# PLANETARY SURFACE INSTRUMENTS WORKSHOP

Edited by

Charles Meyer, Allan H. Treiman, and Theodor Kostiuk

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Cover: MIMOS-II, a miniaturized Mössbauer instrument with two detector channels, developed for use in space missions with very limited power resources like the Small Stations of the Russian Mars ’96 Mission.

# Introduction

The next steps in the exploration of the solar system will include robotic missions to the surfaces of planets, moons, asteroids, and comets. For the greatest possible returns from these missions, their scientific rationales must be closely coordinated with development of appropriate instrumentation and with the constraints of mission and program planning. Instruments on a spacecraft must take measurements that can answer critical scientific questions within the mass, time, and energy constraints of its mission. Unfortunately, this ideal state of cooperation is difficult to achieve. Scientists, engineers, and managers often have distinctly different goals, speak different languages, and work on different timescales.

The Planetary Surface Instruments Workshop, held at the Lunar and Planetary Institute in Houston, Texas, on May 12–13, 1995, was motivated by one problem of timescales: Today, a planetary surface mission could likely proceed from concept to final manifest faster than a critical instrument could be brought from concept to space-readiness. In order to address this potential problem, we hoped this workshop would initiate cooperation on scientific instruments for planetary (and cometary) surface missions *before* specific missions are proposed or started.

Planning and operation of the Planetary Surface Instruments Workshop followed a few simple principles. The workshop focused on high-level scientific problems common to all solid planetary surfaces, and avoided (where possible) issues peculiar to specific solar system bodies. The workshop focused on analytical instrumentation that would be applicable to solid bodies of the inner solar system (including asteroids and passing comets). The workshop did not deal with specific missions in planning or development, including their scientific goals and instrument selections, except as examples of more general scientific, engineering, or management principles. We sought to invite younger and newer participants in planetary missions and spaceflight instrument development, but did not specifically exclude experienced participants. The workshop was run on a “no-frills” basis, had no registration fee, and finished under budget. And finally, we committed to completing this technical report for electronic distribution within three months of the workshop.

The workshop brought together scientists and instrument design engineers from a wide range of fields to consider what scientific instruments could do from a landed robotic spacecraft. Of the 65 scientists and engineers who attended the workshop, 23 were from university institutions, 5 were from overseas, 5 represented commercial interests, and the rest were from government laboratories. A list of participants and their addresses is included at the end of this volume. The attendees were assigned, according to areas of expertise or general scientific discipline, into eight working groups: precise chemical analysis, isotopes and evolved gas analysis, planetary interiors, atmospheres from within, mineralogy, carbon-based compounds and exobiology, regoliths in 3D, and field geology/processes. Each group included generalists and specialists, scientists and engineers, as well as “newcomers” and “old hands.” Many attendees had significant expertise in more than one area, and were encouraged to contribute to other groups. Many attendees had “vested interests” in specific instruments or scientific areas; we encouraged all to be evenhanded in evaluating their work and that of others.

Each group was asked to (1) assess the general scientific questions answerable by robotic spacecraft landed on planetary surfaces, (2) identify the measurements critical to answering those questions, (3) suggest classes of instruments capable of those measurements, and (4) identify areas where the scientifically desired measurements are not feasible using available instruments.

Each group was given free reign to address the tasks as they saw fit, thus their reports reflect the organizational and presentational needs of their subject and do not follow a standard format. The groups each made great efforts to relate instrumental measurements to important scientific problems, and organized themselves to write the chapters of this report. Most of the actual writing was done after the workshop. Although the workshop goal was to address “generic” rather than “specific” solar system objects, most of the workshop groups seem to have focused on instrumentation for Mars and comets as examples of landing targets, perhaps influenced by the authoritative COMPLEX report. Perhaps this was also due to the fact that several proposals were due for Mars Surveyor and ROSETTA/Champollion in the same timeframe as the workshop.

In plenary sessions at the workshop we heard presentations of the “Critical Science Questions” as laid out by COMPLEX (G. Ryder), each of the NASA Science Working Groups (J. Kerridge, A. Treiman, T. Swindle, S. Keddie, and M. Zolensky), and the European and Japanese communities (H. Mizutani and J. Zarnecki). We also heard reports on a JPL approach for packaging instruments into “Sciencecraft” (P. Beauchamp), on one Discovery mission proposal (H. Schmitt), and on the need for a long-term strategy for Mars (S. Saunders). These ideas have been considered and discussed in the enclosed chapters from each of the teams at the workshop.

This exercise has led to a more focused community of scientists interested in exploring planetary surfaces using instrumental techniques. The workshop brought together scientists and instrument design engineers from a wide range of fields to consider what scientific instruments could do from a landed robotic spacecraft. One result is that members of this community are now better able to review proposals and advocate missions to planetary surfaces.

The product of the Planetary Surface Instruments Workshop is this report, which contains the attendees’ responses to the tasks above. The report is intended to provide support and information to the scientific and engineering communities concerned with the planetary bodies and comets, spacecraft mission, and instrumentation design. It is also intended to provide support and information to NASA programs concerned with instrument development, and to the many NASA Science Working Groups regarding ways in which critical scientific questions can be answered by robotic probes to planetary surfaces. Many groups felt that an introductory "tutorial" was important in framing their group's conclusions. Many of the groups also named specific instruments and packages as examples of the current state of instrumentation technology; this naming does not constitute endorsement by NASA or the LPI.

This report should not be considered a final statement; by its preliminary informal nature, it cannot be complete nor completely inclusive. Nor is it intended to supplant the conclusions of NASA and NRC advisory boards or previous conference on instruments for planetary missions. If fact, we hope this report will soon be outdated by the emergence of new scientific questions, new measurement schemes, and new spaceflight instruments suitable for deployment on planetary surfaces.

We are, of course, grateful to all the workshop participants, who gave their expertise, time, and travel funds toward completion of this report, and to those who could not attend but also contributed to this document. We are particularly grateful to the group leaders, who agreed to compile input from each group and render it a coherent whole. We appreciate financial sponsorship from the LPI. The workshop itself would not have been possible without support from the Publications and Program Services Department of the LