable and radioactive nuclides produced by cosmic ray particles in extraterrestrial matter are widely used to reconstruct the irradiation history of the body (e.g. SNC-meteorites [1]) or surface of the body (e.g. moon [2]) as well as the cosmic ray intensity in the past [3]. With respect to this scientific questioning it is intended to measure the spallogenic radionuclides ^{10}Be, ^{26}Al, ^{36}Cl, ^{53}Mn etc. and their target elements in Mars samples by accelerator-mass-spectrometry, low-level techniques and radiochemical neutron activation analysis.

References:
(Exemplary selected publications of the author's studies on this field)

1. R.Sarafin, U.Herpers, P.Signer, R.Wieler, G.Bonani, H.J.Hofmann, E.Morenzoni, M.Nessi, M.Suter and W.Wölfli
"^{10}Be, ^{26}Al, ^{53}Mn, and light noble gases in the Antarctic shergottite EETA 79001 (A)."
Earth and Planetary Science Letters, 75 (1985) 72-76

2. U.Herpers, W.Herr, H.Kulus, R.Michel, K.Thiel and R.Wölfle
"Manganese-53 profile, particle track studies and the rhenium-187 isotopic anomaly of breccia 14305."
Proceedings of the Fourth Lunar Science Conference
(Supplement 4, Geochimica et Cosmochimica Acta)
Vol.2, pp.2157-2169, The M.I.T. Press 1973

3. R.Sarafin, G.Bonani, U.Herpers, P.Signer, H.J.Hofmann, M.Nessi, E.Morenzoni, M.Suter, R.Wieler and W.Wölfli
"Spallogenic nuclides in meteorites by conventional and accelerator mass spectrometry."
Nuclear Instruments and Methods in Physics Research
B5 (1984) 411-414

ORIGINAL PAGE IS
OF POOR QUALITY

HARVARD UNIVERSITY
DEPARTMENT OF EARTH AND PLANETARY SCIENCES

HOFFMAN LABORATORY 20 OXFORD STREET
CAMBRIDGE, MASSACHUSETTS 02138

April 1, 1987

Dr. J.L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

Thanks for your letter of February 10th regarding return samples from Mars. As a former member of the MSWG, I am delighted that Mars is again inching toward center stage. It seems to me that the sequence of missions planned by the USSR is well conceived,and that their plans owe something to our own deliberations. A matching, cooperative, or complementary program by NASA seems almost essential to our continued competitiveness in space.

Returned samples are critical for solving a wide range of Martian problems. First and foremost are problems related to the time scale of Martian evolution. The dating techniques that have been developed during the last three decades should all be applied to returned samples. No less important is the solution of problems surrounding the budget of the volatiles on Mars, the formation of the fluriatile features, and the disappearance of liquid water as an important agent for shaping the surface features of the planet. If the logistic problems of having a rover maneuver through the base of the Valle Marinens, samples from a wide range of horizons might be obtainable. Evidence regarding their weathering, transport, and depositional history would be important both for reconstructing the history of the Martian surface environments and the processes that shaped the internal evolution of the planet. Studies of carbonaceous remains in samples of old sediments might go far toward settling the question whether life was ever present on Mars.

Sincerely yours,

Heinrich D. Holland

HDH/ps

Heinrich D. Holland
Professor of Geochemistry

C-3

CALIFORNIA INSTITUTE OF TECHNOLOGY

DIVISION OF BIOLOGY 156-29

17 April 1987

Dear Dr. Gooding:

On re-reading the letter I sent you yesterday, I realized that I did not mention the possibility that OH radicals generated in the Martian atmosphere may be deposited in the surface as peroxides. I have therefore revised the relevant sentences in the attached rewrite of the letter.

Please discard the earlier letter (dated April 16) and replace it with this one. Thank you.

N. H. Horowitz

PASADENA CALIFORNIA 91125

CALIFORNIA INSTITUTE OF TECHNOLOGY

DIVISION OF BIOLOGY 156-29

17 April 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

This is in reply to your letter of 10 February 1987 requesting input to a report dealing with the scientific goals and requirements of a Mars sample-return mission.

Although your letter does not specify a manned or unmanned mission, I assume that the latter is what you have in mind. If I am wrong in this, and a manned mission is what you are planning, please ignore this letter.

The background for the following comments is contained in my book, To Utopia and Back: The Search for Life in the Solar System, W. H. Freeman, 1986.

One objective of future Mars missions must be to confirm and extend the results of the Viking mission. Among the biologically relevant findings of Viking, the following results relative to the Martian surface material were of major importance: (a) organic matter is absent; (b) the material reacts with water vapor to yield oxygen; (c) life is absent. (One Viking experimenter believes that the Viking results showed life on Mars; he appears to be alone in this belief.)

The most parsimonious interpretation of these findings rests on the extreme dryness of Mars and the production of OH radicals in its lower atmosphere. The dryness and the resulting ultraviolet radiation are incompatible with life; the uv-produced radicals diffuse into the surface, where they destroy organic matter. Their presence in the surface (as radicals or in the form of peroxy compounds) accounts for observation (b) above.

Return of Martian samples to Earth would make it possible to confirm the Viking results by more sensitive and sophisticated means than can ever be deployed on Mars. In addition, those results could be extended in the following ways:

(1). The possibility that organic matter exists at greater depths in the Martian surface could be examined by returning core samples. If organic matter is detected, then it would be important to characterize it. Such characterization could tell whether it had a biological or non-biological (meteoritic) origin.

PASADENA CALIFORNIA 91125

(2). Returned core samples could also be examined for microfossils.

(3). Free radicals in returned material could be identified by Raman and electron spin resonance spectroscopy, peroxides by chemical methods. There is reason to think that the Martian surface contains a greater abundance of reactive species than the Viking results indicated, since the Viking samples came from ground that had been swept by the retro-exhaust of the spacecraft. Quantitative determination of such species in pristine Martian material as a function of depth would be of much interest.

Before being returned to the earth, samples should be tested for the formation of oxygen when brought into contact with water vapor. Viking found no samples that did not show this reaction, but if such are detected in the new mission it would be highly desirable to return them along with reactive samples.

A core, as deep as possible, should be taken from a site where organic matter might have accumulated in an earlier, less hostile period--e.g., the mouth of a wash. Uncontaminated samples should be sealed and stored under Martian (or an inert) atmosphere at a temperature approximating the lowest temperature reached at the relevant Martian latitude.

I hope that these suggestions will be of some use.

Yours truly,

Norman H. Horowitz
Professor Emeritus

Posted: Fri Jun 19, 1987 12:40 PM CDT Msg: CGIH-2624-8193

From: RKAHN
To: jgooding
CC: rkahn
Subj: Mars Sample Science

R. Kahn
June 19, 1987

Jim:

I am glad we had the chance to talk this afternoon. Here are my comments on the Mars sample science issue:

I am particularly interested in being sure that the carbonate and cation content of the samples is preserved, so that both the abundance and the distribution of these constituents within the sample(s) can be measured accurately. The latter is of particular importance because it may hold critical clues to the way in which any carbonates present would have formed. (e.g., Kahn, 1985, The Evolution of CO2 on Mars, Icarus 62, 175-190.) Similar information about salts in the samples would also be of great value in assessing the possibilities for occurrence of low temperature solutions. Gas and ice abundance in the samples, including isotopic ratios, represent another dimension to the type of observations which would be of high priority on my list, for their use in constraining atmospheric (and thereby climate) history.

In the more distant future, ice cores from the polar regions might contain some of the most important information about the climate history of the inner solar system in existence. (I know its a dream, but I figured I'd throw it in for good measure.)

While I am very much an amature in matters geological, I appreciate your efforts in keeping me informed and soliciting my comments.

With thanks and best wishes,

Ralph Kahn

NASA/HQ
Code EE

UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Geology

101 Geology Building
Columbia, Missouri 65211
Receptionist 314-882-6785
Administrative Assistant 882-2040
Chairman 882-6673
Field Course Director 882-3757

MAR 02 1987

February 25, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

Replying to your questionnaire and letter of Feb. 10, relative to Mars samples, I respond from the perspective of the Lunar samples that I studied.

We simulated the weathering of Lunar rocks under earth-surface environment, i.e., water and an oxidizing environment, and compared those experiments with parallel experiments on basalt from Earth. If the opportunity arose, I would like to see the same done on Mars materials.

Ideally a collection should be made of at least 2 groups of materials:

(1) as is, without any heating, processing, or sterilization, and (2) a sterilized sample relating to life studies.

If, or when, a rock sample is heated (sterilization), water, gases, and volatile compounds in the rock will be driven off. These are not only "(OH, F)" or "H_2O+", as traditional chemistry has described them; they may include a dozen other compounds. Moreover, LOI may signify not only "loss on ignition" but also "loss of information", or "lots of information", as we see in Amer. Mineralogist, 71, 1420-1425, 1986.

You are to be complimented for your perspective thinking about collection of the Mars samples. The quality of laboratory results on rock samples can not be any better than the quality of collection of the sample, a fact that has, at times, been forgotten. Praise to you.

Sincerely yours,

W D Keller

Walter D. Keller
Professor Emeritus

WDK:mb

an equal opportunity institution

UH University of Houston University Park

Department of Geosciences
4800 Calhoun Road
Houston, Texas 77004

March 1, 1987

Dr. James L. Gooding
SN2
NASA, Johnson Space Center
Houston, Texas 77058

Dear Jim:

Thank you for your letter (ref: SN2-87-L084) of Feb. 10. I am very pleased to have the opportunity to make "input" to a document dealing with various aspects of a sample return from Mars.

What we are considering is only the first sample return from Mars. While even a random surface sample would be of immense scientific importance, we probably can and should do better than that. However, if we compile a giant "wish list", we can easily define an impossible mission! The mission requirements for the first martian samples should be viewed as only the first step in a continuing program of sample-related exploration of Mars.

In that context, I believe that the sampling scheme should focus on the volatiles, volatiles-rock interactions and volatiles-related sediments and sedimentation. In other words, the focus should be on those features not present in lunar samples that make Mars unique among the terrestrial planets. These samples should yield the most exciting new scientific information, provide the greatest justification for future missions and start a resource information base that will be most useful for the inevitable manned exploration and habitation of the planet.

Specifically, I recommend four types of samples that I list in priority order: (1) A gas-tight, sealed sample of either bulk regolith or a regolith core. We should attempt to keep this sample at martian conditions during its transit to Earth. This sample would be used primarily for biological and paleontological evaluation and direct analysis of volatile components. (2) One or more weathered igneous rocks returned in a known environment but not necessarily with a gas-tight seal. This sample would offer the possibility to study rock-volatiles interactions. (3) A bulk surface sediment or regolith sample returned in a known environment, but not necessarily with a gas-tight seal. This sample primarily for investigation of martian sedimentary processes as well as the usual regolith studies. (4) A few small fragments of freshest available igneous rocks returned in a known environment without gas-tight seal for the usual petrological and geochemical analyses.

In order to select samples properly on the martian surface, the lander should have a high resolution imaging system, gas chromatograph-mass spectrometer with stepwise sample heating, and some sort of major element analyzer in addition to sample collection tools. The GC-MS could be used to make a number of sample analyses of volatiles from shallow subsurface samples obtained by trenching or coring. It is particularly important to establish the stratigraphic context of the samples both at the scales of orbital imagery and local site geology. In my view, this is much more important for Mars than for the Moon.

These are my first impressions and they would certainly be subject to change after discussions with my colleagues in different areas of specialty. There will have to be many compromises made in reaction to spacecraft capabilities. Probably, it will be necessary to organize one or more Science Analysis Teams to develop a set of sample requirements for the mission and to review hardware designs as they are developed. Hopefully, we will be able to avoid making the same mistakes that were made in Viking and Apollo!

Yours is an important task and I wish you every success with it!

Sincerely,

Bert

Elbert A. King
Professor

EAK/pld

ORIGINAL PAGE IS
OF POOR QUALITY

APR 27 1987

PHYSICS LABORATORY
UNIVERSITY OF COPENHAGEN

H. C. Ørsted Institute
Universitetsparken 5
DK-2100 Copenhagen Ø
Denmark

Telephone 01353133
International +45-1353133

April 21 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058
USA

Dear Sir

I am a little in doubt if the enclosed material will be of any use for you. However, I decided to send it as a kind of a response to your letter of February 10 1987 ["Call for input to a Mars Sample-Science Document"].

The material may be worth a footnote in your document. In reality, the only message is the following:

The consortium studies of the putative martian meteorites (SNC-meteorites) should be extended to an in depth investigation of the distribution of iron in these meteorites. This might help us in understanding the role of iron in the evolution of Mars, both the planet as such and its surface features. Mössbauer spectroscopy is an essential tool in such endeavours.

Rocks from Mars itself, igneous, sedimentary and fines from the regolith, will of course be the essential thing - but a study of the iron in SNC-meteorites will help in preparing the right Mössbauer experiments, if and when the precious, collected martian samples reach the Earth.

If you want any more information, or a more formally written statement feel free to write, but specify precisely the length of a statement, if you want one.

Sincerely yours

Jens Martin Knudsen

Enclosures:

1. Remarks on the martian meteorites and Mössbauer spectroscopy.
2. Selected examples of articles.

Martian Meteorites:

What they might and might not tell us about Mars.

The geochemical cycle of the element iron - be it on planetary surfaces, in meteoritic parentbodies or in the solar nebula - is strongly coupled to the cycles of abundant elements like H, O, C and S.

Fe occurs in nature in (at least!) three oxidation states, metallic (Fe(0)), Fe (II) and Fe (III). Furthermore:
The element occurs as the essential ion in magnetically ordered compounds, both in the ferro (ferri) - magnetic, antiferromagnetic and superparamagnetic state.

Due to these properties, and due to its high abundance on the surface of Mars, the element iron is of fundamental importance for the understanding of the evolution of the planet, both its igneous rocks (mantle) and its surface fines.

The highly oxidized iron at the surface of Mars - Fe (III), with a small amount of Fe (IV) as a remote possibility - has evolved from the exposed basaltic rocks on Mars. Therefore:

Assuming that the SNC-meteorites represent martian volcanic rocks, the chemical and physical state of iron in these meteorites should be investigated in depth.

Preliminary studies have been made. Examples of results obtained are:

1) Compared to, say, the eucrite achondrites and Moon rocks, the meteorite Nakhla is more oxidized. By means of Mössbauer spectroscopy it has been shown that Nakhla contains Fe^{3+} in the pyroxenes. These Fe^{3+} ions are very difficult to detect by any other means than Mössbauer spectroscopy. Until now no other achondrite - or no Moon rock - have been found to contain Fe^{3+} in its pyroxenes. The finding of Fe^{3+} in the pyroxenes of Nakhla (a "volcanic rock") supports the view that the parentbody of Nakhla is "large", probably larger than the Moon.

2) The Mössbauer spectra of olivine separated from Nakhla show superparamagnetic relaxation at liquid helium temperatures. This is due to the fact that the iron is innomogeneously distributed in the crystals of olivine. The iron seems to be located in domains (clusters), with linear dimensions so small that the domains (clusters) cannot be detected by the microprobe. The Mössbauer spectrum of olivine from Nakhla at 4K is different from the corresponding spectrum of olivine from for instance Icelandic lava. This is probably due to different thermal histories.
As these two examples demonstrate an in depth investigation of the distribution of iron in crystals of olivine and pyroxene separated from the SNC-meteorites is worth the effort. The results of Mössbauer spectroscopy over a wide range of temperatures should be compared to Mössbauer spectra of well characterized olivines and pyroxenes from the Earth.

What might the iron in SNC-meteorites tell us? Examples:

1) Comparing the oxidation state of iron in SNC-meteorites with for instance the oxidation state of iron in terrestrial kimberlites might tell at least something about the difference in oxidation state of the mantle of the Earth and Mars. The oxidation state of iron in the planets is of importance for the study of condensation processes - and accretion processes - in the solar nebula. Mössbauer spectroscopy is by far the best tool to determine the important ratio Fe^{3+}/Fe^{2+} in any mineral.

2) How did the oxidation of the surface material on Mars take place?
The SNC-meteorites contain very little Fe^{3+}, and very little Fe_3O_4 (magnetite). Especially the comparatively large amount of ferrimagnetic material in the martian fines is surprising. If the ferrimagnetic (superparamagnetic?) material on Mars is γ-Fe_2O_3 (maghemite) it might have as precursor either:
a) Fe_3O_4 b) γ-FeOOH (decomposes by heating, and perhaps under UV, to maghemite) c) Nontronite (palagonite).

It is doubtful that Fe_3O_4 occurs in sufficient amount in the martian baserock to be the sole precursor of the γ-Fe_2O_3 on Mars. Pathways have been studied by several workers, which lead from baserock (SNC-meteorites?) via γ-FeOOH or nontronite to maghemite. Whenever iron-oxides and/or hydroxides form by low temperature weathering (corrosion) the resulting particles are generally so small that they are superparamagnetic. In that case their magnetic properties are complicated. Even antiferromagnetic particles (α-Fe_2O_3) may, in the superparamagnetic state, have a rather high magnetic susceptibility (surface spins, lattice defects). Mössbauer spectroscopy over the critical temperature range is an ideal tool for the study of superparamagnetic particles. More Mössbauer spectroscopy of superparamagnetism in Mars sample analogues (palagonite etc.) should be performed, also the possible creation of superparamagnetic fines through for instance impact decomposition. If for no other purpose then to prepare for the study of returned martian fines by means of Mössbauer spectroscopy.

Conclusions:

The consortium studies of the SNC-meteorites should be expanded to include Mössbauer spectroscopy of iron from temperatures of a few Kelvin and up to temperatures where the iron starts to redistribute itself on the various accessible lattice sites in the crystals.

When a sample return mission finally occurs, we shall be in a better position to ask penetrating questions about the history of the element iron - both in the returned martian fines and in the returned martian rocks - if we expand our knowledge by careful studies of the distribution of iron in SNC-meteorites.

Mössbauer spectroscopy over a wide range of temperatures is an essential aspect of such studies.

Christian Koeberl
INSTITUT FUR GEOCHEMIE
DER UNIVERSITAT WIEN
Dr.-Karl-Lueger-Ring 1
A-1010 Wien
Telefon (0222) 43 00 - 23 36
Austria

Wien, am April 29, 1987

To: Dr. James L. Gooding
Code SN2
NASA Johnson Space Center
Houston, TX 77058 USA

Re: Mars Sample Return Mission - Science Input

Dear Dr. Gooding,

in response to the "Call for Input to a Mars Sample Science Document" I would like to comment on the questions raised together with some general suggestions. Surely the possible retrieval of samples from Mars will have an impact on the whole Planetary Community, comparable only to the boost received in the first years of lunar sample studies. It would be extremely useful to provide a goal of adequate magnitude for the 90's. We all know only too well that without a clear target, standing for at least one decade, efforts will be dispersed and much experience, gathered from lunar and meteorite work, will be lost due to migration to other subjects.

Among the most important factors to consider are side-effects of the study of Martian samples. We can expect a similar development as for lunar sample studies. The development of new analytical techniques and concepts for lunar science produced some invaluable spin-off for fields quite different from the original field of application. The impact on planetary science, earth science, material science, etc., will be immense, if a dedicated effort for a Mars sample return is launched.

This already leads to a very important aspect of Mars sample studies, namely pre-return studies. Clearly, the analytical methods available today will be improved until Martian samples reach our laboratories. However, some techniques will have to be developed or improved specifically for the analysis of Martian samples, with benefits for related investigations. Laboratories working in the field of geo- and cosmochemical analysis should extend their efforts to do so, of course only after some dedicated statement (and funding) from NASA and related agencies. Among the techniques that will have to be improved are the following:

(1) Study of trace elements and isotopes in single minerals within a mineral assemblage, and study of the distribution within single minerals. Neutron activation techniques, radiochemistry, and nuclear microprobes together with mass spectrometric methods are promising for these studies, provided their sensitivity is increased to some extent. Higher fluxes and better detectors are some of the requirements.

(2) Sample preparation techniques are crucial for almost all investigations. Contamination free laboratory environments and preparation procedures do not exist for very small samples to an extent necessary for single

..../2

mineral analyses. Related research and training may be gathered by treating available materials, e.g. Antarctic meteorites, in a similar manner. Also, techniques will be needed for analysing samples at low temperatures, in order to avoid structural changes.

(3) Improved procedures for the analysis of volatile elements are required. Those elements (like the halogens, C, N, S, Tl, In, Bi....) are among the "difficult" elements even today. For some of them, pushing radiochemistry to it's limits may be the answer, for others new techniques are needed.

(4) Isotopic systems other the well-known ones (like Sm-Nd, K-Ar, Rb-Sr) should be explored and quantified. Some valuable information concerning Martian differentiation processes may be hidden here.

Of course this list can be expanded considerably, but I mentioned only a few obvious problems from the geochemical viewpoint. Concerning the four specific questions raised in the "Call.."-letter, I would like to provide my comments as follows.

(1) The requirement of having samples in a terrestrial laboratory rather than sending some instrumentation to the site should be obvious to everybody. Analytical techniques can be altered and refined according to specific sample requirements, which is nearly impossible with remotely controlled equipment (which, in addition, necessarily lacks sensitivity and stability). All aspects of Martian chemistry and processes can be addressed much better on Earth. Single mineral analyses, leading to geochemical and isotopic models of the evolution of specific sites, like volcanic provinces, are possible only on Earth. The determination of volatiles, especially at trace abundances, is another example. All data gathered from the SNC meteorites will be seen in the light of the data provided from Martian samples, and together they may very well lead to more far-reaching conclusions.

(2) It should be a requirement to include samples from more than one location. A single sampling location is statistically insignificant and may lead to biased conclusions. The rover version seems to be most promising. Sample sizes should be at least a few centimeters for single rocks, to provide enough material for diverse studies and cross-checks, together with some remainder for future investigators. Soil samples also should amount to no less than 5 g per site. Most desirable would be the collection of at least one drill core, with 1-3 m coring depth. It is of ultimate importance to record the exact location of each sample, and allow no degradation or alteration within one sample or core, because the study of cosmogenic nuclides depends heavily on environmental data.

(3) Sample degradation should be minimized as far as possible. Many compounds and loose mineral assemblages will be destroyed by elevating the temperature above the environmental level. At temperatures below 100°C mainly (but not exclusively) structural changes can be expected. Temperatures exceeding this limit will lead to more and more severe chemical alterations, with an increasing loss of volatiles - elements and compounds which are crucial to the understanding of many Martian processes. Pressure and shock influences the samples in a similar way - first structural, then chemical changes. Radiation should be shielded from the samples a far as possible to avoid alterations and/or production of cosmogenic nuclides.

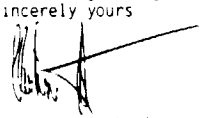
.../3

Sterilization procedures should be avoided since, after Viking, there seems to be no need for them. Also, due to high reactivity of Martian soil, biological activities are not expected, and sterilizing will lead to the destruction of the reactive compounds (which may be interesting to study). Prebiotic structures, unlikely but not impossible to be present, will also be destroyed.

(4) In situ-measurements should include penetrator experiments, HPGe gamma ray studies, RFA, GC, and related experiments. They have to be supplemented, of course, by all necessary sample collection documentations. Also, some kind of record of the state of the samples during the return leg of the mission has to be provided, to ascertain the absence (or degree) of post-collection alterations.

Concluding, it can be said that some international effort may be considered useful, especially concerning the state of Soviet projects. Europe may provide some forum for data exchange between the US and Soviet studies. Clearly, the need is felt for the implementation of a far-reaching goal in planetary geochemistry, and the scientific reasons for going to Mars and returning samples are reasonable, and hopefully find their way to decisionmakers.

With best greetings,
sincerely yours



Christian Koeberl

RIJKSUNIVERSITEIT - GENT

LABORATORIUM voor
MINERALOGIE, PETROGRAFIE
en MICROPEDOLOGIE

Dir.: Prof. Dr. G. STOOPS
Dr. S. GEETS
Dr. R. NIJS

B-9000 GENT 11 augustus 1988
Geologisch Instituut
Krijgslaan 281 S8
Tel. 091 22 57 15 Uitbr. 2666

Uw ref.: SN2-87-L084
O. ref.:

Dr. James L. GOODING
SN2
NASA Johnson Space Center
HOUSTON, TX 77058
U.S.A.

Dear Sir,

As I understood from contacts with Mrs. J. Allton during the International Working Meeting on Soil Micromorphology '88, San Antonio, Texas, you are still interested in ideas for the sampling and return of samples from Martion "soil" (= the upper surface layers).

I enclose some answers to your questions and some considerations about sampling techniques.

As my field of study is mainly mineralogy and micromorphology, I will restrict my remarks to these fields.

I do hope that these ideas may be of interest to your pro-ject and I would be pleased to answer any question you might have.

Sincerely yours,

Carl LANDUYDT.

ANSWERS TO QUESTIONS (1),(2),(3) AND (4) FROM A MICROMORPHOLOGICAL AND MINERALOGICAL POINT OF VIEW

(1) From a detailed micromorphological study, present and/or past soil forming processes (if existing) can be deduced. These processes may reflect climatic and atmospheric conditions and possibly also biological activity (if present).
A detailed mineralogical study could result in additional information. From weathering products, weathering processes can be characterized (chemical, physical, biological) and this information can give indications about soil moisture, temperature, pH, redox conditions, etc.

(2) For micromorphological studies, it is absolutely necessary that returned samples are as undisturbed as possible. Relatively large samples are needed (e.g. cores with a diameter of about 2.5 cm). The larger the samples, the more accurate the analysis will be and the larger structural units can be recognized.
For mineralogical analysis, samples can be disturbed. In order to get representative samples, it would be best to take larger samples from various depths. These can be homogenized (crushed) and split on Mars to return a small quantity (1 g or 0.1 g) from each sampling depth. If unstable minerals are to be expected, atmosphere, temperature and pressure of the sample container should be controlled.
It is probably best to take two sets of samples :
1) Larger, in situ fixated samples for preparation of thin sections (mineralogical, petrographical and micromorphological study)
2) Small samples for chemical and mineralogical (X-ray diffraction) analyses.

(3) As stated above, micromorphological samples should be undisturbed. Vibrations may cause compaction and segregation of different particle size fractions in unconsolidated material and large differences in temperature and pressure may cause cracks and/or alter existing voids. The same counts for shock and large acceleration. Therefore, fixation of the samples prior to their return is highly recommended (see also general considerations on sampling techniques).
If unstable minerals are present, temperature and pressure variations (even small ones) can cause mineral transformations. However, if these changes should occur, the original form of the minerals may still be visible in thin sections of the undisturbed material, giving an indication of its nature.
If sterilization is necessary, can't this be done by irradiation with gamma rays instead of heating?

ORIGINAL PAGE IS
OF POOR QUALITY

(4) It will be difficult to do mineralogical analysis in situ, unless a miniaturized X-ray diffractometer could be transported. Some mechanical characteristics of the soil could be derived from penetrometer tests or from the behaviour of the sampling devices.

SOME CONSIDERATIONS ON UNDISTURBED SAMPLING AND PRESERVATION TECHNIQUES

Murphy (1986) gives some good general ideas about sampling and impregnation techniques of unconsolidated materials.

From pictures of the Martian landscape, it may be concluded that the top surface layers have a rather loose packing and are not consolidated. A good device for taking undisturbed samples is probably a hollow drill, consisting of an outer, rotating wall and an inner non-rotating one (see fig.1). (Such drills are used for taking geological samples on a larger scale, but they can probably easily be miniaturized) The inner shaft can serve as a holder for storing the sample and is replaced after each uplift of the drill (see fig.2).

Even in this way, there is still a danger for disturbing the uppermost material. If possible, a kind of resin (like polyester or epoxy) could first be poured or sprayed on the surface. After impregnation of the soil and curing of the resin, coring could begin. After the drill head is full, the drill is lifted and the sample is stored in a container, which also contains the empty inner shafts/holders of the drill. Of course, all this should be tested in similar conditions in the lab. Specially, the development of a suitable resin might be a problem.

A similar resin might be used for the impregnation of the samples after the sample container is filled, and prior to its return.

Reference

Murphy, C.P. 1986. Thin section preparation of soils and sediments. ABA Publishers, Berkhamsted, UK., 149pp.

Carl LANDUYDT

Gent, August, 12, 1988.

Carl LANDUYDT
Laboratory for Mineralogy,
Petrography and Micropedology
Krijgslaan, 281 - S8,
B-9000 GENT
BELGIUM

Warsaw University
Department of Chemistry
Żwirki i Wigury 101
02-089 Warsaw, Poland

JUL 14 1987

Dr. James L. Gooding
SN2
Nasa Johnson Space Center
Houston

Dear Jim,

Warsaw, June 25, 1987

Thank you very much for your most kind invitation to participate in preparation of exploration of the Mars-returned samples. I am terribly sorry for the delay in writing to you. I should like to focus your attention on some possible objectives of the planned exploration in my opinion a little bit underestimated.

Within my scope are some aspects of the physical structure of distinct Martian materials which are related to their origin and history. The geological history of Mars cannot be understood without a clear picture of the microstructural features of the respective materials. It must be considered not only their bulk densities with possible variations but brought to light all available details of their intrinsic geometry. The involved spectra of pore sizes are badly needed. The molecular surfaces separating the solids from pore spaces are to be studied and evaluated in terms of the fractal approach to their irregularity. The porosity and not excluded dendritic structure of Martian ices seems to be of high importance.

At the moment I am unable to explain whether the existing technology of measurements can assure the availability of the required data. I predict the necessity of a wide study of adsorption of gases and - not ecluded - some liquids on the surfaces of the Martian materials leading under other to determination of their specific surfaces and pore spectra. Small-angle X-rays scattering capable tooperate submillimeter-sized particles seems to have a particular advantage.

I have no personal experience in the above mentioned methods. I cannot even assure you that my present orientation is sufficient to make adequate practical suggestions. However I feel the problem, the entire family of problems. Impressed by the latter I am trying to use the chromatographic method for soecific area determination leading to fractal parametwrs of the molecular surfaces and in later time possibly to the spectra of pore sizes. If we succeed with meteorite samples we would be able to consider on request an extension to Martian samples. The use of X-rays scattering at small angles is also within our scope although largely uncertain.

Summarizing the above: I realize the alternative - to be met without any enthusiasm or to open a dialogue leading to activity in favour of the expected Martian samples along the lines of this letter. The decision is to you.

With best wishes and friendly greetings.

Sincerely

Bruno Lang

ORIGINAL PAGE IS
OF POOR QUALITY

JUL 1 1987

THE ROCKEFELLER UNIVERSITY
1230 YORK AVENUE NEW YORK, NY 10021

JOSHUA LEDERBERG
PRESIDENT

June 23, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Dr. Gooding:

I am responding to your letter of May 27th which reminded me of prior correspondence going back to last February concerning Mars sample-science. Although I was a very enthusiastic member of the Mars Viking Lander experiment team, I have more or less retired from space science in the interval and I do not contemplate playing an active role in a program that will still take some years to reach fruition. So I was not sure how pertinent my remarks would be.

I do however have a single policy point that I would like to leave for the record.

Certainly the scientific value of return samples from Mars would be enormous for a wide range of disciplines. This is sometimes confused with a manned return mission and I hope that you will not fall into that trap since it will necessitate a vast multiplication of resources in a way that will add very little to the scientific utility. On the other hand it seems to me absolutely vital that we secure samples from a variety of locations and I am obviously speaking to the necessity of a rover which would be able to explore a variety of terrains and secure samples that are representative of a number of quite different sites within its purview. I don't have the original copy of the announcement and if there is time I would like to have a look at it and perhaps I would have more to say in response.

Unmanned

Yours sincerely,

Joshua Lederberg

JUL 28 1987

PRO BONO HUMANI GENERIS
The Rockefeller University 1901

THE ROCKEFELLER UNIVERSITY
1230 YORK AVENUE NEW YORK, NY 10021

JOSHUA LEDERBERG
PRESIDENT

July 24, 1987

Dr. James L. Gooding
Space Scientist
Lyndon B. Johnson Space Center
NASA
Houston, Texas 77058

Dear Dr. Gooding:

I am continuing to dribble some responses to the Mars sample-science document. The question of sterilization will evidently loom as the central issue in defining the requirements for sample return. Here we have a paradox: some part of the very great interest in returning to Mars is surely our last ditch effort to see if there are microniches that might allow for some surviving biota, despite the substantially negative results of the Viking missions and the very harsh environment in the regions sampled thereby. If we could but premise that there just is no life there, then of course we could relax the sterilization requirements. But if we insist on that as a proven premise, we undercut a substantial part of the justification for the mission. And from a strictly scientific standpoint we have so far sampled only one (equatorial) habitat -- the least promising that Mars might afford.

At this point I might be persuaded to return samples from Mars to Earth without sterilization (albeit with some careful attention to quarantine!) iff they are demonstrably from habitats like those sampled by the 1976 missions. To assess how well we know that will require some attention to the further automated instrumentation that will be on the lander experiments.

One of the purposes of the Rover will be to try to seek out as diversified a set of terrains (is that still the right word?) and of course these contradict the idea that we can predict what's likely to be in them. We will also surely be

looking for fossils, especially in connection with the ancient riverine features. For the most part these pose no very special problems of preservation except for needing substantial samples or else extensive onboard processing.

Some of the most striking features of the Viking/Lander experiments spoke to the prevalence of (presumably photochemically induced and unstable) oxidants and it would be important to get a handle on just what these surface chemical structures are, as part of our design of sample return. A good deal of this could be done during the course of the landing and preparation for return: but as we well know, if we do not think about it now, it is not going to happen. Recall, we never did get even a conductimetric measurement of surface materials in the 1976 mission. These unstable oxidants which may be of very substantial importance in understanding the regolith (and contribute to our expectation that the zone of Mars is self-sterilizing) may pose the most difficult problems of chemical stability in trying to think how to package the samples for return. Maybe it is just not feasible, and we better think very carefully about what experiments to do in situ. Other than that, keeping material cold, dry and dark (which is what we do in the chemical laboratory) would seem to be the paradigm for conservation.

As to the kinds of samples we want to look for I would put the greatest emphasis on lateral extension -- that is indeed the Rover! -- in looking for the most interesting sites. At some places it will undoubtedly be an advantage to take borings that can give some idea of the geological history and stratigraphy and the possibility of permafrost. And I hope we can go sufficiently poleward that we can get at least some sample of habitats that are exposed to or influenced by seasonal water ice and frosting. I do not know how far the planning has gone on the Rover to know to what extent we can rely on on-board intelligence and how far we will need to, and be able to, direct its exploratory movements from Earth.

Forgive these rather scattered remarks; but I just do not have the background documentation in front of me that would enable me to respond in more coherent detail.

I am sure we are going to change our minds about the kinds of samples we want in real time, as we get

pictures of specific target specimens -- for example fossil suspects!

Yours sincerely,

Joshua Lederberg

P.S. I enclose a note that Carl Sagan and I wrote years ago on microhabitats. That line of reasoning has had emphatic corroboration by the recent discoveries of deep sea vents, and unique macro-- and micro-- flora on Earth's ocean floors.

JUN 22 1987

BIOSPHERICS INCORPORATED
Technologies for Environment and Health

June 16, 1987

Dr. James L. Gooding
SN2-87-L328
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

This is in response to your request for my input concerning the Mars Sample-Science Document to be prepared.

As stated in my talk at the Mars Conference held on the 10th Anniversary of the Viking Mission (Proceedings in process), I am most concerned that the issue of life on Mars is not receiving adequate consideration in future NASA plans. On an objective scientific basis, the issue not only remains open, but tilts on the side that the Labeled Release Mars experiment probably detected microbial activity in the Mars surface material.

I was not invited to attend any of the workshops mentioned in your May 27, 1987 letter to me, but since you state that the meetings made an effort to obtain "opinions from the widest possible cross-section of the scientific community," I am encouraged that someone was invited to present the possibility that there is life on Mars.

Concerning the specific questions posed in your request of February 10, 1987:

(1) The aspects of Martian history that can uniquely be addressed by direct analysis of samples returned to Earth include searches for physical or biochemical fossils of living organisms.

(2) The above can be accomplished with approximately 1g of sample. Several samples would be preferable, including those from apparently different types of surface material and from different depths.

(3) Heating above 100°C may have an adverse effect on attempts to detect and identify biochemical fossils. I do not believe that pressure, radiation or shock, within the probable ranges that a return sample mission would apply, would be adverse factors.

Corporate Headquarters • Laboratory Division • Engineering and Instrumentation Divisions • PD Communications

4928 Wyaconda Road
Rockville, Maryland 20852-2400
(301) 770-7700
Telex 898 072

(4) The most important in situ measurements that could be made on Mars to supplement or replace information that might be lost from degraded samples being returned would certainly be those looking for life in the surface matter.

I have reviewed the Conclusions of 1974 JSC Report on Mars Sample Return. Obviously this is a document designed for the study of the geochemical, physical evolution of Mars. The lack of any biological orientation to the proposed mission is fully stated in paragraph D, page 72, "Hopefully, sterilization will not be required." Thus, in 1974, before the Viking had even landed on Mars, this document was hoping that life would not be present since it might interfere with the objectives of the mission being planned.

Life, indeed, might interfere with a return sample mission to Mars. A scientific approach under the present state of affairs would require that the lander conduct life detection experiments on Mars and that the sample return mission have adequate capabilities to deal with the possibility of a positive response. That is, as much as possible should be done to characterize the nature of any organisms found in the surface material while still on the planet because the rigors of space travel and the environmental changes that necessarily must be imposed on the sample might not only kill the organisms but destroy much valuable biochemical and morphological information that might otherwise have been extracted by scientific analysis.

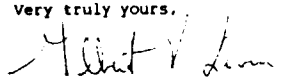
I note with considerable puzzlement that none of the plans currently being developed by NASA for further exploration of Mars, by orbiter, lander, return sample or manned mission, contemplates the Mars life issue. It seems that the Soviets do regard this as an open question. However, I prefer not to view the problem in a political light, but to consider the issue on scientific merit alone. On that basis, it is hard to understand why data which were clearly consistent with the presence of life, and which data met all the pre-flight criteria for a positive determination, are being neglected in this paramount area. Moreover, no acceptable nonbiological hypothesis has yet been advanced to duplicate and satisfactorily explain the Labeled Release Mars data.

Here then, I believe, is the starting place for a Mars return sample mission. The Labeled Release experiment, having provoked a strong reaction from the Mars "soil," should, as is customarily the case with scientific pursuits, be repeated for verification. The updated instrument, however, should have capabilities beyond those of Viking's. In particular, the left-handed and right-handed organic compounds should be carried separately

so that they might be individually applied to the Mars surface material. A positive response from one isotopic compound but not its enantiomer would probably be accepted as proof of life by biologists and biochemists. Such a response would establish the need for sterilization of the return Mars sample and could be a decisive factor in determining the entire treatment of the sample. Other variations of the Labled Release experiment involving temperature control, pH measurement and control, atmospheric analysis and control, and the like, could completely determine the life issue. Furthermore, such experiements would document the sample and provide important parameters for assessments of a nonbiological nature prior to sample changes induced by handling, sterilization and transportation. A tool exists which has evoked sharp responses from the Martian surface material. It seems only logical that this tool of entry to Mars science should be expanded, refined and used.

But, most importantly, the information at hand does not permit premature closing of the door on the single most important scientific issue in our solar system.

Very truly yours,



Gilbert V. Levin, Ph.D.
President

GVL/lm

JUN 4 1987

Mars Sample-Science Input

John S. Lewis

One of the most important goals for Mars sample science is the characterization of volatile-bearing regolith samples for the purpose of improving our knowledge of global inventories of the volatile elements. The volatile elements H, C, S, Cl an F may in part enter into rather stable phyllosilicates, carbonates, sulfates, and halides that resist thermal decomposition at 500K. However, a very substantial component of interlayer water, adsorbed carbon dioxide and water can be present throughout the entire regolith. At latitudes greater than about 30°, water ice and hydrates must be important constituents of both the permafrost layer and seasonal and nocturnal precipitation. We already have spectroscopic detection of ozone very strongly concentrated in the polar caps, and it is possible that other minor constituents with dipole moments, such as volcanic sulfur dioxide and halogen acids, may also be present in the polar ice in detectable amounts. The most informative samples for such science will be those taken at the lowest ambient temperatures. Such samples include both cold regolith containing permafrost and genuine polar ice. On the latter, the full range of techniques used in the analysis of polar ice cores on Earth can be brought to bear. A historical record of dust storm activity, climate (precipitation and isotopic composition of condensate), relatively recent comet and asteroid infall (siderophile element concentration) and possibly volcanic gas emission may be extricable from such cores.

The delicacy of such evidence and the wide range of analytical techniques required to extract the useful information seem to require that a fully refrigerated sample be returned to Earth (or delivered via aerocapture to an orbital receiving facility). Even simple melting of the sealed ice sample may destroy much of the valuable evidence. All layering (and hence all time-resolved chronological information) will be lost. Further, certain reactive gaseous constituents will almost certainly be consumed. The problem gases are ozone, hydrogen chloride, hydrogen fluoride, and sulfur trioxide (which would react to form oxides and salts), carbonyl sulfide (easily oxidized to CO or carbon dioxide with loss of sulfur), and sulfur dioxide (which at the very least will disproportionate into SO_3 and sulfur). The cores, if kept cold and confined, can be reasonably robust against moderate mechanical shock and will not generate significant gas pressures. Radiation is not a problem, since even a few years of exposure to cosmic rays while in transit will have only about the same effect as a few years sitting on the polar surface of Mars. (I assume here that the spacecraft structures, insulation, core jacket, and other mass will contribute about the same amount of shielding as the Martian atmosphere.)

The value of a clean sample of the Martian atmosphere,

free from contamination by volatiles released from the "solid" sample, is so self-evident that I will not take the time here to elaborate on it.

Sterilization of Samples

From the perspective of samples that bear information about the volatile budget and climate cycles of Mars, sterilization would cause a devastating loss of crucial data. It is a little hard for me to believe that there are still people who harbor paranoid delusions about the invasion of Earth by Martian life forms (and vice versa). The gross excesses and fatally flawed execution of the Apollo quarantine effort are still fresh in my memory. The enormous expense of sterilizing (and documenting the sterilization of) the Viking Mars lander is also well known. But now we are smarter: it would be folly to ignore the new facts we have learned since 1970. First of all, killing ultraviolet light with wavelength as short as 2000 Angstroms floods the Martian surface in the daytime. Atomic oxygen and ozone are manufactured right on the surface. Both of these species are used as biocides on Earth. The Martian surface environment is deadly to terrestrial organisms, which evolved under enormously more benign conditions beneath a thick ozone layer.

Second, the Viking landers found not only no unambiguous evidence of life, but no soil organic matter at the level of about one part per billion. The organic matter sought by the Viking landers cannot be present because of the action of ozone and atomic oxygen. The UV flux at the surface of Mars is capable of destroying DNA and disrupting protein structure. Any organism adapted to life on Mars would be optimized for temperature, radiation, and chemical conditions that do not occur and never have occurred on Earth since the time of the origin of life. The idea that such organisms could even survive in Texas is bizarre. The idea that they would be biochemically compatible with terrestrial life and capable of infecting humans or other life forms is so astronomically improbable that it does not even bear serious discussion.

Finally, there is the very strong evidence that the SNC meteorites originated on Mars, from which they were ejected by hypervelocity impacts. For every multi-kilogram SNC meteorite rock ejected by an impact, vast numbers of smaller regolith particles are also thrown into space. The celestial mechanics of sweepup of such particles by the terrestrial planets is rather well understood: those particles that are ejected (or perturbed) into Earth-crossing orbits have nearly a 50% chance of falling on Earth as micrometeorites. Those that find themselves in nearly circular obits near Mars will spiral in toward the Sun under the Poynting-Robertson force, until they eventually encounter Earth. Micrometeorites, because of their very high surface:volume ratios, survive entry with relatively modest thermal alteration. Thus Earth has been "seeded" with vast quantities of Mars surface material. (The reverse is almost impossible because of the very high escape velocity of Earth.) If, contrary to all reason and evidence, there are

soil microorganisms on Mars today, then they have already been delivered to Earth in astronomical quantities by natural processes, falling indiscriminately on the polar regions, dry deserts, oceans, tropical foests, arctic tundra, and farm land. A few more kilograms of material carefully sequestered in laboratories could not reasonably cause a meaningful increase in the hazard.

Phobos and Deimos

The easiest form of Martian sample to return to Earth is unquestionably regolith material from one of the Martian moons. Viking Orbiter tracking and photometric data suggest that both bodies are composed of a very dark, primitive material with a density characteristic of carbonaceous chondrites. Return of material from either of these satellites to Earth is energetically and technically less demanding than automated return of lunar samples. The latter capability was developed in the late 1960s by the Soviet Union, at that time laboring under a very serious handicap of inferior basic technology. An automated Phobos or Deimos sample return in the 1990s should not stretch the capabilities of even NASA.

At the very least, the Martian moons will provide us with samples of volatile-rich primitive preplanetary materials. With the exception of the near-Earth asteroids, these bodies are easier to sample than any other bodies in the Solar System. The present population of near-Earth asteroids must have been collected from a very wide range of heliocentric distances. There is a chance that the Martian moons may possibly sample the raw material out of which Mars formed.

Since both the Soviet Union and the United States are, after gaps of fifteen years, resuming the exploration of the Mars system, we need to consider not only the scientific significance of being able to study a sample of the raw material out of which Mars formed, but also the practical role of these satellites in the exploration of Mars. Studies done at JPL indicate that the extraction of water from the carbonaceous regolith of Phobos should provide an inexpensive source of hydrogen and oxygen propellants for use by manned expeditions within the Mars system and for return to Earth. Very large reductions in launch costs can be realized by the use of propellants manufactured in space. Thus the chemical and physical characterization of the material of Phobos and Deimos may be a crucial part of making a manned Mars mission economically acceptable.

In summary, a sample return program that concentrates only on Mars, to the exclusion of its much more accessible and primitive satellites, makes little sense. An earlier, easier satellite mission, with its promise of making future, more ambitious missions to the surface of Mars much more practical, could and should be done first. It provides the incentive for developing much of the hardware and knowhow needed for a Mars sample return, is much simpler to execute, and is clearly not a dead end. The desire to sample primitive material in the

terrestrial planet region, frustrated by the discovery of the highly differentiated nature of the Moon by the Surveyor landers in the 1960s, can now be focussed very sharply on these two moons. No other body in the inner solar system is both small enough to avoid differentiation and in an orbit that assures that it has actually been in the inner Solar System since the era of planetary formation.

The requirements for handling Phobos or Deimos samples are also much less stringent than for the most volatile-rich Mars samples. Vacuum storage at the mean daytime temperature of one of these very black moons would require a bare minimum of thermal control. Sterilization would of course not be advocated by even the most ardent xenobiophiles.

The Soviets are aware of the attractions of Phobos and Deimos. The 1988 Phobos mission represents an investment of close to a billion rubles in their study. The American program wholly omits any mention of them. In fact, there is a good chance that Mars Orbiter will literally fly between these moons for several months, before settling down into its final close Mars orbit, without even bothering to look at them. The reason for this short-sightedness is incomprehensible.

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

9 June 1987

Dr. James L. Gooding
Code SN2/Curatorial Branch
Planetary and Earth Science Div.
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

In response to your request for input for a Mars Sample-Science document, I make the comments below. These are written solely from my perspective as a trace element (ppm-ppt levels) analyst of siderophile, chalcophile and lithophile mobile elements that track geochemical processes involving mild to strong heating. Most of these elements can only be determined by radiochemical neutron activation analysis (RNAA).

With regard to your first question, it is only through analysis of returned samples that we can establish the geochemical and thermal history of Mars (or any planet). Remote analysis can give approximate major element compositions and identify, perhaps, whether a basaltic or other type surface is present but that is about it. Trace elements are present only in small proportions: if they are fractionated by a process, a small absolute change caused by it will result in a large relative change. Naturally, to determine those low concentrations, returned samples must be used. Analysis of a single sample can give broad generalities but, by analyzing a number of samples of different types for various trace constitutents, one can determine compositional trends and infer detailed genetic processes.

As an illustration, consider the shergottites which, after all, are of putative Martian origin. I attach the abstract and Table 1 from our recent consortium paper (Laul et al., GCA 50 909, 1986). The right-hand (very short) column in Table 1 gives the Viking data (remote lander): the other long columns give results of laboratory measurements of Shergotty. From the Shergotty data alone, one can deduce only that it's volatile-rich. (One can do petrology and chronology but I'm speaking only of chemistry.) By comparing Shergotty data with results for other shergottites, one can begin to unravel the complex history of the SPB (see abstract). The kinds of measurements done in this work and their interpretation (right or wrong) just cannot be done in any other way.

Now to your 2d question, sample kind and quantity. Consider the lunar meteorites, each of which weighed 30-50 grams and the amount of information they contained. We can certainly get by with such samples, or, if necessary, much smaller ones (at some risk because of biased sampling). After all, only about 1 g of each was used up by Consortium members. A 50 g sample and lots

CHEMISTRY BUILDING • WEST LAFAYETTE IN 47907-3699

of smaller ones of various types would be minimal. I assume that sampling would be done by unmanned probe, in which case, it may not be possible to select specimens too carefully. About the best that could be done would be to visit several different sites and terrain types. One regolith core would be useful but samples mainly should be surface chips. I would opt for samples never exposed to Martian water, to those in the eroded zones and impact ejecta.

Since I believe that we already have Martian material on Earth (in the form of shergottites, at least), returned samples should not be degraded further. If Earth were going to be contaminated by Martian material, it already has been on several occasions. Assuming that samples to be sterilized, treatment with radiation would be least objectionable provided that this could be done without powdering the sample or otherwise altering its physical form. Heating (under dry conditions) could be done for a few hours without affecting us too badly. A temperature of $\leq 300^{\circ}C$ should be OK for us. On the other hand, such heating will affect light element isotopes. I cannot imagine how other techniques could be productive. Above all, chemical sterilization must be avoided from our standpoint.

As might be deduced from my remarks relative to question 1, there is no known in situ Martian measurement to replace information lost during sterilization. It is this plus the absence of any evidence that sterilization is warranted, that causes me to argue against this practice.

I trust that these remarks are useful and I apologize for not having provided the information sooner. I was involved with an NSF renewal proposal.

With best regards,

Michael E. Lipschutz
Professor of Chemistry

MEL/gs

Yale University

Department of Geology and Geophysics
Kline Geology Laboratory
P.O. Box 6666
New Haven, Connecticut 06511-8130
U.S.A.

Campus address
Kline Geology Laboratory
210 Whitney Avenue
Telephone
203 432-3114

March 30, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding

In response to your request for comments on a Mars sample return I would like to respond to your questions from an experimental petrologist's point of view.

(1) Through high-pressure melting experiments on silicate liquid compositions an experimental petrologist can constrain the composition of minerals in the planetary interior and estimate the depth of melting.

(2) In order to determine the appropriate liquid compositions on which to conduct these experiments, it is necessary to have conducted a thorough petrographic examination of igneous samples including microprobe analysis over and above bulk chemical analysis. Only if the igneous sample is very fine-grained or glassy and free of phenocrysts can its bulk composition be safely assumed to that of a quenched liquid. Otherwise further petrographic/microprobe analysis is required to establish the efficacy of the bulk composition as a liquid composition. This sort of sample analysis requires a terrestrial sample return.

If the retrieved samples are fine-grained basalts, then samples on the order of 2-3 cm are probably adequate. If samples happen to be coarse-grained cumulates or are breccias, then 2-3 cm sized samples are likely to cause important uncertainties regarding homogeneity. The sample return capacity should be designed to suit the sampled terrain: volcanic flows should yield fine-grained samples, whereas the ancient cratered terrain may, by analogy with the Moon, yield coarse-grained cumulates and breccias.

(3) Temperatures on the order of 200 - 300°C for a day or two should not be a problem.

(4) In situ bulk chemical analyses of soil samples should be carried out and compared with terrestrial-based analyses in order to establish ground truth for remote sensing analyses, which should expand our knowledge of Mars-wide volcanic compositions.

I hope these comments are of some help. I appreciate the effort you are making to keep the sample return gears moving.

Sincerely,

John Longhi
Associate Professor

INPUT TO MARS SAMPLE-SCIENCE DOCUMENT

Rocco L. Mancinelli
Mail Stop 239-12
Solar System Exploration Branch
NASA-Ames Research Center
Moffett Field, CA 94035

INPUT TO MARS SAMPLE-SCIENCE DOCUMENT

The record of the origin and early evolution of life on Earth has been erased by extensive surface activity. On Mars, however, large fractions of the surface date back to this early time period. Beneath the surface, Mars may very well contain the best preserved record of the events that transpired on the early terrestrial planets. Consequently, it is entirely possible that even if no life exists on Mars today, it holds the better record of the chemical and biological events which may have led to the origin and early evolution of life.

Understanding the geochemical cycling of the biogenic elements (C, H, N, O, P, S) and their compounds (*e.g.* CO_2, H_2O, NO_x) on early Mars, as recorded in a possible Martian sediment, would provide a useful tool in understanding biological evolution. Isotopic signatures are used to understand early Earth and to analyse the interaction between biological and abiological chemical cycles (see *e.g.* Schidlowski *et al.*, 1983; Knoll *et al.*, 1986). Of primary interest is the fractionation of the heavy isotope of carbon, ^{13}C, with respect to the common isotope, ^{12}C. Biological metabolism of CO_2 preferentially selects the lighter isotope. In Earth sediment, there is a distinct difference between the isotopic composition of carbonate carbon and that of organic carbon i.e., the lighter ^{12}C isotope is more abundant in organic carbon (Schidlowski *et al.*, 1983). The pattern of isotopic variation among hydrocarbons of increasing carbon number can be used to infer the nature of their formation (DesMarais *et al.*, 1981), including abiotic processes. The source of diagenic carbonates formed during decomposition of organic matter (abiotic as well as biotic) can be inferred from their isotopic ratios (Irwin *et al.*, 1977). Typically, carbonates have $\delta^{13}C$ values ranging from $\sim$ -2 to +2 ‰, whereas organics found in sediment depleted in ^{13}C have typical $\delta^{13}C$ values of $\sim$ -27 $\pm$ 7‰ (Schidlowski *et al.*, 1983; Knoll *et al.*, 1986).

We know that the current Martian CO_2 ^{12}C:^{13}C ratio is 90‰ (Owen *et al.*, 1977). However, we do not know the value of $\delta^{13}C$ for carbonates that might be buried beneath the Martian surface. The abundance of ^{13}C may vary in both carbonate minerals and any organic material that may be found. Such variations can be primary (reflecting changes in the carbonate that was deposited)

or secondary (reflecting biological processing of organic material, precipitation and mixture of new carbonates, or isotopic exchange with species in solution). Consequently, some method for distinguishing primary and secondary effects must be used. To accomplish this directly is difficult at best for Earth samples (Brand and Veizer, 1981), and because of our limited knowledge of Mars impossible, for any Martian samples, even if organic-C and carbonate exist on that planet. However, there are no secondary processes that always cause a shift in the isotopic compositions of carbonate and organic carbon in the same direction, at the same rate. Instead, secondary processes usually alter the isotopic composition of either organic carbon or carbonate carbon, but not both (Hayes, 1983; Irwin *et al.*, 1977). The magnitudes of such shifts are controlled by different and unrelated factors (Knoll *et al.*, 1986). Formation of carbonate from CO_2, and synthesis of organic material are primary processes that usually maintain a constant isotopic difference between carbonate and organic carbon. The resolution between primary and secondary isotopic variations can be accomplished by comparing the $\delta^{13}C$ of carbonate carbon with that of organic carbon from samples taken as a depth profile, as well as from different sites (Knoll *et al.*, 1986; Schopf, 1983).

The $\delta^{15}N$ within the Earth's environment is not constant. Slight variations in the natural abundances of ^{15}N and ^{14}N occur during abiotic and biotic nitrogen transformations (*e.g.*, Junk and Svec, 1958; Hauck, 1973, Hauck and Bremner, 1976; Wada and Hattori, 1976, 1978; Saino and Hattori, 1980; Sweeney and Kaplan, 1980; Wada, 1980; Letolle, 1980; Bremner and Hauck, 1982; Kohl and Shearer, 1980; Delwiche *et al.*, 1979). Biological processing of nitrogen does not result in a consistent isotopic shift of nitrogen in a particular direction, like that of carbon. For example, biological nitrification results in ^{15}N depleted NO_3^-, whereas biological denitrification results in ^{15}N enriched NO_3^- (Hauck and Bremner, 1976; Bremner and Hauck, 1982). Consequently, isotopic shifts of nitrogen are difficult to interpret without some knowledge of the system. However, on Mars we do have some knowledge of the system. The isotopic variation of N ($^{15}N/^{14}N$) on Mars, in particular, is interesting because the isotopic ratio is believed to have varied monotonically with time, enriching the atmosphere with the heavier isotope (McElroy *et al.*, 1977; Fox and Dalgarno, 1983). This preferential atmospheric escape of ^{14}N compared to ^{15}N is the only isotopic fractionation of nitrogen postulated. This can be accounted for by the apparent lack of long term recycling of atmospheric constituents. Hence, the N isotopic ratio of compounds within the sediment would have undergone few transformations, and may reflect the time of their incorporation. Significant deviations from the predicted isotopic ratio would indicate here-to-fore unknown perturbations to the system, possibly biological in origin. Banin and Navrot (1979) suggested that fixed nitrogen and organic carbon are key elements that are enriched through biological processes above their natural geochemical abundances. Therefore, they may be indicators of biological activity in possible Martian sediment. The feasibility of identifying biological marker organic compounds, such as kerogen material (Hayes *et al.*, 1983; Rullkötter *et al.*, 1985), must also be considered important.

Sulfur is an important biogenic element comprising approximately 0.1% dry weight of organic material. Biological cycles of sulfur, such as the reduction of sulfate to sulfide in anaerobic environments and the oxidation of sulfides in aerobic environments, have distinct isotopic effects on the relative concentrations of ^{34}S and ^{32}S. Tracking these isotopic changes through the Earth's fossil record seems to be correlated to major changes in the atmosphere and the biogeochemical cycling of sulfur (Schidlowski *et al.*, 1983). The soil of Mars is known to be rich in sulfur, in forms which may be, or have been, available to a biological system (Clark, 1979). In addition, other compounds and elements such as P, PO_4^{2-}, O, and O_2 are important to exobiology and may have been, or currently are, important to Mars.

Another important determination would be that of possible organic composition of the sample. No organic compounds were detected in the Martian regolith by the Viking lander gas chromatograph/mass spectrometer, whose limits of detectability were less than parts per billion for heavy organics and parts per million for light organics (Biemann *et al.*, 1977). In fact, the concentration of organics appears to be less than expected merely from the influx of carbonaceous chondrites (Mazur *et al.*, 1978; Biemann *et al.*, 1976, 1977). The inability to detect organic compounds in regolith samples does not itself exclude the possibility of organics existing beneath the surface. In fact, Yung and Pinto (1978) have shown that vast amounts of hydrocarbons may have been produced on primordial Mars. Furthermore, the production of organic matter from CO_2 in the presence of ultraviolet light and ferrous iron was reported by Getoff (1962) and supported by Baur (1978). In addition, Tseng and Chang (1974) found that ultraviolet light can produce formic acid from a mixture of CO_2 and H_2O at temperatures as low as 200 °K. The primary question is, does organic matter exist beneath the Martian surface or anyuwhere on the immediate surface.

As a consequence it would be very desirable to determine what types of C, N, and S com-

pounds exist within the Martian soil as well as their isotopic composition. In addition, direct analysis of samples returned to Earth would provide the most effective means for searching for micro-fossils within the sample.

It would be highly desirable to obtain samples as undisturbed cores collected from as many sites as possible. However, the measurements discussed above only require a few mg of sample for the various analyses. Sub-samples of the core should be collected every few mm or cm to determine the depth-profile of the biogenic elements and their compounds.

Important biological compounds are all very sensitive to heat, as well as different types of radiation. There is no lower temperature requirement, however the upper temperature limit should not exceed the *in situ* maximum. This temperature maximum will vary depending upon the location and depth at which the sample is collected. As a guideline maximum limit the temperature of the sample should not exceed 100° C, or kept lower if possible. The samples should be protected from exposure to strong radiation.

Because of the instability, or volatility of certain types of biologically important molecules some measurements should be made *in situ* on the Martian surface or this information would otherwise be lost. One of the most important of these is water potential. Regolith samples collected at the two Viking lander sites were found to contain approximately 1-3% H_2O, by weight, when heated in a step-wise fashion to 500° C. Most of the water was released between 200° - 300° C, indicating the presence of mineral hydrates of low to moderate thermal stability (Biemann *et al.*, 1977; Anderson and Tice, 1979). In addition, duricrust was found at one of the Viking lander sites indicating the possibility of the presence of hygroscopic minerals on Mars. Water vapor measurements made by the Viking orbiter indicated that the water content of the atmosphere fluctuated as a function of geographic location, topography, season, and time of day, with the maximum being 100 precipitable micrometers in the North Polar region during mid-summer (Farmer *et al.*, 1976, 1977). With the exception of the North Polar region, which is thought to be at saturation (Farmer *et al.*, 1976, 1977), the relative humidity at the surface of the remainder of the planet is unknown. It is of great exobiological importance to determine the water potential (the free energy of water in a system) within the Martian regolith.

Other important measurements that should be made on the Martian surface include those involving adsorbed gases and other volatile compounds. For example, it has been shown from data obtained by the Viking mission that certain gas molecules especially CO_2 become adsorbed onto particles of the Martian regolith. It is also possible that various gases such as N_2, O_2, or N_2O may be adsorbed onto surface regolith particles. It would be necessary characterize the different gas and volatile species that are adsorbed onto the particles, or trapped in pores beneath the surface.

1 References

Anderson, D. M., and A. R. Tice, The analysis bof water in the Martian Regolith. *J. Molec. Evol.* **14**, 33-38 (1979)

Banin, A. and J. Navrot, Chemical Fingerprints of Life in Terrestrial Soils and Their Possible Use for the Detection of Life on Mars and Other Planets. *Icarus* **37**, 347-350 (1979)

Baur, M.E., Thermodynamics of heterogeneous iron carbon systems: Implications for the terrestrial primitive seeking atmosphere. *Chem. Geol.* **22**. 189-206 (1978)

Biemann, K., J. Oro, P. Toulmin III, L.E. Orgel, A.O. Nier, D.M. Anderson, P.G. Simmonds, D. Flory, A.V. Diaz, D.R. Rushneck, and J.A. Biller, Search for organic and volatile inorganic compounds in two surface samples from Chryse Planitia region of Mars. *Science* **194**, 72-76 (1976)

Biemann, K., J. Oro, P. Toulmin III, L.E. Orgel, A.O. Nier, D.M. Anderson, P.G. Simmonds, D. Flory, A.V. Diaz, D.R. Rushneck, J.A. Biller, and A.L. LaFleur, The search for organic substances and inorganic volatile compounds in the surface of Mars. *J. Geophys. Res.* **82**, 4641-4658 (1977)

Brand, U., and J. Veizer, Chemical diagenesis of a multicomponent carbonate system. 2. Stable isotopes. *J. Sedim. Petrol.* **51**, 987-997 (1981)

Bremner, J.M., and R.D. Hauck, Advances in methodology for research on nitrogen transformations in soils. In: ***Nitrogen in Agricultural Soils***, F.J. Stevenson, *ed.*, pp. 467-502, American Society of Agronomy, Madison, Wisconsin (1982)

Clark, B.C., and A.K. Baird, Volatiles in the Martian Regolith. *Geophys. Res. Lets.* **10**, 811-814 (1979)

DesMarais, D.J., J.H. Donchin, N.L. Nehring, and A.H. Truesdell, Molecular carbon isotope evidence for the origin of geothermal hydrocarbons. *Nature* **292**, 826-828 (1981)

Delwiche, C.C., and P.L. Steyn, Nitrogen isotope fractionation in soils and microbial reactions. *Environ. Sci. Technol.* **4**, 929-935 (1970)

Farmer, C. B., D. W. Davies, and D. D. LaPorte, *Science* **193**, (1976).

Farmer, C. B., D. W. Davies, A. L. Holland, D. D. LaPorte, and P. E. Doms *J. Geophys. Res.* **82**, (1977)

Fox, J.L. and A. Dalgarno, Nitrogen escape from Mars. *J. Geophys. Res.* **88**, 9027-9032 (1983)

Getoff, N., Reduktion der Kohlensäure in Wässeriger Lösung unter Entwirkung von UV-Licht. *Z. Naturforsch B: Anorg. Chem., Org. Chem., Biophys., Biol.* **17**, 87-90 (1962)

Hauck, R.D., Nitrogen tracers in nitrogen cycle studies - past use and future needs. *J. Environ. Qual.* **2**, 317-327 (1973)

Hauck, R.D., and J.M. Bremner, Use of tracers for soil and fertilizer nitrogen research. *Adv. Agron.* **28**, 219-266 (1976)

Hayes, J.M., I.R. Kaplan, and K.W. Wedeking, Precambrian organic geochemistry, preservation of the record. In: *Earth's Earliest Biosphere; Its Origin and Evolution*, J.W. Schopf *ed.*, pp. 93-134, Princeton University Press, New Jersey, (1983)

Hunten, D., Possible oxidant sources in the atmosphere and surface of Mars. *J. Mol. Evol.* **14**, 57-64 (1979)

Irwin, H., C. Curtis, and N. Coleman, Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature* **269**, 209-213 (1977)

Junk, G., and H.S. Svec, The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. *Geochim. Cosmochim. Acta* **14**, 234-239 (1958)

Knoll, A.H., J.M. Hayes, A.J. Kaufman, K. Swett, and I.B. Lambert, Secular variation in isotope ratios from uppr proterozoic successions of Svalbard and east Greenland. *Nature* **321**, 832-838 (1986)

Kohl, D.H., and G. Shearer, Isotopic fractionation associated with symbiotic N_2-fixation and uptake of NO_3^- by plants. *Plant Physiol.* **66**, 51-56 (1980)

Letolle, R. ^{15}N in the natural environment. In: *Handbook of Environmental Isotope Geochemistry*, P. Fritz and J. Ch. Fontes *eds.*, pp. 407-443, Elsevier, Amsterdam (1980)

Mazur, P., E.S. Barghoorn, H.O. Halvorson, T.H. Jukes, I.R. Kaplan and L. Margulis, Biological implications of the Viking mission to Mars. *Space Sci. Rev.*, **22**, 3-34 (1978)

McElroy, M.B., T.Y. Kong, and Y.L. Yung, Photochemistry and evolution of Mars' atmosphere: A Viking perspective, *J. Geophys. Res.* **82**, 4379-4388 (1977)

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)

Rullkötter, J., B. Spiro, and A. Nissenbaum, Biological marker characteristics of oils and asphalts from carbonate source rocks in a rapidly subsiding graben, Dead Sea, Israel. *Geochim. Cosmochim. Acta* **49**, 1357-1370 (1985)

Saino, T., and A. Hattori, ^{15}N natural abundance in oceanic suspended particulate matter. *Nature* **283**, 752-754 (1980)

Schidlowski, M., J.M. Hayes, and I.R. Kaplan, Isotopic inferences of ancient biochemistries: Carbon, sulphur, hydrogen, and nitrogen. In: *Earth's Earliest Biosphere; Its Origin and Evolution*, J.W. Schopf (ed)., pp. 149-186, Princeton University Press, N.J. (1983)

Schopf, J.W., editor *Earth's Earliest Biosphere; Its Origin and Evolution* Princeton University Press, N.J. (1983)

Sweeney, R.E., and I.R. Kaplan, Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chem.* **9**, 81-94 (1980)

Tseng, S.S., and S. Chang, Photo-induced free radicals on a simulated Martian surface. *Nature* **248**, 575-577 (1974)

Wada, E., and A. Hattori, Natural abundance of ^{15}N in particulate organic matter in the north Pacific Ocean, *Geochim. Cosmochim. Acta* **40**, 249-251 (1976)

Wada, E., and A. Hattori, Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. *Geomicrobiol.* **1**, 85-101 (1978)

Wada. E., Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In: *Isotope Marine Chemistry*, E.D. Goldberg, Y. Horibe, and K. Saruhashi (*eds.*,) pp. 375-398, Uchida Rokakuho, Tokyo, Japan (1980)

Yung, Y.L., and J.P. Pinto, Primitive atmosphere and implications for the formation of channels on Mars. *Nature* **273**, 730-732 (1978)

JUL 7 1987

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY, B-017
LA JOLLA, CALIFORNIA 92093

July 1, 1987

Dr. James L. Gooding
SN2
NASA/Johnson Space Center
Houston, TX 77058

Dear Jim:

This is in response to the recent reminder regarding input to a Mars sample document. The expected contributions by our group to the study of Mars will be along two lines of research:

(1) Evolution of the martian surface, crater ages, erosion and transport phenomena based on the irradiation history of selected well documented returned samples.

(2) The volatiles (N_2, noble gases, extinct radioactivities) and the evolution of Mars and its atmosphere. This will require gas, soil and rock samples, and if possible subsurface gas samples taken by a coring device.

The atmosphere of Mars causes an attenuation of the primary cosmic ray flux which is minor for galactic cosmic rays, significant for solar cosmic rays and is shielding the solar wind. Using techniques already developed for the study of the lunar surface, we will attempt to investigate the exposure history of Mars, crater ages, ages of lava flows, their erosion and vertical and lateral transport phenonema. In addition to the techniques already at hand, we will explore new methods using noble gas radioisotopes and secondary neutron effects. These attempts will depend on the availability of novel instrumentation which still needs to be developed. The planning of rover trips, the design of a coring device and sample documentation will be most critical.

If we assume, as some people like to do, that the EETA 79001 data do provide some information on the gas inventory of Mars, then the discrepancies in isotopic signatures between the glass and igneous phases would indicate isotopic disequilibrium. The time/space evolution should be explored by coring both regolith and bedrock material, which in turn may possibly be correlated with siotopic signatures from (vesicular?) samples from different formations.

I will be glad to provide more specific input regarding our sample requirements at a later date.

Sincerely yours,

Kurt Marti

KM/fk

JUL 2 1987

June 30, 1987

To: Jim Gooding/SN2

From: Gordon McKay/SN4

Subj: Mars Sample Requirements

Operating in reaction mode, I find that today is the deadline for input to your Mars Sample-Science Document, so here goes.

I am primarily interested in the magmatic evolution of Mars, and the chronology thereof. Questions of interest to me include the composition and evolution of the martian mantle, and the production of magmas from that mantle. These questions can be best addressed by returned samples of fresh, unweathered, primitive basalt.

From such material it may be possible, through high pressure phase equilibrium studies, to determine the depth of origin and the nature of the mineral assemblage in the basalt source region. It may also be possible through isotopic studies to determine the time of crystallization of the basalt, and the initial isotopic ratios of Sr, Nd, Hf, and possibly other elements. This information will give clues to the evolution through time of the martian mantle.

The principle mass requirements for phase equilibrium studies are that the sample be large enough to be representative of the melt from which the basalt crystallized. Larry Haskin can tell us more about how large such a sample should be, but in part it depends on grain size. It is difficult to put a hard number on mass, but a few grams of a medium- to fine-grained basalt would probably be adequate. The sample should have remained a chemically closed system (Oops! I got interrupted by some sort of fire, and now find that it is July 2. Maybe you will consider this letter, even though it is after your deadline.) since it crystallized, so that the melt composition can be accurately determined.

Chronological studies require a very similar sample. An additional requirement is that it should not have been subjected to thermal or shock metamorphism... look at the problems we have had dating the shergottites.

Sample handling would have to be pretty severe before the studies outlined above would be compromised. It might be best for chronological studies to keep the temperature from getting too high, but 100°C is probably OK. Experimental studies would not be affected by any reasonable T.

Little information about these samples would be degraded by handling, so other than normal sample documentation, no *in situ* measurements are needed for the studies outlined above.

The Florida State University
Tallahassee, Florida 32306-2043
Department of Biological Science
Polar Desert Research Center

JUN 22 1987

June 17, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

The principal investigator of our NASA funded research, Prof. E. Imre Friedmann, is on sabbatical in Kiel, West Germany, and will not return until the end of August, 1987.

In order to contribute to and to meet your production schedule of the Mars Sample-Science Document, I am writing in Dr. Friedmann's stead.

Enclosed is a reply to your "call for input" and, for your information, the following synopsis of our research. In extreme hot and cold deserts, microorganisms live sheltered within the pore spaces of sandstone rocks. Metabolic activity creates a characteristic pattern in the rock, and, at least in Antarctica, the once colonized rock may become silicified. This process preserves the characteristic biological-weathering pattern and thereby forms a trace fossil of previous microbial activity. Our study of cryptoendolithic microorganisms and trace fossil formation may aid the search for evidence of past life on early Mars.

I hope the needed information is provided in the enclosed reply, and, if any questions arise, please call.

Sincerely,

Michael A. Meyer, Ph.D.
Associate Director

MARS SAMPLE-SCIENCE DOCUMENT

1) Did life ever develop on Mars? This question can be addressed by:

   a) searching for trace fossils indicative of previous microbial activity,

   b) returning trace-fossil sub-samples for analyses, including:

      i) light and electron microscopy for identification of possible cellular structures

      ii) chemical analysis, with emphasis on microdistribution, as evidence of biological activity

      iii) interactive study of sub-samples, with experiments designed to develop a scenario of physical-chemical processes that may account for patterns observed.

2) The samples needed would be from rocks (probably porous) that exhibit a pattern unaccounted for by physical or chemical processes. The returned sample, approximately 1 cm^3, should preserve vertical and horizontal gradients that demarcate the observed pattern. Several samples may be needed to acquire all constituents of the pattern. More importantly, finding evidence beyond an unexplained pattern may require additional samples to increase the probability of finding fossil remnants of possible organisms.

3) The characteristic pattern of colonized Antarctic rocks is resistant to temperatures of at least 400°C. However, we have no expectations as to what compounds may contribute to a recognizable trace fossil on Mars. Also, the same procedure designed to insure sterilization may, in fact, destroy complex compounds and higher ordered structures that would be indicative of previous life. Therefore, sample return should be designed to maintain <u>in</u> <u>situ</u> sampling conditions.

4) Measurements made <u>in</u> <u>situ</u> should include analysis of pattern constituents and documentation of pattern orientation in the parent rock and sub-samples.

JUN 17 1987

DFVLR Deutsche Forschungs- und Versuchsanstalt
für Luft- und Raumfahrt e.V.

Forschungsbereich Nachrichtentechnik und Erkundung
Institut für Optoelektronik
Institutsdirektor Professor Dr. F. Lanzl

DFVLR Oberpfaffenhofen 8031 Weßling

8031 Weßling
Telefon Sammel Nr. [illegible]
Telex [illegible]
Telegramme DFVLR 8031 Oberpfaffenhofen

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058
USA

Ihr Gesprächspartner: Dr. G. Neukum
Hausanschluß 26: 731

Unser Zeichen AZ: NE-OE-PE
Datum: 12 June 1987

Mars Sample Science Input
Ref.: Circular letters of 10 February 1987 and 27 May 1987

1) Among the aspects of martian history that can uniquely or best be addressed by direct analysis of samples returned to earth are

(i) determining absolute ages from radiometric measurements and combining those measurements with dating information from cratering data, in order to firmly establish the martian cratering chronology (as was done similarly for the earth's moon from Apollo data) and hence to be able to determine absolute ages from martian crater statistics for any surface unit globally

(ii) obtaining "ground truth" data from martian samples in the lab and in situ measurements at the landing sites for the interpretation of orbital remote sensing data; i.e. measuring the photometric and spectral properties from UV to mid infrared of returned martian soil and rocks in the lab and of soils and rocks at the landing or roving sites and comparing those data with orbital data. Only in this way can we get close to a quantitative understanding of the reflectance behavior of the different martian rock units and hence to a quantitative interpretation of the physical, mineralogical/petrological and chemical properties of martian surface rocks and of the weathering and other alteration processes that have acted on them.

2) The types and quantities of samples needed to support the above analyses are whole rocks, fine materials (soils), and (desirably) unchanged pieces of the uppermost "duricrust". Rocks of different weathering states are needed from specific areas.

For the dating goal, rocks should be as pristine as possible from a geologically simple area with a (desirably) one-stage emplacement history of the local formation. We need as a minimum at least one highland site for old ages, one (better two or more) intermediate-aged sites (Lunae Planum age to northern plains ages), and one very young one (Tharsis volcanoes or young surrounding plains).

For the photometric/spectroscopic goal samples should be returned over a wide range of different geological regions and physically different materials, such as blocks of hard, consolidated rocks (both fresh and weathered) or assorted loose, particulate materials (soils, alluvial fans, dune materials, wind-blown and impact-derived debris including various types of soil forming crusts) which provide ground truth for comparison with the remote measurements of the morphological, physical and chemical properties of the martian surface. An appropriate candidate is the Oxia Palus Quadrangle where the surface displays a wide variation in color, albedo and thermal properties. Sampling in this area would help to decide whether the surficial units may be used to characterize the bedrock geology or whether they are completely decoupled from the underlaying bedrock. For this area enough Viking orbiter images exist from which numerical values of the photometric parameters can be derived which best explain the remotely sensed reflectances.

3(The average scattering behavior of rough particulate surfaces depends on many physical properties of the individual surface particles, such as size, shape, refraction index, internal structure, the occurrence of inclusions of other particles, absorptivity, how these particles and clumps of particles are oriented in the uppermost scattering surface layer and how the regolith compacts with depth. In order to provide photometric calibration for the orbital remote measurements, acquisition of a typical soil sample with a representative size distribution (eolian fines to sand-sized particles) should be carried out without disturbing the textural characteristics and the vertical structure of the sampled surface. The environment imposed on the samples during return to Earth should maintain as closely as possible the temperature and pressure conditions which the sample experienced on Mars. Much potential information about particle compaction and textural surface characteristics will be lost by heating the sample and removing surface adsorbed water or melting interparticle water ice or frozen CO_2. Proper precautions are required to protect the samples from uncontrolled contamination by the terrestrial environment. Infiltration of H_2O into the pores of rocky surfaces, adsorption of small amounts of water by clay minerals, dissolving the cementing agents that hold the individual grains together, re-carbonation in a humid environment, compressing the pore volume by higher atmospheric pressure

will also affect the structural characteristics of the primary, dry silicate minerals. In addition to the above contamination effects, oxidation by the terrestrial environment will alter the chemical and mineralogical information, which is determined by spectral absorption features, i.e. oxidation will change the primary element ratios such as Fe^{2+}/Fe^{3+}. Moreover, alteration of the original soil sample will seriously affect the albedo of the single particles and severely limit the use of spectro-photometric measurements of the returned samples under laboratory conditions as calibrations for regional and global mapping efforts of the physical, elemental, and mineralogical characteristics of martian surface materials.

4) In situ measurements on Mars to supplement or replace information that might be lost from degraded samples should be (i) multispectal imaging of the soil and rock materials collected at the landing/roving sites and of the surroundings and (ii) in situ determination of their photometric and spectral properties and of the materials at the landing/roving sites in general by means of spectrophotometrically measuring the passively reflected sunlight in the range from UV to near (or desirably mid) infrared, possibly also by means of an active remote sensing experiment (tunable laser).

Oberpfaffenhofen, 12 June 1987

Gerhard Neukum
Head, Planetary Remote Sensing Section
Institute for Optoelectronics

StonyBrook

Astronomy Program
Department of Earth and Space Sciences
State University of New York at Stony Brook
Stony Brook, New York 11794-2100
telephone (516) 632-8221

APR 7 1987

March 30, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Dr. Gooding:

I am writing in response to your letter of the 10th requesting suggestions for a report on future Mars sample return missions.

My main request is that care be taken to acquire and preserve a sample of Martian atmosphere, and to collect rocks and soil with Martian atmosphere in an undisturbed state. The latter request could potentially satisfy the former; both are important.

Undisturbed Martian atmosphere should be analyzed for composition and isotope ratios, to improve on the Viking results. This experiment would also test the hypothesis that SNC meteorites indeed originated on Mars. To prevent chemical and physical reactions, the sample should be kept as close to Martian conditions as possible.

The advantage of bringing back soil and rocks in contact with the atmosphere is that it would then be possible to investigate the highly oxidizing character of the Martian soil that was discovered by the Viking biology experiments. Since the oxidizing agent(s) may be very unstable, this is another argument for preserving local conditions as carefully as possible.

As a precaution, since the atmospheric measurements are so important, I would personally favor bringing back a separate atmospheric sample in addition to the rocks + soil + atmosphere.

Sincerely,

Tobias Owen

TO:mo

NOV 23 1987

Date: Nov. 19, 1987

To: Jim Gooding
Steve Squyres
Mike Drake

From: David Paige

Re: Mars Polar Sample Cores

To aid you in getting your Mars Sample Return presentations and documents together, I've put together this list that outlines some of the points that were brought up at this week's workshop. It is by no means complete, but I hope you will find it useful.

1. SAMPLE LOCATION

Ice cores should be obtained at the north residual polar cap. The first priority would be to be obtain cores on level surfaces in areas that have not experienced significant rearosion. Cores from exposed layered deposits off the residual cap would also be highly desirable. The north polar area is preferred because 1) Available geologic data indicates the north polar terrains are younger, 2) The nature and physical properties of the north polar condensates are better understood than those in the south.

2. CORE CHARACTERISTICS

Cores to a depth of a few meters should provide significant information about Mars climate variations. The rates at which ice and dust are accumulating (or possibly eroding?) at the poles are presently not well constrained. If the polar caps have formed gradually over the entire geologic history of the planet, then a one meter core could sample over 1 million years of climatic history. If the caps have formed, or reformed recently, then a one meter core might contain as little as 10 thousand years of climatic history. Since the expected timescales for martian climatic oscillations range from 10 thousand to 1 million years, it might be desirable to obtain cores in areas where ice accumulation rates are low. This is especially true since per unit mass, the information content of the dust within the cores should be higher than the information content of the ice. Continuous cores would be highly desirable. Since rocks are not likely to be abundant, core diameters do not need to be very large.

3. THINGS TO MEASURE

A. On Mars

1. Dust content with depth
2. Ice grain morphology and size with depth

B. On Earth

1. Water ice isotopic composition with depth
2. Dust composition, abundance and morphology with depth
3. Short lived cosmogenic nuclide abundances in dust with depth (to estimate depostion rates)
4. Trapped atmospheric gas composition with depth
5. Other contaminants such as clathrates and organic matter
6. Whatever else you like

4. REQUIREMENTS FOR SAMPLE PRESERVATION

The big question here is whether to let the ice melt. It is common in terrestrial studies to subdivide frozen cores at regularly spaced intervals and put the individual pieces into separate sealed containers and then let the ice melt. This is certainly an option, although the science tradeoffs need to be explored more fully. Cores from the north polar cap must be kept at a maximum of 205K to preserve internal structure, since this is the maximum observed ice surface temperature during the summer season.

MAR 27 1987

DEPARTMENT OF PHYSICS

University of California
Santa Barbara, California 93106

Telephone (805) 961-3405

March 21, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

This is in reply to your letter of February 10, 1987. I will not be analyzing Mars samples upon their return, but I thought I might just suggest a few contraints on their collection that I believe should, if possible, be observed.

I think it is imperative that samples be retrieved from as wide a variety of terrains as possible. Otherwise, a single sample could lead to a limited interpretation of Mars history, or worse, a misinterpretation. What would we conclude about the Earth's history if all we had was a piece of oolitic limestone from Indiana? If the sample return is to be severely limited to one or two areas, I believe the return not to be worth the condiserable expense involved.

It would be desirable to return samples from as many volcanic constructs as possible, but I think a minimum return should be from three areas determined to be the youngest, oldest and somewhere in the middle from the crater counts. The dating of these samples would yeild both a crude time history of Martian volcanism and a much needed piece of ground truth concerning the history of the cratering flux at Mars.

Next it would be desirable to verify the former existence of liquid water on the surface by seeking samples of sedimentary rocks in likely places determined by the apparent stream topography.

It seems that we would have to have someone there with a means of rapid transport over great distances to do the sample collection properly. Such a requirement may preclude our ever having a good representation of Mars' surface rocks.

Sincerely Yours,

Stanton J. Peale

Stanton J. Peale
Professor of Physics

JUN 24 1987

United States Department of the Interior
GEOLOGICAL SURVEY
BOX 25046 MS 963
DENVER FEDERAL CENTER
DENVER, COLORADO 80225
Branch of Isotope Geology

June 22, 1987

Dr. James L. Gooding
SN2
Johnson Space Center, NASA
Houston, TX 77058

Dear Dr. Gooding:

This note is in reply to your letter regarding the Mars sample-science document.

As Drake et al. (1987) emphasized, the advantage of studying planetary returned samples instead of accepting in situ measurements cannot be overstated. A wider range of state-of-the-art analytical techniques with higher sensitivities and accuracies can be applied to returned samples. Measurements of U-Th-Pb, Sm-Nd, Rb-Sr, and Lu-Hf systematics for chronology of planetary specimens cannot be done in situ with desirable precision.

Drake et al. (1987) evaluated oxygen isotopes, noble gases, and siderophile trace element abundances for important measurements that would constrain theories regarding the assembly of the planets. I argue that the radiometric systems listed above, especially U-Th-Pb, can provide some vital information on the evolutionary history of the planetary body, because the U-Th-Pb system has three decay systems, two of which envolve U-Pb. Our group was the first to suggest that the Nakhla meteorite may be originated from a large planetary body, probably from Mars, based on U-Th-Pb, Sm-Nd, and REE abundances (Nakamura et al., 1982). Some detailed studies of SCN meteorites (e.g. Bogard and Johnson, 1983; McSween, 1985; Laul, 1986) strongly support a Martian origin for the meteorites.

SNC meteorites have distinctly low $^{206}Pb/^{204}Pb$ values between 12 and 15 (Nakamura et al., 1982; Chen and Wasserburg, 1986); whereas, those for the earth and the moon are 18-20 and 150-500, respectively. these values indicate that the SNC meteorites evolved in an unique environment of a low $^{238}U/^{204}Pb$ (μ) = 5 during the history of the solar system. This μ value is distinctly lower than that for the earth (8), the moon (50-100), and eucrites (100-150), which implies that the parent planetary body was rich in volatile elements compared to the earth, and may be Mars. The volatile-rich Mars interpretation, however, contradicts Anders and Owen (1977) who maintain that Mars is intrinsically poorer in volatiles than the earth (Chen and Wasserburg, 1986). As lead is a chalcophile element and could be removed to the Martian core as is often inferred from terrestrial basalts regarding the earth's core (^{206}Pb richer than the geochron), the smaller core of Mars may have been less effective in the removal of Martian Pb (Chen and Wasserburg, 1986). Detailed isotopic analyses of Martian samples would provide an unique opportunity to investigate this paradox.

Analytical techniques used in the study of U-Th-Pb, Sm-Nd, and Rb-Sr systematics have been improved tremendously during Apollo sample investigations. Expecting future improvements, analysis of three systematics

using only a few hundredths of a gram of returned Martian sample would provide ample information regarding the accretionary and evolutionary history of the planetary bodies of our solar system.

Sincerely yours,

Mitsunobu Tatsumoto

Wayne R. Premo

References

Anders E. and Owen T. (1977) Mars and Earth: Origin and abundance of volatiles. Science 198, 453.

Bogard, D. D. and Johnson, P. (1983) Martian gases in an Antarctic meteorite? Science 221, 651.

Chen J. H., and Wasserburg, G. J. (1986) Formation ages and evolution of Shergotty and its parent planet from U-Th-Pb systematics. Geochim. Cosmochim Acta 50, 955.

Drake, M. J., Boynton, W. V., and Blanchard, D. P. (1987) The case for Planetary sample return missions: 1. Origin of the solar system. Eos 105.
Laul J. C. (1986) The Shergotty consortium and SNC meteorites: An overview Geochim. Cosmochim. Acta 50, 875.

McSween, H. Y. (1985) SNC meteorites: Clues to Martian petrologic evolution? Rev. Geophy. 23, 391.

Nakamura,N., Unruh, D. M., Tatsumoto, M., and Hutchison, R. (1982) Origin and evolution of the Nakhla meteorite inferred from the Sm-Nd and U-Pb systematics and REE, Ba, Sr, Rb, and K abundances. Geochim. Cosmochim. Acta 46, 1555.

(GOLDEN JUBILEE YEAR 1986-87)

Phone: Off: 71961 33

Department of Geology
Osmania University
Hyderabad-500 007 (A. P.)

JUL 2 1987

Dr. A.S.P.Rao,

June [illegible], 1987

Dr. James L. Gooding,
Space Scientist,
NASA Johnson Space Center,
Houston, TX 77058,
USA.

Atten of: SN2 - 87 - L3[illegible] SN[illegible] - [illegible] - L[illegible]

Dear Dr. Gooding,

Thank you very much for your two letters and I submit the following in response to your letter.

A) Marchan rocks should be collected in order to determine the following:-

a) Age of the Marchan surface rocks

b) Petrographic of Martian surface rocks

c) Geochemistry and biochemistry of the Martian surface rocks

d) Weathering phenomenon on Martian surface leading to clues to the understadinding of climatic conditions on Mars.

B) Martian atmosphere should be collected and analysed to know the following:-

a) Isotopic ratios of $^{12}C/^{13}C$ and $^{14}N/^{15}N$

b) Interdependancy between martian atmosphere and its surface rocks.

c) Size and age of Mars and their effect on its atmosphere.

Thanking you very much for giving me this opportunity and looking forward for highly interactive environment.

Yours Sincerely,

(A.S.P.RAO)

JUL 1 1987

Albuquerque, June 8, 1987

Dr. J. L. Gooding

Mail Code SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim,

Thank you for your letter of May 27, 1987. I have to admit that this letter took me by surprise as I have regarded the earlier "dear-colleague" letter as an open invitation commonly used by the LPI to poll the interest in the subject. Well, I am certainly interested and the first letter has decorated my bulletin board where it has been visible ever since its arrival.

Up to this point my *only martian* involvement has been on shock metamorphism in ALHA 77005,21 and some familiarity with martian weathering processes. However, I possess no deep knowledge on martian geology and surface and atmospheric processes. I could probably contribute to science definition requirements of a martian sample return mission. On the other hand, and arguing from my ignorance, I suggest that the lunar experience probably provides a very good first-order scenario.

In summary, I do not see how I could meaningfully contribute to a Mars Sample-Science Document. Please do not hesitate to contact me if you are of a different opinion concerning this matter.

Sincerely Yours,

Frans

Frans J. M. Rietmeijer

Department of Geology
University of New Mexico
Albuquerque, NM 87131

(505) 277 - 2039

ORIGINAL PAGE IS
OF POOR QUALITY

National Aeronautics and Space Administration
Ames Research Center
Moffett Field, California 94035

MAR 04 1987

NASA

SSA:245-6

February 28, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Jim,

Thanks for sending me a copy of your call for input for the Mars sample-science document. While I don't consider myself to be an expert on Mars-related problems in general, I would like to take this opportunity to make a couple of brief comments.

One of the problems related to Mars that has always intrigued me is the classic "where's the CO_2?" question. While the standard answer is that it's locked up in carbonates, I have the impression that the formation process is somewhat uncertain. The uncertainty may be largely due to the fact that the inferred CO_3 deposits have not been identified on Mars. While carbonate formation usually involves water-related processes, I understand that gas phase reactions have also been suggested (see the diagrams at the end of the last page).

The result of such a gas phase reaction (if it happens) would not be a carbonate mineral in the normal sense, but could tie up CO_2. CO_3 anions made in this way are expected to have spectral properties that differ from classic carbonates since the bonding is different. Lou Allamandola and I are interested in this type of reaction since it may have important implications for grain-gas chemistry in interstellar clouds, and may explain part of the 6.8 μm infrared absorption around protostars. We're presently involved in several experiments in which we intend to address the formation of CO_3 from CO_2 "catalysis" on substrates like CaO, CaOH, Fe_3O_4, etc.

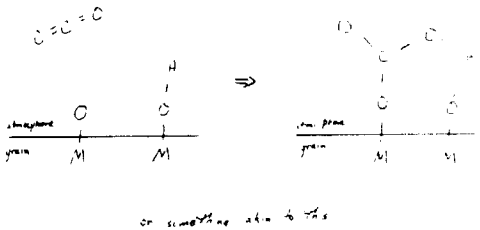
If this sort of reaction scheme turns out to be significant, it would be very interesting to examine any returned martian samples for evidence of this process. Infrared spectroscopy (the technique I'm most familiar with) offers one of the ways in which the samples could be examined for this effect. Various chemical tests could probably also be derived (I think one of the explanations for the excess CO_2 given off in the Mars life experiments was the production of CO_2 from surface corrolated CO_3, i.e. the reverse of the process I mentioned above).

In as far as they relate to this topic, I can answer the four questions you asked in the Call for Input. (1) The aspect of Martian history that can be address is the evolution of its atmosphere, specifically its loss of CO_2. (2) Since the process is a surface effect, the appropriate samples should maximize surface to volume ratios. This means that fine grain materials would probably be best (< 1 mm, 1-50 μm sized grains may be the most appropriate). The IDP community might be useful here. (3) I'm not sure what to say concerning sample degradation except that, being a surface process, the effect may be more easily lost than volume-related information. For this reason it would be desirable to minimize sample degradation, especially, I imagine, that due to high temperatures and high shock pressures. (4) If we were armed with the appropriate laboratory data, it might be possible to look for the spectral signatures of CO_3 "coatings" using a spectrometer onboard the lander. Simple onboard chemical experiments designed to remove CO_3 "coatings" could presumably also be designed. Pristine sample return is, of course, the desirable way to go.

I hope this is of some use to you. I wanted to keep this short since I'm not really a "Mars-expert" and because I suspect you are going to be deluged with "advice." However, if you have questions or comments please feel free to write or call me. My number is (415)-694-6849. Good luck!

Sincerely,

Scott Sandford
Research Astrophysicist



or something akin to this

ORIGINAL PAGE IS
OF POOR QUALITY

McMaster University
1280 MAIN STREET WEST
HAMILTON ONTARIO
CANADA L8S 4M1

Department of Geology
PHONE (416) 525-9140
TELEX 061-8347

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

July 3, 1987

Dear Dr. Gooding,

This letter is only intended to express our long-term interest in contributing to studies of returned Mars samples. We would be interested in carrying out studies of stable and radiogenic isotopes on rocks and soils, if such materials are made available. We are also doing studies of electron spin resonance in terrestrial materials, with the intention of learning about the history of ion bombardment and electron/hole trapping.

Please keep me posted on further announcements regarding this program. We do not wish to include any text material in the document under preparation.

Sincerely,

Henry P. Schwarcz
McMaster Isotopic, Nuclear and
Geochemical Studies group (MINGS)

cc: RH Mcnutt

A CENTURY OF DISCOVERY UN SIECLE DE DECOUVERTES

JUN 30 1987

BRITISH MUSEUM (NATURAL HISTORY)
Cromwell Road London SW7 5BD

Telegrams Nathemus London SW7
Telephone National 01-589-6323 Ext
International +441-589-6323

Your reference

Our reference

Date 18.6.1987

Dear Dr. Gooding,

Thank you for the invitation to participate in providing input to your Mars sample-science programme. My own expertise, however, is confined to the study of the morphology and classifiaction of the exoskeleton of micro scopic organisms i.e. diatoms. For these purposes minute samples, up to a gram, of unconsolidated material - soft sediments are used for light microscope and Scanning Electron microscope studies. The smaller the particle the better for biological organisms I am familiar with which are in the order of 5-800µm in size, with an average of 100µm. Coring facilities would be useful to determine whether there is a fossil record to be established ; siliscous materials can withstand most sterilising techniques.

Every success in your enterprise,

Sincerely,

Patricia A. Sims

THE UNIVERSITY OF CHICAGO

DEPARTMENT OF THE GEOPHYSICAL SCIENCES

5734 SOUTH ELLIS AVENUE

CHICAGO • ILLINOIS 60637

MAR 02 1987

February 27, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear James,

In response to your call for input to a Mars Sample-Science Document, I believe that we went through all the questions about sample size, etc. in the 1970's. Although there is no evidence for biological activity on Mars, and no reason to expect any danger of biological contamination of the Earth, it would be prudent to do biological testing of a Mars sample in the Receiving Laboratory prior to release of samples. Ideally, the samples should be transferred from Mars without change of any chemical and physical conditions. If any conditions are changed, they should be designed to minimize any chemical and physical reactions. Hence, I favor transfer of sample into hermetic insulated containers for which the temperature is controlled as far as possible and monitored during transfer to Earth. Furthermore, all measurements (e.g. X-ray diffraction) should be made with the sample held in a chamber under the same conditions on Mars. Measurements should be made of P, T, atmospheric chemistry at the Martian surface. High-resolution photographs should be taken of samples before transfer to the containers. The problem of packing the sample to minimize damage from acceleration is not easy; perhaps a spring-loaded piston in a cylindrical container would help. Perhaps some samples might be treated crudely to minimize overall cost.

All the standard analytical techniques should be used on Earth: microscopy, diffraction, absorption, resonance, isotopes, etc. The experience from lunar samples is that the whole battery of techniques is needed, and that it is futile to pick just one or two techniques. At this time, I expect that chemical alteration of minerals with the implications for atmospheric chemistry will be particularly important. Ideally one would find a historical sequence of alteration events, but it would be naive to expect a simple answer. It is difficult to specify size and type of samples, but I would try to get one sample as deep as possible under the Martian surface. In addition, a range of centimeter-size cobbles would be useful.

Yours sincerely,

JOSEPH V. SMITH
Louis Block Professor
of Physical Sciences

JVSncw

APR 2 1987

INPUT TO MARS SAMPLE SCIENCE DOCUMENT

Carol Stoker
NASA Ames Research Center, Moffett Field, CA

Q1: What aspects of Martian history can be uniquely addressed by direct analysis of samples returned to Earth?

A: The question of the existance of present life on Mars can only be addressed by return of biologically preserved (i.e. not sterilized) samples of Mars material. The Viking biology experiments are often interpreted as having provided strong inferential evidence that there is no life on Mars. However, a serious look at the evidence is far from convincing. In fact, three of the four Viking Biology experiment yielded positive (for life) results according to the experimental design. Generally, the positive results are attributed to spurious signals produced by an unusual soil mineralogy and the presence of superoxide compounds in the Martian soil. It is interesting to note that production of superoxide compounds in the Martian atmosphere was predicted prior to the Viking mission (Hunten and McElroy, 1970). Yet, three biology experiments were chosen for the Viking mission that would all yield "false positives" if superoxides were present in the soil.

Although the Viking Biology data are consistent with a chemical explanation for the phenomena observed, they do not prove that no biology was present or even detected. The biological signal may have been swamped by the 'noise' of the chemical signal, the incubation time of the experiments may have been too short for very sparse bacteria to grow sufficiently to produce a measurable signal, or (I think most likely) the experimental designs were too inflexible and too anthropomorphic to really test for an alien biology.

The current view that Viking found no life is based on two lines of evidence. The first is that the abundance of complex organic compounds at the two Viking sites was below the detection threshold of the GCMS. The second is that the conditions on Mars are cold and dry (which was known before Viking). The first line of evidence could be explained as follows: Clearly, Mars has no globally distributed, active biosphere and it is really the detritus of such a biosphere that is responsible for the amount of organic material found in even very sterile soils on Earth. However, if life were confined to selective clement niches on Mars, and bacteria outside of these niches were in the form of dormant spores, then very little organic material would be built up in regions where the bacteria were not actively growing. Add to this the active destruction of organic compounds by UV light and oxidants in the soil, and a low global abundance of organic carbon is easily consistent with the presence of life confined to restricted niches. The cold, dry conditions on Mars, and particularly the lack of liquid water, virtually guarantees that growing organisms are

confined to restricted niches. Nevertheless, all martian soils could contain small numbers of viable microbe spores. The best way to find out is to subject samples of martian soil to a wide range of culturing procedures to look for growth.

There are really two reasons to look for extant life on Mars. First, to take advantage of the potential for for discovering extraterrestrial life. Such a discovery would be of tremendous scientific importance. But, suppose there is no extant life on Mars. Proving this to a reasonable degree of certainty is almost as important as finding life on Mars, particularly in view of future, possibly manned, missions. Thus, proving that there is no life in the Martian soils is the second reason to look for life on Mars. The attempt to culture unaltered Martian soil must be done to insure that Martian materials do not biologically contaminate Earth. A failure to do this with the first Mars sample return mission will mean that it will have to be done with a subsequent mission before any human mission can "set foot" on Mars. If it is not done, a public outcry is sure to ensue. Since eventual human missions to Mars are a virtual certainty, it makes sense to verify that biological contamination can't occur as soon as possible, in case there is a sudden political mandate to land humans on Mars.

Another, biologically relevant use for a sample of Mars surface material is to study the oxidizing character of the Martian soil, the interaction of photochemically produced oxidants with soil mineralogy, and the processes by which organic compounds are decomposed. Again, analysis of unaltered samples is important because the Viking biology experiments showed that the soil samples degassed when exposed to water vapor. Presumably loosely bound oxidants were coming off. If organic compounds are decomposed on Mars, it is important to know the mechanisms involved before sending future missions especially manned missions. For example, this information could influence the choice of materials used in future missions.

A third issue that must be addressed with samples of Mars materials that are not chemically altered from their normal state on the surface is their potential toxicity to living terrestrial organisms. The evidence from Viking that the soil contains strong oxidants suggests that these material could be chemically toxic to terrestrial organisms, particularly humans. A range of organisms (everything from bacteria to mammals) should be exposed to Martian soil to test for toxic effects. Again, this must be done before engaging in human exploration of the Martian surface.

Finally, in view of the evidence for a clement early Mars, Mars surface samples could be chosen to afford the highest probability of finding evidence of fossil life.

Q2: What types and quantities of samples are needed to support the analysis related to (1)?

A2: To search for extant biology, the best sample would be from an environment likely to have even occasional liquid water. The edge of the polar caps would be a good choice. A core of 10 cm length from the polar layered terrain would be ideal. However, a sample of aeolian material from anywhere on the surface would be valuable to look for widely distributed biology. This type of sample could be used to verify that biology only occurs in restricted niches and is absent or nonviable elsewhere. A few grams of soil would be adequate for these tests. Again, a core of material would be best to get some material that has been protected from destructive UV light at the surface.

To study the oxidizing character of the soil, a few grams of oxidized surface material from anywhere would suffice. A core of 10 cm length or longer would be preferable since this would allow us to determine whether the oxidizing conditions and the organic depletion varies with depth. These same samples could be used to test for biological toxicity of Martian soils as well as search for life.

To search for evidence of fossil life, we would probably need a core of material from an ancient lake bed. There are several candidate sites in Vallis Marineris, for example (Nedell et al., 1987).

Q3: What degree of sample degradation can be tolerated without defeating the analysis goals?

A3: Of course, if the samples are sterilized, it will be impossible to search for extant biology. To search for biology, the best procedure is to keep the samples within the limits of the range of conditions they experience on Mars. Subsamples from this reservoir can then be used to try various culturing procedures. (Temperature near 0 C, No limits for pressure, radiation, acceleration or shock.)

To study the oxidizing character of the soil, one must be careful not to degas the samples. Viking biology results suggest that the samples were partially degassed when heated and largely degassed when exposed to either liquid water or water vapor. Thus, these samples must be kept cold (within the range of temperature experienced on Mars, near 0 C should suffice), and they should be kept in either a Mars atmosphere at low total pressure or a pure N_2 atmosphere. Care should be taken to keep the absolute humidity close to that on Mars.

The search for fossil life on Mars does not place restrictions on sample handling.

REFERENCES

Hunten, D.M. and McElroy, M.B. (1970) *J. Geophys. Res.* 75,5989-6001.

Nedell, S. S., S.W. Squyres and D.W. Anderson (1987). *Icarus*, in press.

The University of Georgia College of Agriculture

Agronomy Division

Our Profession Feeds The World

$
DEPARTMENT OF AGRONOMY
ATHENS, GEORGIA 30602

ROOM 3111
MILLER PLANT SCIENCES BUILDING
(404) 542-0801

June 17, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, Texas 77058

Dear Dr. Gooding:

This letter is in response of your inquiry for input to a Mars sample-science project: SN2-87-L084. I regret to inform you that I don't know anything about extra-terrestrial materials or soils, since I haven't been involved in analyzing lunar substances or any other materials from meteorites that have fallen on earth.

I think that many people have already given you their responses, and in order not to bore you with things that you already know I will touch only a few topics that may have been forgotten.

(1) As a soil scientist I am inclined to subject the Mars samples to analyses that we do with soil samples, e.g. analyses required to determine the physical, chemical and biological characteristics needed in soil genesis, morphology, classification and soil fertility.

(2) The conclusion in the 1974 JCS report indicates the collection of lunar materials of 2-20 mm in diameter only. This type of sample may delete a very important fraction for analysis, e.g. the clay fraction (<0.002 mm). It is also nice to know whether the Mars material contains some clay minerals. The question then is what types of minerals are present; have they been formed through processes similar as in soil genesis? What kind of electrochemical properties do these clay minerals have?

Another important aspect is the organic matter content. We realize that lunar and martian materials do not contain organic material. If organic matter, in the form of humic acid, is added, will these materials be converted into a soil? Humic acid is very beneficial in terrestrial soils, and will affect plant growth both directly and indirectly. It is capable of chelating toxic concentrations of Al, Fe, Cu and Mn, and releasing these elements again in quantities less harmful to plant growth. Briefly, in my experiments plants grow always better in the presence of some organic matter. I will be glad to send you some of my reprints if needed.

Thanking you for the opportunity to express my biased opinion as a soil scientist, I am,

Sincerely,

Kim H. Tan

Dr. Kim H. Tan
Professor of Agronomy

AN EQUAL OPPORTUNITY/AFFIRMATIVE ACTION INSTITUTION

United States Department of the Interior

GEOLOGICAL SURVEY

Kenneth L. Tanaka
Branch of Astrogeology
2255 N. Gemini Dr.
Flagstaff, AZ 86001
(602) 527-7208

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Jim:

Here are my comments that you can use for the Mars Sample-Science Document. I have emphasized, in a broad manner, how research based on Viking images has identified key geologic problems that may be resolved by returned samples:

"Geological analysis of the Viking Orbiter images of Mars has raised many fundamental questions regarding the history of the planet. Returned samples could resolve or greatly contribute to answering such questions; the research based on lunar samples has demonstrated the value of returned samples.

"An obvious area of focus is geochronology. Geologic mapping of Mars at 1:15,000,000 scale is now complete and is supplemented by local detailed mapping of regions of geologic interest. Stratigraphic relations and crater densities have been determined for major geologic units. However, the correlation of crater densities and absolute age of the rocks remains unresolved. Lava flows form well-preserved stratigraphic markers that would provide ideal specimens for the determination of a crater-density chronology that could be applied to the remainder of the planet.

"Also of vital interest is the petrology of Martian rocks. Based on the Viking images, researchers have proposed a wide array of rock types for Mars. Proposed volcanic rocks include lava flows of rhyolitic to basaltic composition, pyroclastic flows and airfall, and lahars. Fluvial, lacustrine glacial, periglacial, polar, and eolian sediments and products have formed or have been at least postulated. Even deep plutonic and metamorphic rocks may be exposed in the walls of Valles Marineris. Identifying the origin of diverse rock units (such as northern plains material and various basin deposits) will illuminate the relative roles of volcanic, weathering, erosional, and sedimentary processes in the evolved Martian landscape. Moreover, knowledge of rock types from key areas could help answer questions regarding the ancient climate of Mars (Did rain fall? Did lakes form?), tectonic history (Did the Tharsis bulge cause the planet's axial pole to shift), and the northern lowlands region (When and how did it form?).

"The Viking data set has given us many tantalizing indications of geologic processes occurring over spatial and temporal scales and within environmental conditions much different than on Earth. Rocks samples of Mars will test our hypotheses and stimulate further growth in our knowledge of the planet."

I hope this is useful to you

Regards,

Ken

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO · SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY, B-017
LA JOLLA, CALIFORNIA 92093

May 5, 1987

Dr. James L. Gooding, SN2
NASA/Johnson Space Center
Houston, Texas 77058

Dear Jim:

Sorry to be slow, but I wanted to speak with more experience before writing.

Regarding the Mars-sample science document we wish to contribute to the Martian sample return program, specifically, we wish to utilize our recently developed sulfur isotope techniques for high precision $^{34}S/^{32}S$, $^{33}S/^{32}S$ and $^{36}S/^{32}S$ measurements. We presently have the ability to measure the $\delta^{34}S$ and $\delta^{33}S$ to ± 0.02‰ on 16 micrograms of sulfur. ^{36}S may be measured on samples approximately 10 times that. We have the complete fluorination, chemical separation, via gas chromatography, and mass spectrometry developed and working on a wide range of samples, including terrestrial sulfur samples. We plan to commence meteoritic measurements in the very near future. There are several questions which may be addressed with sulfur, including crustal history, volatile (atmosphere) interactions and, possibly, aqueous alterations. The ability to measure all of the stable isotopes at ultra-high precision also permits us to look at differences between the different "planteary" or solar system reservoirs as exist for oxygen and possibly titanium. The fact that sulfur possesses a rich variety of redox states, both oxidizing and reducing, adds an important dimension. The relatively high abundance (6-9 wt%) due to minerals such as pyrrhotite and troilite drastically reduce sample requirements. The oxidation state of sulfur in the surface environments at, e.g. Chryse and Utopia Planital, is of particular interest. The range of observed sulfur minerals (FeS, FeS_2, Na_2SO_4, $MgSO_4$) offers a wide range of components to be individually studied by isotopic analysis.

The measurement of ^{36}S also allows us to determine the cosmic ray exposure age, since this is a spallation product from iron. It has previously been shown that this is a sensitive means by which exposure ages may be determined.

In summary, the following are the general subjects which may be addressed by sulfur isotopic analysis:

(1) General sulfur reservoir (Martian) isotopic composition as it applies to other solar system reservoirs.

(2) Crustal/Surface processes:

  (a) Redox chemistry.

  (b) "Aqueous" effects.

  (c) Agglutionation processes--(Martian fines are sulfur enriched due to this process.

(3) Cosmic (and solar) exposure history.

In conclusion, I might add that, at present, we are the only laboratory in the world with the capability to measure all four isotopes at high precision.

I hope this little section is of some use.

Sincerely,

Mark H. Thiemens
Associate Professor

MHT/mis

THE OHIO STATE UNIVERSITY

Byrd Polar Research Center

108 Mendenhall Laboratory
125 South Oval Mall
Columbus, OH 43210-1308

Phone 614-292-6531
Telex 4945696
OSUPOLAR

April 20, 1987

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston, TX 77058

Dear Dr. Gooding:

Some time ago I recived a copy of a document entitled, "Call For Input to a Mars Sample-Science Document." I will address the questions in the order asked from what little I know from the Viking missions of Orbiter and Lander.

1. Being a glaciologist, perhaps explains why I believe the polar ice caps on Mars are the most interesting geological features on the planet. Perhaps these ice caps contain within their stratigraphy a record of past climate which might aid in understanding the climate of our earth. One is immediately impressed by the layered nature of these ice caps and wonders if this distinct dust layering might be used in some way to provide a dating technique. The important questions concerning the ice caps are: What is the annual mass accretion or loss on these ice caps? How thick is the ice and what is responsible for their swirled appearance? These polar caps, since they are quite cold and likely frozen to the bedrock, may contain a record of the Martian ancient climate which might help us better understand that of the earth. Records of dust fall and type of dust could be important. Perhaps there are ancient gas bubbles trapped in the ice which could provide an archive of the ancient Martian atmosphere.

2. Two shallow ice cores could potentially be removed from the base of the margin of the ice cap. These samples, because of the flow law of ice (if the ice caps are thick enought to flow now or in the past), potentially would represent some of the older ice stored in the ice caps. These samples could be as small as 20 cm in length and 10 cm in diameter and could provide dust/gas samples of the ancient Martian atmosphere and stable isotope samples.

3. The degree of sample degradation which could be tolerated would depend on the measurements to be made. For most dust studies the samples could be melted and only the insoluble particulates returned. If, however, one wanted to examine stratigraphy, soluble anions or cations, stable isotopes, and the composition of any gas in bubbles, then the samples would need to be returned frozen.

4. On site the ice core could be photographed for stratigraphic features to ensure a record even if the core melted in transit. Perhaps ice thickness determinations could be made at the area of sample collection and ice temperatures could be measured at the bottom of the borehole.

We have in the past and continue to conduct research programs in Antarctica and Greenland as well as high altitude, low altitude and mid altitude ice caps (such as the 5,670 meter Quelccaya ice cap in Peru and the 5,400 meter Dunde ice cap in China) in an attempt to reconstruct the earth's past climate and environment from ice core stratigraphic records. The ice caps on Mars potentially will provide a record of the solar system climate when it is driven solely by solar radiation in the absence of the impact of oceans and atmosphere.

Sincerely yours,

Lonnie G. Thompson
Research Scientist

LGT/lb

Apr. 17, 1987

Allan H. Treiman
Geology Department
725 Commonwealth Ave.
Boston University
Boston MA 02215

Dr. James L. Gooding
SN2
NASA Johnson Space Center
Houston TX 77058

Dear Dr. Gooding;

Thank you for your letter of Feb. 10, 1987, concerning sample selection during the Mars Sample Return Mission. I am quite interested in the mission, and feel I could contribute in two areas: geologic inferences from the SNC meteorites, putative samples of Mars; and petrologic and geologic criteria for selection of return samples. My contribution in these areas comes from research into the petrology and petrogenesis of the SNC meteorites, and broad experience with igneous rocks: basaltic, granitic, alkaline, and ultrabasic.

Before addressing the four questions about sample return in your letter, let me comment on the constraints the SNC meteorites provide on our expectations of Martian surface geology (item 2.4 of the Draft Outline, Mars Sample Science Document: Martian Meteorites: What they might and might not tell us about Mars). There is much information still hidden in the SNC meteorites about the geology, petrology, and tectonics of Mars. Further study of the SNC meteorites is essential to provide models of what the Mars Rover may encounter, and what kinds of samples might be available.

My own work has focussed on just this question: in what geologic settings did the SNC meteorites form? I have presented evidence that the nakhlites and Chassigny formed in differentiated flows or shallow intrusions of ultrabasic magma, in contrast to previous theories of formation in plutons of 'tholeiitic' magma. Ultrabasic magma compositions are in general accord with the composition of the Martian soil, and suggest that mechanical weathering is dominant over chemical weathering at the Martian surface. Formation of the SNCs in differentiated, near surface, bodies is in accord with Martian surface geology and constraints of possible impact ejection mechanisms; formation of the SNCs in plutons is not in easy accord with either constraint.

Moving on to the four questions posed for sample return, let me reiterate that my area of special interest and expertise is the petrology and geology of the SNC meteorites, igneous rocks putatively from Mars. My scientific concerns would be planetary differentiation, magma formation and differentiation, and igneous and volcanologic processes on Mars as they compare to those on Earth.

(1) What aspects of Martian history can be uniquely (or best) addressed by direct analysis of samples returned to Earth?

Little petrologic or petrogenetic study can be done without returned samples ''in hand''. For example, compare the far-reaching conclusions based on study of the SNC meteorites to the few, equivocal results derived from the Viking analyses of Martian soil. Data which may be obtained only from a returned sample include: petrography, mineral compositions, bulk compositions including trace elements and trapped gases, stable isotope compositions, and radio-isotope compositions. From these data would come interpretations about the formation and differentiation of Mars, processes within the Martian mantle, processes of magma generation and differentiation, alteration and weathering processes on the Martian surface, and age-dating of specific rock samples and geologic terrains on Mars. Petrologic study must be considered one of the primary purposes behind sample return from Mars.

(2) What types and quantities of samples are needed to support the analyses realted to (1)?

Ideally, samples would include one of everything. Within the restrictions of a real mission, limited collections could partially address the concerns posed above. We should minimally aim for: a suite of samples taken in situ from many accesesible areas of known geologic relations and crater-count age; a suite of samples from a single flow; a suite of samples of different flows from a single eruptive center; and a suite of samples from an alluvial deposit. Each of these objectives would address particular scientific questions; for instance the last objective would be important for understanding the variety of rocks outside of the Rover's scope, and for understanding the composition of the crust, core, and mantle. But such a selection would do little towards defining the age, petrology and spectral reflectance characters of a known petrologic unit.

As a geologist, I think it is supremely important to obtain samples from known geologic contexts, and if possible directly from outcrops. With proper photographic documentation and geodetic locations, a geologic sample becomes a clue to a particular formation (or flow), a particular terrane, a particular geologic and tectonic environment. Without geologic context, a returned sample is little better than a meteorite.

(3) What degrees of sample degradation can be tolerated without defeating the analysis goals?

The data of primary interest to the igneous petrologist and volcanologist is relatively insensitive to the rigors of sample return and decontamination. Samples solid enough to be picked up by mechanical arms are likely to survive blast-off and recovery. Temperatures needed for decontamination, I assume less than 200C, will not cause any important change in the primary igneous materials, isotopic systems, or gas systematics (except adsorbed atmospheric gas, which will be measured independently). Materials likely to suffer during thermal decontamination are low-temperature alteration minerals, like those identified in the Antarctic shergottites. Others are more competent to comment on their degradation than I am.

(4) What in situ measurements should be made on Mars to supplement or replace information available in returned samples?

The most helpful data from the planet surface would be full multi-spectral imaging, including stereoscopic image pairs, of the sample collection sites. Imaging is particularly those sites where material could be plucked in situ from coherent or stratified geological units.

Multispectral imaging would provide reflectance spectra under Martian conditions of samples to be known upon return. The spectra would provide ground truth in interpretation of imaging of the rest of the planet. Imaging at different sun angles, if possible within mission constraints, would also be valuable.

Stereoscopic images would allow three-dimensional reconstruction of the sample sites and of the orientations of geological structures (e.g., faults, igneous layering, sedimentary bedding). Knowing the site geometry would allow the imaging/recovery team to apply many of the techniques of structural and sedimentary geology; for instance, one could reconstruct bedforms in sediments, and thereby constrain flow directions and velocities.

I hope that my comments will be helpful in summarizing the case for sample return from Mars. If I can be of further help, please let me know. I will try to attend the Sample Return Workshop this fall; if so, I'll see you then.

Sincerely yours,

Allan Treiman

Allan H. Treiman
Assistant Professor

MATERIAL ANALYSES OF RETURNED MARTIAN SAMPLES: SCIENTIFIC GOALS AND SAMPLE REQUIREMENTS

Michael Anthony Velbel
Department of Geological Sciences
206 Natural Science Building
Michigan State University
East Lansing, Michigan 48824-1115

The Mars Sample Return Mission will further our understanding of the geologic history of Mars, by enabling direct study of surficial materials. The history of martian internal processes, and the history of the planet's fluid envelopes, are recorded in igneous and sedimentary materials presently exposed at the martian surface. The known history of vigorous surficial activity on Mars suggests that much, if not most, of the surficial material available on the martian surface has been modified by exogenic processes involving physical and/or chemical interactions with the martian atmosphere, and with any hydrosphere which may once have existed. Consequently, all recovered materials will have to be examined from the perspective of the martian sedimentary cycle.

The physicochemical conditions of the martian sedimentary cycle differ from Earth's, but the principles of investigating the sedimentary cycles are similar. Individual compartments of the martian sedimentary cycle, including provenance, weathering, dispersal, and diagenesis, each shed light on some aspect of the geologic history of Mars. Some compartments are dominated by physical surficial processes, others by chemical and mineralogical surficial processes. Thus, in order to facilitate discussion of how we can utilize different compartments to investigate different surficial processes, the compartments can be reorganized (relative to the sequence in which grains actually pass through them) into two pairs related to one another by similarity of processes: I) Provenance and dispersal; and II) Weathering and diagenesis.

SCIENTIFIC GOALS AND SAMPLE SPECIFICATIONS

I. Provenance and Dispersal

A. Provenance studies reveal the nature of the parent crystalline rocks from which regoliths and sediments are derived. Certainly, substantial efforts will be made to collect in situ primary crystalline rock. Rock samples will allow investigation of traditional questions of igneous petrology, such as the nature, source, and timing of magmatic processes, with all their attendant implications for the overall evolution of the crust and interior of the planet. Despite this, if our experiences with the earth, moon, and meteorites are any guide, much of what will be learned about martian igneous petrology will have to be approached in the same way sedimentary petrologists study the provenance of terrestrial sandstones. Much of the lithic material that will be widely available and easy to collect will

have been transported to the sampling site either as ejecta, or by fluids such as water or wind. The resulting sediments will therefore certainly contain grains of primary rock-forming minerals, and clasts of igneous rocks, including varieties which originate outside the operating range of the rover. These exotic clasts will supplement the petrological and geochronological information of whatever in situ samples may be accessible.

Bulk chemistry of major and trace elements could be analyzed by the lander/rover, in a manner similar to the Viking XRF analyses. Most other forms of analysis, however, including mineralogical, crystallographic, and major/trace/isotopic compositional analyses of individual mineral phases in the samples and clasts, would require both the capability to isolate individual clasts and/or grains (usually done on earth with the aid of various optical microscopes and sample manipulation devices), and an array of different analytical instruments. Optical, petrographic, and electron microscopes, microprobes, X-ray fluorescence and diffraction, and various mass spectrometers, are the minimum equipment required to approach complete characterization of lithic materials. Given the astronomical odds against being able to miniaturize the entire suite of instrumentation sufficiently to enable them to be included aboard the lander and/or rover, even fairly routine characterization seems to require direct analysis of returned samples.

Chips, clods, or cores must be of sufficient size for preparing petrographic thin-sections/microprobe mounts. Seeking provenance information in sedimentary materials would benefit from sieving, raking, or screening unconsolidated sediment to enrich the sample in sand- to fine-pebble-size material. Thirty to fifty grams per sample would be considered adequate for such studies in terrestrial terms, allowing for optical examination (binocular & petrographic microscopy), and sufficient material for microprobe, chemical, mineralogical, and/or isotopic analysis of selected separates.

B. Dispersal of sedimentary materials is often studied simultaneously with provenance. As noted above, clastic sediments by definition contain grains exotic to the depositional environment, and martian sediments should be no exception. Once the grains themselves have been characterized and linked to physical (or at least generic, conceptual) source areas, the question shifts from "Where and how did the grains originate?" to "How did they get from there to here?"

This study bears great similarities to terrestrial basin analysis. Stratigraphy, sedimentology (including paleocurrent analysis, and depositional environment analysis), and sedimentary petrology, all play a role. For Mars, much of the stratigraphic and sedimentological information on dispersal patterns (e.g., physical stratigraphy, paleocurrent analysis of flow and wind directions) will be acquired from orbital data (e.g., Viking orbiter, Mars Observer, Mars Sample Return Orbiter). Other information, relating to transport and depositional processes (e.g., sedimentary structures and bedforms), will require a lander imaging capability (cf. Viking landers).

Studies of dispersal systems will have considerable

significance for understanding the evolution of Mars at scales larger than those directly accessible to the rover. For example, exotic clasts will provide information about lithologies which do not occur in place within the range of the rover traverse. Determination of where these clasts originated will require analysis of the dispersal system. In addition to the petrological significance alluded to in the provenance section above, clast geochronology may also place useful constraints on the time of deposition of the surficial deposits, since the sedimentary deposits must be younger than any clasts they contain. This application of the principle of included fragments, to put absolute-age limits on the operation of the dispersal system and the resultant surfical deposits, will also provide the basis for absolute-age calibration of martian crater statistics, an exercise with planet-wide implications.

Any chip, clod, core, or sieve sample suitable for provenance analysis would provide the material required for dispersal analysis, providing that the stratigraphic and sedimentological context of the sample were established by orbiter, lander, and rover imaging.

II. Weathering and Diagenesis

Weathering studies examine the manner in which crystalline parent materials are chemically and mineralogically modified at a planetary surface by interaction with the atmosphere and/or hydrosphere. Weathering sensu stricto includes only those chemical and mineralogical alterations taking place before the solid products are transported from the site of the primary-rock/volatile interaction. Diagenesis includes all physical, chemical, and mineralogical changes experienced by sedimentary particles after they are transported and deposited. On Earth, the distinction between pre-transport and post-depositional alteration is significant, because of the pronounced differences in the physicochemical environmental conditions. Terrestrial weathering takes place under subaerial conditions, whereas post-depositional alterations (diagenesis) generally take place in subaqueous environments. While most workers would agree that such planetary surface alterations taking place before transport should be called weathering, surface reactions which act on materials after they are transported are called either weathering or diagenesis, depending on one's disciplinary perspective.

On Mars, post-depositional processes take place at or very near the planet's surface; thus, martian diagenesis takes place under surface conditions which are essentially identical to weathering processes experienced by the materials before they were transported. The processes are so similar, in fact, that many workers would continue to refer to them as weathering. Because of this fundamental similarity of pre- vs. post-depositional environmental conditions on Mars, I have chosen to discuss weathering and diagenesis together, distinguishing instead between surface alteration of untransported primary crystalline material on the one hand, and surface alteration of transported parent materials on the other. Making the distinction on the basis of parent material emphasizes the

fundamental similarity of conditions and processes. Studies of the diagenesis of martian sedimentary materials offer the same opportunities for understanding crust/volatile interactions as studies of weathering of untransported crystalline rock.

A. Rock weathering. During weathering, primary rock-forming minerals react with volatiles. Products of such weathering reactions include residual primary rock-forming minerals, secondary minerals, and altered volatiles. Although reactant and product volatiles may no longer exist, considerable insight into their nature, abundance, and properties can be achieved by examining the reactant and product minerals. The compositional and textural relationships among reactants and products record mineral stability and elemental mobility, which in turn result from the thermodynamics and kinetics of the weathering system (including its volatiles). Thus, study of weathering products enables us identify, reconstruct, and characterize weathering factors, conditions, and processes, including atmospheric composition, and the solute characteristics of any liquid water which may have existed when the weathering reactions took place.

Even on Earth, where high temperatures and abundant water faciliate relatively rapid kinetics (at least in comparison with present martian conditions), the mechanisms of weathering reactions often prevent the attainment of thermodynamic equilibrium. Most naturally weathered materials therefore represent various intermediate stages between unaltered parent materials and the ultimate weathering products. At least four analytical approaches are required to elicit the maximum amount of information from these transitional materials. They are; 1) bulk chemistry; 2) bulk mineralogy, to identify the phases among which the elements are distributed; 3) petrographic analysis, to determine the textural relationships among reactants and products; and 4) mineralogical, crystallographic, and compositional analysis of the individual reactant and product phases. Bulk chemistry and mineralogy could conceivably be performed in situ, but, as noted in the discussion of provenance, the complete array of techniques which is available in terrestrial laboratories is not readily transported to the martian surface.

Weathering studies of primary crystalline rock would require that chips or cores be taken from outer surfaces of outcrops or boulders. A single sample of any weathered surface would be an incidental acquisition during the course of coring outcrops or boulders for igneous petrology. However, the quantity of material thus acquired would be minimal. If the weathering of outcrop/boulder surfaces is to be a priority in its own right, methods must be devised for collecting larger quantities of surficial weathering rinds on such surfaces. At least two possibilities come to mind. The less practical involves "paring" weathered rinds from outcrop or boulder surfaces. Doing so without destroying the suitability of the sample for petrographic analysis seems only a remote possibility, given the extensive sample manipulation which would be required. More practical, but less efficient in terms of optimal sample packing for the return trip, would be deliberately seeking individual small (20-50 gm)

weathered pebbles. Such specimens would generally have a higher yield of weathered surface per total volume collected.

Both options would require fairly advanced rover capability for visually recognizing and selecting pebbles of weathered rock. Color imaging, spectral analysis of the surface color of prospective samples, remote elemental analysis of surfaces of prospective samples, the ability to quickly estimate the bulk density of a prospective sample, or some combination of the above, would facilitate intelligent sample selection. Alternatively, sieving or screening of sand- to fine pebble-size material might also yield some proportion of such material, but at this point the small size of the individual grains, and the correspondingly small yield of weathered material, once again becomes the limiting concern.

B. Sediment weathering/diagenesis. Sedimentary materials collected for diagenesis studies would often contain transported grains and clasts of primary crustal materials, thus being at least somewhat suitable for provenance and dispersal studies. However, the converse is not true; samples collected for provenance and dispersal studies are not suitable for studies of weathering and diagenesis. Studying mineral assemblages formed at planetary surface conditions imposes significant additional constraints on sample handling and preservation.

Great care must be taken to preserve textural relationships if studies of diagenesis are to succeed, so screened or sieved samples are not suitable for weathering or diagenesis studies. The paragenetic relations of detrital grains to post-depositional mineral cements must be investigated using optical and electron petrography, in order to determine both reactant-product relations, and the relative sequence of chemical events in the history of the sample. Clods of moderately indurated regolith (such as the inferred sulfatic duricrusts of the Viking lander sites) would have to be sampled and returned intact. Clods would have to be carefully documented, handled and stored; proper interpretation of alteration textures requires knowledge of sample orientation in the landscape, and many of the likely cements and alteration minerals are sensitive to changes in temperature and atmospheric content of water vapor, carbon dioxide, &c. Studies of crust/volatile interactions via mineral weathering and diagenesis would be severely compromised by temperature or pressure excursions beyond the stability limits of the alteration minerals. In the case of poorly consolidated regolith clods or duricrusts, it is essential to avoid physical disruption of textures and fabrics, and of physical properties such as porosity, permeability, and bulk density, by acceleration and/or shock. Samples in the 30-50 gram range, suitably collected and preserved for petrographic and mineralogical analysis, would be sufficient for most purposes.

SAMPLE HANDLING AND COMPENSATORY DATA REQUIREMENTS

As can be seen from the previous sections, requirements for sample preservation and the prevention of sample degradation

differ with the objectives of the study. Provenance and dispersal studies will not be severely affected by moderate heating or shocking of the sample. On the other hand, studies of mineral weathering and diagenesis would be severely compromised by temperature or pressure excursions to any significantly non-martian conditions, and by physical disruption of textures and fabrics.

In order to minimize information loss due to sample degradation during return to Earth, it might be valuable to plan for some analytical redundancy. For example, the lander/rover instrument package might contain an XRF or similar capability. Samples could be analyzed for all major elements (especially volatiles) at the martian surface, and then again after sample return. Any non-isochemical redistribution of elements could thus be detected; it might then be possible to back-calculate from the terrestrial mineralogical and chemical analysis, using the differences in pre- vs. post- return bulk chemistry to reconstruct what the primary properties (and minerals) were. Isochemical redistribution of elements would be much more difficult to detect, and it is not clear that significantly refined mineralogical and/or petrogrpaphic data could be acquired at the martian surface to make an adequate pre-disturbance characterization of the sample, for comparison with its returned state. Nevertheless, some redundant analytical capabilities should be deployed on the rover. Some information on primary properties might thus be retrieved which would otherwise be lost due to sample degradation during return and/or processing.

ORIGINAL PAGE IS
OF POOR QUALITY

VRIJE UNIVERSITEIT

NATUURKUNDIG LABORATORIUM

Natuurkundig Laboratorium
Postbus 7161
1007 MC Amsterdam
Telefoon 020 - 548 3571

Dr. J.L. Bodding
SN2
NASA Johnson Space Center
Houston, TX 77058
U.S.A.

uw kenmerk	uw brief van	ons kenmerk	datum	bijlage(n)
		N/RDV/rv	June 17, 1987	

onderwerp

Dear Dr. Bodding,

In reply to your call for input to a mars sample-science document the following.

My group has in principle great interest in future participation in research on mars material. Our special interests are focussed on the use of our microprobes; in our institution we have possibilities to use a nuclear microprobe, an electron microprobe and a Raman microspectrometer. The consequence of this situation is that we try to collect data on the in situ distribution of trace elements, from a selected number of elements the in situ distribution of isotopic anomalies and, paying special interest to the element C, the in situ determination of some information on the chemical state of C using Raman spectrometry. Collection of these data give ample opportunities for reconstruction of forming processes of the minerals involved and to collect information on temperatures and pressures during the formation, although martian samples may have suffered from metamorphosis. In any case, what we will need are slices of the unperturbed samples from which we will produce the maps as mentioned above and correlate them with textures, petrology etc.

The consequence of this is that as little degradation as possible is tolerated. To give rough estimates, temperatures exceeding 300°C are undesirable because migration of the volatiles will defeat the analytical goals. High pressures should be avoided to maintain original structures and to prevent loss of possible gaseous inclusions.

Bezoekadres: De Boelelaan 1081 1081 HV Amsterdam

In situ measurements on Mars with comparabel analytical output are not feasible.

I hope that information given here will suit your purpose to some extent.

Sincerely yours,

Dr. R.D. Vis.

ORIGINAL PAGE IS
OF POOR QUALITY

Re SN2-87-L084

February 24, 1987

Jim -

Thanks for your Feb. 10 circular. To answer your questions:

(1) Detailed MIN/Pet studies cannot be done *in situ* so all aspects related to detailed min/pet must be done with returned samples. The internal volcanic processes, sedamentation history, and climate variability are only some of the aspects of martian history for which sample return provides required material. My own specialty - experimental petrology to understand planetary differentiation based on observed rock types - certainly cannot be done without detailed min/pet as a prerequisite.

(2) Depending on rock type and gram size, a few grams to a few kgm of each. As broad a selection of fresh rock as possible is desirable rather than a lot of one type.

(3) For the all important age dating, this certainly depends on method used. Others beside myself could answer that better. For detailed min/pet and geochemistry, 200°C and a few bars shouldn't upset very much.

(4) From a min/pet standpoint, remote XRF/XRD would be useful in making choices for return samples. My general input is, gook luck!

Best regards,

Dave Walker
Prof. of Geological Sciences
Lamont - Doherty, Palisades N.Y. 10964

Chevron Oil Field Research Company
A Chevron Corporation Subsidiary
P O Box 446, La Habra, CA 90631

March 17, 1987

Dr. James L. Gooding
SN2
NASA - Johnson Space Center
Houston, TX 77058

Dear Jim:

I am delighted to respond to your request for input to a Mars Surface Sample Return Mission (MSSRM). MSSRM is surely the mission that will teach us the most about Mars and Mars' relation to earth. Congratulations to you, JSC, and NASA for pushing ahead with MSSRM.

I confine my remarks to your question 2: "What types and quantities of samples are needed to support analyses directed to understanding Martian solid body geologic development?"

Sample All Geologic Units

MSSRM must sample typical materials from each of the major geologic units on Mars. These are the samples that constrain geologic history and processes. Samples of unusual materials should be a subordinate goal. There are four geologic units on Mars that must be sampled:

1. Cratered (southern) highlands,
2. Volcanic (northern) plains,
3. Recent volcanic constructs,
4. Layered (polar) terrain.

The distances on Mars that separate these units dictate that four spacecraft are required - one targeted for each geologic unit. A roving sampler is useful to collect representative and unique samples within a landing site.

A roving sampler is not a good mechanism to collect samples from two geologic units from a single landing site. There are two problems: range and psychology. The range problem is obvious - designs tend to provide for 10's to 100's of kilometers, but to unambiguously move from one geologic unit into another requires 100's to 1000's of kilometers. The psychology problem is more subtle - I have difficulty believing that scientists will command a rover to pass "unique" objects (e.g., a spotted boulder) to head for a distant goal. Such action would be required for a rover to traverse from one geologic unit to another, but such action is not in the nature of scientists.

Collect Lots of Small Samples

The sample collection should be biased to lots of fist-sized samples and away from large samples. Apollo collected large rocks and soil samples from each mission. The history of sample analysis suggests that a larger number of smaller samples can yield population studies and the possibility of unique samples. Only small fractions of large samples are used. Large samples appear to be a poor use of returned mass allowances.

Good luck in your fight for MSSRM.

Sincerely,

J. L. Warner

Jeffrey L. Warner

MAY 18 1987

Department of Geography

The Queen's University of Belfast
Belfast BT7 1NN Northern Ireland Telex 74487

Tel 245133 Ext 3350

Dr. J.L. Gooding
SN2
NASA Johnson Space Center
Houston
Texas TX 77058
USA

12th May 1987

Dear Dr. Gooding

Mars Sample

I am on the NASA mailing list fpor things scientific and recently received your letter re the 'mars sample- science document'. Although I am not a NASA investigator I wondered if I might make some comments.

These relate particularly to the weathering aspects of martian regolith, particularly to what might be termed 'desert varnish' or its martian equivalent. I am aware of your work in this area of course - indeed you have sent me some reprints before now - so I hope you will not think me too intrusive.

As you know, it has been suggested that (terrestrial) varnish may be of microbial origin. Altough I am not happy about this explanation if there is bacterial action it probably came *after* inorganic fixing of of Mn/Fe) I do believe that it should be considered as a possibility. This is especially so if, as I gather, you are still looking at possible organic life. I do not know what sterilization might do to surfaces which could have bateria/fungal hyphae on them. Would it be far-fetched (or worthwhile) to have an SEM to look at specimens actually on Mars? Technically, I am sure this is feasible. I venture to suggest it just in case no one else has!

On returned samples, an along more conventional lines, I think that it would be worthwhile looking at weathering surfaces in some detail. This might say as much about terrestrial conditions for the formation of desert varnish as anything but the comparison might be useful. For instance, I think that UV photons are a likely source of driving some reactions (on earth) which are not normally considered as being important. On Mars, there is probably more than than enough energy from this source.

Conventional techniques (microprobe) could be usefully employed to look at cross sectional and surface elemental distributions. There are some pretty sophisticated techniques which could be used to give important information on surface and near-surface changes in chemistry of such varnishes and coatings. Proton probes and Auger spring to mind as well as the more traditional Mössbauer for looking at the Fe component. In some of the terrestrial varnishes, Fe/Mn/Si gels play a role in forming the crust and I think that there might be some pay-off here with respect to the water-balance on Mars.

Specifically, to answer your questions:

1. Surface chemistry of oxidation of minerals, energy input and water balance. Also the importance of dust transport (as trapped in any varnish - earth analogy).

2. Any specimens of rocks, preferably of known orientation, e.g. compare exposed boulder surface to the hidden base or near base. Quantity sufficient to make thin sections through and for surface probe samples across. Probably about 5cm² would do.

3. Probably not important as long as temperatures did not exceed normal martian surface temperatures.

4. SEM (see above) would be useful, especially if coupled with some simple analysis. I assume IR reflectance would be done anyway. EDS on the SEM??

I hope that you might find these comments useful.

Yours Sincerely,

Brian Whalley

V. Brian Whalley

JUL 8 1987

THE OPEN UNIVERSITY

DIRECT LINE 0908 652079.

6th July, 1987.

J.L.Gooding,
SN2,
NASA Johnson Space Center,
Houston,
Texas 77058,
U.S.A.

Dear Jim,

Enclosed is our contribution to the Mars Sample-Science Document. Apologies for the delay in replying which ultimately has been caused by our involvement in organization of the Meteoritical Society meeting in Newcastle. I hope our comments are of some value and that they can be assimilated into the report - we are very keen to be associated with this important project.

Yours sincerely,

I.P.Wright.

Mars sample-return mission

Low temperature geochemistry and light element stable isotopic studies.

I.P.Wright and C.T.Pillinger.
Planetary Sciences Unit, Department Of Earth Sciences, The Open University,
Walton Hall, Milton Keynes, MK7 6AA, England.

July, 1987.

The un-manned Viking Lander experiments conducted on Mars demonstrated clearly NASA's ability to perform a variety of analytical tasks at a remote site. The sucess of these investigations should not be underestimated. Indeed, during the following ten years or so, Viking's in-situ measurements of the martian environment have been of paramount importance in efforts to assess the likelihood that SNC meteorites originated on Mars. While isolated pieces of rock from unknown specific locations are of limited use for the comprehension of regional geological processes, the interest generated by the study of SNC meteorites illustrates the importance of in-depth laboratory analyses of chemical and mineralogical composition - a feat which cannot be accomplished by un-manned space probes.

A full understanding of the evolution of martian geology, through analyses of rocks and surface fines, involves an appreciation of the role that low temperature geochemistry has played. During its history Mars has clearly been shaped topographically by the action of fluids of some description; furthermore it has seasonal and permanent ice caps, an atmosphere, it suffers from climatological processes, including pressure changes, and is subjected to violent dust storms etc. Thus, any study which attempts to elucidate the origins of martian rocks will need to consider the nature of any secondary alteration effects which may have acted to disturb the primary characteristics of the rocks. This in turn will establish a complete picture of the various geological interactions which take place in the martian environment.

The techniques involved during investigation of low temperature geochemical processes involve the use of observational equipment (such as optical and electron microscopy etc.), analytical instruments (such as electron probe, ATEM, XRF etc.) and mass spectrometry. Although the exact mineralogical forms of low temperature species are established by analytical instrumentation, the content and stable isotopic composition of componenets comprised of the elements hydrogen, carbon, nitrogen, oxygen and sulfur (referred to as "light elements") are conventionally analysed by conversion to a gaseous form using a variety of chemical procedures, acid-dissolution, fluorination, pyrolysis etc., followed by manometry and analysis on a mass spectrometer. In some cases the technique of incremental heating, with or without oxygen, allows the speciation and isotopic composition of different components to be readily inferred. In many situations where light elements are involved extreme care has to be taken so that extraneous material

ORIGINAL PAGE IS
OF POOR QUALITY

is not added to the sample prior to analysis. Similarly, care has to be exercised to ensure that isotopic exchange reactions are avoided particularly when the extent of isotopic fractionation between coexisting minerals is the subject of investigation.

We envisage that light element studies can be sub-divided into three main categories; (1) processes that occur during late-stage magmatism in operation within the crust/mantle or at the surface (2) effects which act to modify the chemical or mineralogical make-up of any rocks residing at or near the surface of the crust (secondary alteration processes) and (3) various tertiary processes which may also be investigated by measurement of the distribution and isotopic composition of light elements; these include effects related to impact phenomena (shock-alteration, brecciation, emplacement of atmospheric gases etc.)

(1) Late-stage magmatism.

There is a considerable knowledge concerning the general geological features of Mars; this information has been pieced together from the results of various imaging and other scientific experiments carried by visiting spacecraft. One significant result is that the lithosphere is thought to be thicker on Mars than on Earth and this has acted to prevent the initiation of plate tectonics. As a corollary, the majority of igneous rocks present at the surface of Mars are thought to be fairly primitive basalts of some description. Notwithstanding this, it is known from imaging studies that there is a wide diversity of geological units present on Mars and furthermore these can be demonstrated to have different ages. However, at present, the specific description of rock types is unknown. In light of the extent and time-scales over which volcanic activity has taken place on Mars, it is necessary to consider that advanced stages of igneous processing may have left their mark on the martian rocks. It is possible that, within the older samples of Mars, may be preserved the results of various differentiation or crystal-fractionation events and even highly-evolved rocks. Furthermore, minerals formed from residual magmatic fluids may occur as late-stage rocks analgous to pegamatites or quartz veins present on Earth. The study of such rocks, should they exist on Mars, could contribute substantially to our understanding of mineralization processes and the role of volatile element behaviour during the early, and subsequent, evolution of the planet. Thus, a search should be made for the effects of late-stage magmatic products among as diverse a suite of returned samples as can be selected. In support of the acquisition of rocks of this kind it should be stressed that the effects of circulating groundwaters, particularly of magmatic origin (operating early in the history of Mars), need to be fully assessed by the analysis of late-stage magmatic products.

Late-stage minerals and rocks would not be a ubiquitous feature but would instead be related to plutonic or other intrusive features and thus landing-site selection, or mobility in terms of sampling, will be important. It is considered that these materials would be fairly coherent and could be collected as competent masses of rock taken from outcropping exposures. Obviously the field relations of such rocks are extremely important and require as detailed documentation as can be acquired remotely. A major concern is that samples collected at the surface may have been subjected to atmospheric weathering processes which have subsequently altered the original state of the rock. Thus, if possible, rocks should be broken from a surface formation by the equivalent of geological hammering in order to obtain fresh specimens. In addition it would be desirable to sink a borehole into a rock outcrop thought to be geologically undisturbed. The depth requirement for such a borehole is a subject which would require some debate but clearly should be deep enough to penetrate beyond the effects of suface weathering. Material collected from the walls of the most recent craters or other geological features (fault scarps etc.) should be considered as a means of sampling rocks of greater depths within the crust. Perhaps the best way to obtain data concerning magmatic volatiles is to analyse species trapped (in solid-solution or in fluid inclusions) in primary igneous rocks of fresh, unaltered composition. Samples collected for this sort of study should necessarily not be from surface flows as degassing would have resulted in a loss of volatiles at the time of eruption. Thus, it may be expeditious to analyse material recently ejected from depth by cratering events despite problems created by the lack of knowledge concerning sample location and the possibility of shock-degassing or shock-implantation of gases.

As far as the laboratory analyses are concerned, grams of material from each available rock type should suffice and we would advocate that diversity should take priority when deciding which samples should be on the manifest for the return voyage to Earth. The protocol of collecting, documenting and storing samples should follow along the lines of those used by the Apollo missions.

(2) Secondary alteration effects.

In some ways acquisition of rocks and minerals for this kind of study is straightforward as, in principle, it is possible to simply collect material from the martian surface on the basis that surface samples are likely to be most altered. The techniques applied on the Moon for the collection of soil, breccias and rocks can be applied to Mars suface material. However, from Viking images and other data the martian surface and environment today is clearly more geologically active than that of the Moon. By far the most important differences are the interaction of surface solids with atmospheric gases and also the cycling of volatile materials within and upon the martian surface. Furthermore, in the past freshly erupted volcanic rocks may have reacted with surface, or sub-surface, ice thereby generating a number of secondary products. Undoubtedly much debate will concern the exact location of any proposed Mars sample return mission but, in general terms, it would be advantageous to obtain specimens from dispersed environments in order to sample a variety of secondary alteration phenomena. In particular, it would be desirable to collect samples associated with the flood-produced channels and the plains where fluids may once have accumulated. Samples from within the areas covered by the seasonal polar caps would also be informative to assess the effects of severe frost weathering. Obviously these environments are widely separated and thus again the most profitable mission to Mars needs to have the capability to move over large distances

of the surface.

Samples of surface fines and weathered rocks should be sealed in gas-tight containers filled with ambient martian atmosphere wherever possible so that the products of weathering are not altered, degraded, exchanged etc. (as might be the case if exposed to earth-like atmospheric conditions or hard vacuum during return). When received in the laboratory the solid samples will be analysed for their volatile element inventory and inorganic salt contents. Isotopic measurements will be used to trace the inter-relationships of the active parts of the environment. The head space gases should be analysed in order to provide samples of the martian atmosphere at the collection sites - it will then be possible to understand the nature of the interaction of the surface material and the atmosphere. Wind-borne dust samples should be collected in any area in which the surface samples are acquired; their high surface areas should provide a wealth of information relating to soil-gas interaction. Obviously if low temperature geochemical processes are currently in operation, or have taken place in the past, then samples of surface fines and rocks will need to be stored at low temperature (i.e. equivalent to that of martian winter at the collection site) in order to avoid degredation of any highly volatile compounds or phase changes etc.

In addition to samples collected directly from the surface, it will be necessary to acquire material from depth within the regolith. Here a slightly different approach is required in that it can be expected that the sub-surface environment has witnessed a long history of cycling of volatile components. For example, depending on the sampling location there may be seasonal effects giving rise to the presence of groundwater or ice layers etc; in addition,the flow of volatiles through the surface layers may have built up a duricrust layer of volatile-rich salt compounds. Furthermore, depending on the porosity of the regolith, the interaction of atmospheric gases may extend to well below the surface horizon. As such it will be necessary to acquire bulk samples from a number of shallow trenches (appropriately documented in the field) so that the near-surface stratigraphy can be investigated. At least one core of ≥ 1 metre in length should be drilled in order to investigate in detail the depth relationships of surface weathering processes. Again it is desirable to preserve any volatiles which are frozen in-situ and thus, if possible, samples should be stored at low temperatures to prevent sublimation/evaporation of ices etc.

At the very surface of Mars the highly oxidising environment conspires to convert any carbonaceous materials to carbon dioxide gas, which is subsequently cycled into the atmosphere. This conclusion is arrived at from the results of the Viking Lander gas chromatography-mass spectrometry experiments, which demonstrated there to be negligible quantities of organic compounds in surface materials. However, it is clear that these measurements will need to be repeated by using the most up-to-date equipment available in the laboratory, particularly since samples collected from some depth in the regolith may have been sufficiently shielded from the effects of oxidation and radiation etc, to allow preservation or even synthesis of organic compounds. Supposing a succesful detection of solvent-extractable or macromolecular organic materials, isotopic measurements, in and within individual compounds, should be made in order to help constrain their origin (most importantly it would be necessary to assess whether the organics had a meteoritic source or were indigenous to Mars). If such an investigation is to be successful then obviously appropriate precautions need be taken during collection to ensure minimum levels of contamination by sample handling and storage procedures.

(3) Tertiary alteration effects.

The effects of shock events at the martian surface, caused by impacting bolides, need to be investigated using the full complement of analytical equipment. A primary goal of such studies would be to assess the amounts and nature of extraneous (meteoritic, cometary etc.) material present within the martian regolith. If any of the geological processes in operation on Mars have concentrated meteoritic debris, like glacial phenomena in Antractica, then collection and analysis of this material could prove instrumental in trying to comprehend the meteorite source populations. Light element isotopic studies will be informative in serving to trace the progress of assimilation of foreign material into the regolith. Older regolith breccia materials may contain useful indicators of impact processes which took place in the distant past. Samples collected from crater ejecta may help clarify the lobe-structure which is typical of the larger structures on Mars.

Another significant aim of a Mars sample return mission should be to try and explain the origin and evolution of the atmosphere and to search for the existence of an early hydrosphere. In this context, it is interesting to note that SNC meteorites are believed to contain samples of the martian atmosphere imparted into the sample during a shock event (possibly the impact phenomenon which caused the meteoroids to be ejected from the surface of the planet). Thus in order to investigate the evolution of the atmosphere it may be possible to analyse the gases contained within shock-produced or shock-affected rocks of different ages.

Conclusions

At the outset there are conflicting theories regarding the volatile inventory of Mars; some suggest that the planet is, and always has been, volatile-poor (relative to the Earth) while others claim that it was originally volatile-rich. This is a question which can be answered by returned samples - there is considerable scope with current methods to provide a full understanding of the geochemistry of martian volatile components. In order to study the products of low temperature processes in martian samples it is highly important to analyse samples which can be guaranteed to have not reacted with terrestrial fluids or the Earth's atmosphere. This is an extremely important point and one which the acquisition of martian (SNC) meteorites can never hope to satisfy. The goal of efforts to charcterise the martian inventory of low temperature minerals and light element-bearing materials should be to reconstruct their evolutionary history and to see what information can be gleaned concerning the physical conditions under which they formed (it would be very disappointing indeed if the exercise were to end up in trying to distinguish the effects of martian processes from those of terrestrial alteration or contamination). It is imperative that samples

are returned to Earth for detailed laboratory analysis because the instrumentation needed to make such determinations is complex and requires skillful operation. It is considered that, for the foreseeable future, the chemistry and extraction procedures necessary to process the elements of interest are unlikely to be adaptable to automated machines. We must emphasise that the isotopic effects in the processes of interest at the martian surface are likely to be subtle and thus, highly accurate and unabiguous results need to be obtained if we are to make significant headway in attempts to comprehend the geological cycles which have operated in the past, and are currently taking place, on Mars.

Response to: Call for Input to a Mars Sample-Science Document

Aaron P. Zent

Planetary Geosciences Division

Hawaii Institute of Geophysics

University of Hawaii

Honolulu, Hawaii, 96822

April 9, 1987

The principal focus of my Mars-related research has been the origin and evolution of the Martian volatile inventory. The study can be subdivided into four major sub-topics: 1) What is the bulk volatile inventory of Mars?; 2) How did the planet's thermal history mediate access of that inventory to the surface?; 3) How are the available volatiles partitioned among the available geochemical sinks?; and 4) What are the principal physical and chemical cycles in which the volatiles currently participate?

Significant new results can be achieved in these areas by acquisition of appropriate samples, or by the appropriate *in situ* analyses. Below, I discuss the current problems in each area in highly abbreviated versions, describe samples most likely to contribute to their resolution, and describe qualitatively the degradation tolerances for each sample.

1) Bulk Volatile Abundance. Both theoretical and experimental evidence are converging on a scenario involving very high initial volatile abundances, followed by massive degassing and loss of most of the volatile inventory from the planet. The current paradigm, proposed by Wanke and Dreibus, is based upon the contention that the SNC meteorites are indeed of Martian origin. If that is the case, the considerable chalcophile depletion and volatile enrichment (relative to Earth) of the SNC's points to homogeneous accretion of Mars, followed by partitioning of the chalcophiles into sulphides and thence the core during differentiation. One of the most critical determinations to be made from a Mars sample return mission is whether the SNC meteorites are of Martian origin, and whether the volatile enrichment and chalcophile depletion characteristic of the SNC's is characteristic of the bulk Martian crust. Therefore, a primary goal of a Mars sample return mission should be the collection of a small suite (minimum 5) of unrelated, unweathered igneous rocks. Possible criteria for selection of returned samples include a diversity of XRF analyses, a diversity of grain sizes in order to sample intrusive and extrusive rocks, and samples with and without vesicles. Samples with grain size large enough for mineral separations should be assured. If, as expected, the SNC meteorites prove to be of Martian origin, then this additional set of igneous rocks will greatly aid in constraining the bulk initial volatile abundance of Mars.

As a rule, all samples should be maintained and transported at the conditions under which they were collected. However, bulk volatile abundances should be estimable from relatively pristine samples that have experienced a variety of pressure and temperature histories. I do not know the mobility of moderately volatile elements (from which high bulk abundances are inferred) during shock events, but any attempt to decode the early history of Mars should be based on samples that have experienced minimal shock. It is suggested that an effort be made to obtain igneous samples from bedrock in exposure, rather than collecting rocks from the surface which may prove to be crater ejecta.

Thermal History. The thermal history of Mars controls the planetary differentiation and degassing, the translation of bulk volatile abundance to surface inventory. Collection of the igneous suite would allow Rb-Sr, U-Pb, Nd-Sm and other dating methods to be applied to units previously characterized from orbital imagery. Establishing the ages of specific geologic units on the Martian surface should also be a primary goal of any Mars sample return mission. Even a few samples from a geographically restricted area would allow substantial progress in pinning Martian degassing to a timeline, and in calibrating the all-important crater size frequency curves.

It is critical to the goals of thermal history calibration that a number of the returned samples be minimally, or not at all shocked, nor weathered. It becomes clear that the most important measurements to be made on returned Martian samples may require some degree of mobility on the part of the lander, since relatively pristine bedrock exposures cannot be guaranteed at the landing site from orbit. Further, some coring mechanism may be necessary to access unweathered samples.

Geochemical Sinks. A number a geochemical sinks are available to the Martian volatile inventory. Most important may be irreversible loss to space due to atmospheric cratering at the tail-end of accretion. Dating igneous Martian samples collected *in situ* will allow dating specific units on the Martian surface, and will allow comparison of Martian degassing history, which provided volatiles to the surface environment, and the Martian cratering flux history, which likely represents the greatest volatile sink in Martian history. The currentlty available volatile inventory is probably the result of the temporal superposition of these two competing processes. Establishing firm dates for a few well characterized geologic units should allow photogeologic extrapolation to much of the Martian cratering flux history.

Samples collected uniquely for determination of the geochemical fate of the currently available volatile inventory must be of a somewhat different nature. After loss to space, the regolith probably represents the most extensive volatile reservoir. Volatiles (principally CO_2 and H_2O) can be stored in the regolith as surface and subsurface condensates, adsorbates, in mineral structures, etc. Abundances and proportions will vary strongly with pressure, temperature, and hence depth in the regolith column. If at all possible, the second priority sampling device for a Mars sample return mission should permit acquisition and return of core samples of unconsolidated soil, and perhaps ice, at least 1 m in length. The length of the core must be sufficient to sample beneath the annual thermal skin depth. The necessity of acquiring unweathered and unshocked igneous material supports the inclusion of a coring device. Martian regolith cores, acquired at only two latitudes would aid in establishing absolute volatile abundances, their partitioning into various physical-chemical states, and the latitudinal and depth dependence of both abundance and phase partitioning.

Preserving the state and vertical distribution of highly volatile compounds in a 1 m core during transport over ~ 10^8 km to Earth is likely to be an expensive proposition. Fortunately, it needn't be mandated in the mission profile, although every effort should be made to include it. The scientifically optimal solution of course is just that: transport of the entire core to Earth without incurring deceptive redistribution and/or reaction of the volatiles. However, a number of more economical options may be adopted without jeopardising the most salient data. One possibility is to sample the core at pre-specified intervals, and maintain the sub-samples separately during transport to Earth. A second option is to monitor the pressure and temperature of the core or sub-samples continuously during transport, without heroic efforts to control either. A third, and most attractive possibility, is *in situ* analysis of the samples in support of and to complement, analysis of returned samples.

The principal goal of *in situ* analysis of the Martian cores should be to measure the abundance and physical-chemical state of H_2O and CO_2 as a function of depth, latitude, and possibly season, since *in situ* analyses could continue after the samples leave. Three techniques are suggested; 1) Thermogravimetry, 2) Differential Scanning Calorimetry, and 3) Mass Spectrometry. The techniques should be integrated to the fullest possible extent, so that results from one experiment may be quickly and unambiguously related to results from the others. An advantage of the *in situ* analysis of the cores is that information lost through sterilization of the returned samples can be recovered. Mineralogical analyses of soilsamples are best performed in terrestrial laboratories.

Current Cycles. Determination of the annual and long-term cycles experienced by the Martian volatile inventory is not well suited to sample return missions, although the *in situ* analyses described in the previous section would contribute greatly to their understanding. One further analysis, to be conducted on the sub-samples of the cores, would be an adsorption analysis of the pore size distribution in the regolith column. The thermogravimetric device recommended above could be augmented to permit the adsorption experiment to be conducted, without significantly increasing payload mass.

In conclusion, three separate goals should be realised: 1) A suite of unrelated, unweathered igneous materials should be returned to Earth from well documented sites in well characterised geological units. These samples would allow determination of the bulk volatile inventory of Mars, the thermal history of the planet, and the competition between planetary degassing and atmospheric cratering. 2) A coring device should be used to collect samples for *in situ* analyses, including thermogravimetry, differential scanning calorimetry, mass spectrometry, and adsorption studies. 3) Sectioned cores of weathered soil should be returned in as pristine a state as economically possible.

The necessity of collecting both unweathered samples of igneous materials, and depth-resolved samples for analysis, strongly argues for the inclusion of some kind of coring device. Further, since exposures of bedrock cannot be guaranteed at the landing site, the lander should have mobility on the order of 100's of meters at least. The great importance returning and measuring a representative sample of Martian materials argues strongly for at least two lander/return vehicles, preferably at well separated latitudes. A logical split in tasks would be to land an equatorial sampler that would sample a large igneous unit, and a higher latitude sampler that would emphasise weathered samples.

NASA
National Aeronautics and Space Administration

REPORT DOCUMENTATION PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-4184		

4. Title and Subtitle	5. Report Date
Scientific Guidelines for Preservation of Samples Collected From Mars	April 1990
	6. Performing Organization Code: SN21
7. Author(s): James L. Gooding, Editor	8. Performing Organization Report No.: S-604
9. Performing Organization Name and Address: Planetary Science Branch, NASA/Johnson Space Center, Houston, TX 77058	10. Work Unit No.
	11. Contract or Grant No.
12. Sponsoring Agency Name and Address: Solar System Exploration Division, NASA/Johnson Space Center, Houston, TX 77058	13. Type of Report and Period Covered: Technical Memorandum
	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The maximum scientific value of Martian geologic and atmospheric samples is retained when the samples are preserved in the conditions that applied prior to their collection. Any sample degradation equates to loss of information. Based on detailed review of pertinent scientific literature, and advice from experts in planetary sample analysis, number values are recommended for key parameters in the environmental control of collected samples with respect to material contamination, temperature, head-space gas pressure, ionizing radiation, magnetic fields, and acceleration/shock. Parametric values recommended for the most sensitive geologic samples should also be adequate to preserve any biogenic compounds or exobiological relics.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Mars, Sample preservation	Unclassified - Unlimited Subject Category 91

19. Security Classification (of this report)	20. Security Classification (of this page)	21. No. of pages	22. Price

The principal goal of *in situ* analysis of the Martian cores should be to measure the abundance and physical-chemical state of H_2O and CO_2 as a function of depth, latitude, and possibly season, since *in situ* analyses could continue after the samples leave. Three techniques are suggested; 1) Thermogravimetry, 2) Differential Scanning Calorimetry, and 3) Mass Spectrometry. The techniques should be integrated to the fullest possible extent, so that results from one experiment may be quickly and unambiguously related to results from the others. An advantage of the *in situ* analysis of the cores is that information lost through sterilisation of the returned samples can be recovered. Mineralogical analyses of soilsamples are best performed in terrestrial laboratories.

Current Cycles. Determination of the annual and long-term cycles experienced by the Martian volatile inventory is not well suited to sample return missions, although the *in situ* analyses described in the previous section would contribute greatly to their understanding. One further analysis, to be conducted on the sub-samples of the cores, would be an adsorption analysis of the pore size distribution in the regolith column. The thermogravimetric device recommended above could be augmented to permit the adsorption experiment to be conducted, without significantly increasing payload mass.

In conclusion, three separate goals should be realised: 1) A suite of unrelated, unweathered igneous materials should be returned to Earth from well documented sites in well characterised geological units. These samples would allow determination of the bulk volatile inventory of Mars, the thermal history of the planet, and the competition between planetary degassing and atmospheric cratering. 2) A coring device should be used to collect samples for *in situ* analyses, including thermogravimetry, differential scanning calorimetry, mass spectrometry, and adsorption studies. 3) Sectioned cores of weathered soil should be returned in as pristine a state as economically possible.

The necessity of collecting both unweathered samples of igneous materials, and depth-resolved samples for analysis, strongly argues for the inclusion of some kind of coring device. Further, since exposures of bedrock cannot be guaranteed at the landing site, the lander should have mobility on the order of 100's of meters at least. The great importance returning and measuring a representative sample of Martian materials argues strongly for at least two lander/return vehicles, preferably at well separated latitudes. A logical split in tasks would be to land an equatorial sampler that would sample a large igneous unit, and a higher latitude sampler that would emphasise weathered samples.

APPENDIX B4

ESTIMATES OF MARTIAN "OXIDANT" ABUNDANCES IN SEDIMENT SAMPLES AT THE *VIKING* LANDING SITES

James L. Gooding

SN21/Planetary Science Branch,
NASA/Johnson Space Center, Houston, TX 77058.

Introduction. The life-detection experiments on the *Viking* Landers obtained apparently positive responses which, after initial evaluation as possible biological activity, were inferred to be signatures of highly reactive inorganic chemical agents in the Martian sediment samples. As reviewed by Klein [1], the complete set of results indicated that at least two (and possibly three or more) different agents occurred in the samples. Given the fundamentally different nature of the three biology experiments and their results, it was concluded that, at the minimum, the set of reactive agents possessed the capacities to evolve molecular oxygen by reaction with water, to oxidize simple organic compounds in aqueous solution, and to fix gaseous carbon dioxide into forms that are non-volatile under nominal Martian surface conditions. Despite those very different properties, the oxidization reactions received more popular attention and the reactive agents became known collectively as "oxidants". Although the experiment teams explored various explanations for the *Viking* results, derived values for the abundances of the "oxidants" were apparently never published.

The simple calculations presented here purport to use the *Viking* measurements to estimate the concentrations of reactive agents in the original sediment samples. Such estimates are needed both to support preservation plans for returned Martian samples and to assist in design of future Mars surface experiments. As will be shown, there is no single, preferred concentration value. Instead, it is found that the "oxidant" concentrations were probably in the range of a few parts per billion (ppb) to a few hundred parts per million (ppm) by weight.

Data and Assumptions. Upper limits for abundances of the reactants can be estimated from the most active samples (i.e., those giving the greatest "positive" results) in the *Viking* Lander gas-exchange (GEX), labelled release (LR) and carbon assimilation (CA; also known as pyrolytic release, PR) experiments. Other samples showed less activity, presumably because they contained lower abundances of the active chemical agents. Data used here are those reported by the original investigator teams [2-5]. Assuming a bulk density of 1.5 g/cm^3 for the delivered soil samples of specified volume, the masses of the samples analyzed were approximately 1.5 g (GEX), 0.75 g (LR), and 0.38 g (CA/PR), respectively. For simplicity, instrument-based differences between actual decay rates and measured count rates are ignored here for LR and CA/PR.

Most interpreters of the *Viking* biology results have favored one or more metal peroxides or superoxides as the active agents for the observed phenomena. Because computational results of the type presented below depend on the molecular weight (hence, identity) assumed for the oxidant and the stoichiometry assumed for the pertinent reactions, caution must be exercised in interpreting the derived numbers; they are intended to represent only the order-of-magnitude concentrations of the compounds in question. For simplicity, the following results assume the stoichiometry appropriate for alkali-metal peroxides (M_2O_2) as model reactants and express results in equivalent concentrations of H_2O_2. It should not be inferred, however, that this procedure represents an endorsement of H_2O_2 as the active agent in any of the *Viking* biology experiments. Alternative models, based on catalytic properties of clay minerals [6,7] deserve separate attention and are not treated here.

Results for GEX. The GEX, VL-1 "Sandy Flats" (first cycle, humid) sample released 790 nmol O_2 after wetting of 1 cm^3 of soil with 0.56 cm^3 of aqueous nutrients [5]. If evolution of O_2 was an inorganic process, for which the organic nutrients were simply spectators in a water/peroxide reaction, each mole of O_2 produced would require consumption of two moles of peroxide:

$$M_2O_2 + H_2O \rightarrow 1/2\ O_2 + 2\ MOH.$$

Therefore, the abundance of peroxide would be $2(7.9 \times 10^{-7}$ mol)/1.5 g = 1.05×10^{-6} mol/g sample. If the peroxide was H_2O_2 (f.w. 34.0), the implied abundance would be

$$(1.05 \times 10^{-6})(34.0) = 36 \text{ ppm}.$$

Using laboratory simulations with photo-oxidized MnO_2 to duplicate the GEX results, Blackburn et al. [8] pointed out that 790 nmol of O_2 could be produced by only 1.9×10^{18} atoms of activated Mn. That amount would correspond to only 1.2×10^{-4} g Mn/g sample, or only 120 ppm Mn in the sample. If the oxidant was MnO_3H (f.w. 103.9), as suggested by Blackburn et al. [8], then its equivalent concentration would have been $(1.2 \times 10^{-4})(103.9/54.9) = 230$ ppm.

Results for LR. The LR, VL-2, under "Notch Rock" (third cycle) sample produced 15,500 dpm of ^{14}C after injection of 0.115 cm^3 of aqueous nutrient onto 0.5 cm^3 of sample [3]. The nutrient consisted of 7 organic compounds, each at a concentration of 2.5×10^{-4} M and with an average labelled activity of 8 μCi/μmol [2].

The carbon gas evolved (presumably CO_2) contained *at the minimum* the number of carbon atoms equivalent to the measured radioactivity. Most likely (but not substantiated by the experiment), the evolved gas also contained non-radioactive carbon in the same proportion as the ^{14}C/(total C) ratio in the original nutrients. Therefore, at least two different estimates for oxidant abundance are possible. The number of ^{14}C atoms should be related to the decay rate according to $N = (1/\lambda)(dN/dt)$, where $\lambda = 1.21 \times 10^{-4}\ y^{-1} = 2.30 \times 10^{-10}\ m^{-1}$. Therefore, using the measured activity, the minimum (all ^{14}C) "efficiency" of carbon consumption was $[(1.55 \times 10^4\ m^{-1})/(2.30 \times 10^{-10}\ m^{-1})]/[(6.02 \times 10^{23}\ mol^{-1})(0.75\ g)] = 1.49 \times 10^{-10}$ mol C/g sample. A second, higher estimate could be made by assuming that the specific activity (on a molar basis) of the evolved gas was not changed by the oxidation reaction(s). (The most plausible change, but one not addressed by the experiment, would have been mass-dependent fractionation of the carbon isotopes by oxidation). The assumption of constant specific activity in the nutrients and the evolved gas permits a gas yield of $[(1.55 \times 10^4\ m^{-1})(1\ m/60\ s)]/[8\ Ci/mol)(3.7 \times 10^{10}\ s^{-1}/Ci)(0.75\ g)] = 1.16 \times 10^{-9}$ mol C/g sample.

If the oxidation reaction involved a 1:1 molecular ratio of oxidant to nutrient (e.g., M_2O_2/HCOONa), then the decarboxylation "efficiency" number also corresponds to the moles of oxidant per gram of sample. Reducing the yields to a basis of H_2O_2 concentrations, as done above for GEX, gives the following two estimated concentrations:

$$(1.49 \times 10^{-10})(34.0) = 5.1 \text{ ppb} \qquad (1.16 \times 10^{9})(34.0) = 39 \text{ ppb}.$$

A third estimate can be made by accepting the interpretation [1,2] that the equivalent of one ^{14}C-labelled nutrient was quantitatively oxidized by the most reactive sample. (Although partial oxidation of several different nutrients cannot be excluded by available data, quantitative consumption of the formate nutrient became the favored interpretation, because of the model simplicity offered by a one-carbon compound). Given the concentration and volume of each LR inoculation, the absolute quantity of each nutrient in the subject experiment was $(2.5 \times 10^{-4}\ mol/10^3\ cm^3)(0.115\ cm^3) = 2.9 \times 10^{-8}$ mol. Assuming the same 1:1 stoichiometry for oxidation used above and an H_2O_2 basis, the alternative estimate for the "oxidant" concentration would be

$$(2.9 \times 10^{-8})(34.0)/(0.75) = 1.3 \text{ ppm}.$$

Results for CA/PR. The CA/PR, VL-1, "Sandy Flats" (C1) sample produced 842 dpm of ^{14}C (corrected Peak 2) after incubation of 0.25 cm^3 of sample [4] with 20 μl of ^{14}C-labelled CO_2 and CO (98:2 by volume; total activity of 22 μCi) in a 4 cm^3 test cell filled with Martian atmosphere (95% CO_2) at 7.6 mb pressure and a temperature of 17° C [2]. The ^{14}C spike increased the total cell pressure by 2.2 mb [2].

By analogy with LR, the simplest *minimum* estimate for the carbon actually fixed can be found from the number of ^{14}C atoms that were fixed. Following the first-order decay method used for LR, the minimum "efficiency" for carbon fixation in CA/PR was $[(8.42 \times 10^{2}\ m^{-1})/(2.30 \times 10^{-10}\ m^{-1})]/[(6.02 \times 10^{23}\ mol^{-1})(0.38\ g)] = 1.60 \times 10^{-11}$ mol C/g sample. Again, by analogy with LR (and ignoring possible mass-dependent fractionation of carbon during reaction), an alternative estimate can be made by assuming no change in specific molar activity during carbon fixation (i.e., Martian CO_2 was fixed along with the labelled CO_2). For ideal gas behavior, the total activity per mole of CO_2 in the cell before reaction would be $(2.2 \times 10^{-5}\ Ci)/[((7.6 + 2.2)/1013\ atm)(4 \times 10^{-3}\ l)(0.95)/(8.21 \times 10^{-2}\ l\ atm\ K^{-1}\ mol^{-1})(290\ K)] = 1.42 \times 10^{1}$ Ci/mol. From the measured ^{14}C activity in the fixed carbon, the "efficiency" of fixation would follow as $[(8.42 \times 10^{2}\ m^{-1})(1\ m/60\ s)]/[(1.42 \times 10^{1}\ Ci/mol)(3.7 \times 10^{10}\ s^{-1}/Ci)(0.38\ g)] = 7.03 \times 10^{-11}$ mol C/g sample.

The experiment team originally suggested [2] a conversion factor of $(2.6 \times 10^{-11}$ mol $CO_2/81$ dpm) $= 3.2 \times 10^{-13}$ mol C/m^{-1} ^{14}C which, by the reasoning presented here, would have led to a fixation "efficiency" of $(3.2 \times 10^{-13})(8.42 \times 10^{2})/(0.38) = 7.09 \times 10^{-10}$ mol C/g sample.

On an H_2O_2-equivalent basis, the consequent estimates for fixation-reactant concentration according to these three different model assumptions would be

$$(1.60 \times 10^{-11})(34.0) = 0.54\ ppb \qquad (7.03 \times 10^{-11})(34.0) = 2.4\ ppb \qquad (7.09 \times 10^{-10})(34.0) = 24\ ppb.$$

An additional complication exists in CA/PR because CO is not distinguished from CO_2 among the reactants and products [2,4]. Because the $^{14}CO_2$ in the experimental gas spike possessed a lower specific activity than the ^{14}CO, the three estimates given immediately above could actually be lower (by as much as a factor of 3) if CO was a major reaction participant [4].

It is important to note that, as originally pointed out by the experiment team [2,4], the active agent detected by the CA/PR experiment might not be an "oxidant". In principle, either an oxidizing or reducing agent (or a third category, "organic-synthetic catalyst") might have produced the carbon fixation.

Summary and Conclusions. The simplest interpretations (i.e., those with the fewest model assumptions) of the three *Viking* biology experiments imply abundances for the unidentified oxidants/reactants comprising 36 ppm (GEX), 5 ppb (LR), and 0.5 ppb (CA/PR), when expressed in equivalent concentrations of H_2O_2. The LR and CA/PR results, in particular, are open to a wide range of model assumptions that can support other H_2O_2-equivalent concentrations up to 24 ppb (CA/PR) or 1 ppm (LR). The values so derived are fundamentally uncertain because both the molecular weights of the reactants and the stoichiometry of the subject reactions remain unknown. The important point is not the specific number values but the fact that the chemical agents responsible for the Viking biology results occurred at exceedingly small concentrations. Even if several different oxidants/reactants were involved, they would require either very high molecular weights (at least 10 times that of H_2O_2) or disproportionately large reaction coefficients (i.e., high reactant/evolved-gas ratio) in order for their total concentrations to exceed a few hundred ppm by weight in the samples.

The trace levels of the "oxidants" must be appreciated both for Mars sample-return missions and for design of future *in situ* Mars sample analyzers. It will be scientifically important to carefully preserve at least some subset of samples in a way that maximizes the opportunity to study these rare, metastable compounds in the laboratory; their low abundances will mean that they may be difficult to isolate for identification. Any experiments proposed to identify the "oxidants" *in situ* must be able to perform diagnostic analyses of analytes that occur at the ppb to ppm levels.

References

[1] Klein H. P. (1978) The Viking biological experiments on Mars. *Icarus, 34,* 666-674.

[2] Klein H. P., Horowitz N. H., Levin G. V., Oyama, V. I., Lederberg J., Rich A., Hubbard J. S., Hobby G. L., Straat P. A., Berdahl B. J., Carle G. C., Brown F. S., and Johnson R. D. (1976) The Viking biological investigation: preliminary results. *Science, 194,* 99-105.

[3] Levin G. V. and Straat P. A. (1976) Viking labelled release biology experiment: interim results. *Science, 194,* 1322-1329.

[4] Horowitz N. H., Hobby G. L., and Hubbard G. S. (1977) Viking on Mars: the carbon assimilation experiment. J. Geophys. Res., 82, 4659-4662.

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

[6] Banin A. and Margulies L. (1983) Simulation of Viking biology experiments suggest smectites not palagonites as martian soil analogues. *Nature, 305,* 523-525.

[7] Burt D. M. (1989) Iron-rich clay minerals on Mars: Potential sources or sinks for hydrogen and indicators of hydrogen loss over time. *Proc. 19th Lunar Planet. Sci. Conf.,* 423-432.

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

NASA
National Aeronautics and Space Administration

REPORT DOCUMENTATION PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-4184		

4. Title and Subtitle	5. Report Date
Scientific Guidelines for Preservation of Samples Collected From Mars	April 1990
	6. Performing Organization Code: SN21
7. Author(s): James L. Gooding, Editor	8. Performing Organization Report No.: S-604
9. Performing Organization Name and Address: Planetary Science Branch, NASA/Johnson Space Center, Houston, TX 77058	10. Work Unit No.
	11. Contract or Grant No.
12. Sponsoring Agency Name and Address: Solar System Exploration Division, NASA/Johnson Space Center, Houston, TX 77058	13. Type of Report and Period Covered: Technical Memorandum
	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The maximum scientific value of Martian geologic and atmospheric samples is retained when the samples are preserved in the conditions that applied prior to their collection. Any sample degradation equates to loss of information. Based on detailed review of pertinent scientific literature, and advice from experts in planetary sample analysis, number values are recommended for key parameters in the environmental control of collected samples with respect to material contamination, temperature, head-space gas pressure, ionizing radiation, magnetic fields, and acceleration/shock. Parametric values recommended for the most sensitive geologic samples should also be adequate to preserve any biogenic compounds or exobiological relics.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Mars, Sample preservation	Unclassified - Unlimited Subject Category 91

19. Security Classification (of this report)	20. Security Classification (of this page)	21. No. of pages	22. Price
Unclassified	Unclassified	242	A11

For sale by the National Technical Information Service, Springfield, VA 22161-2171

NASA-Langley, 1990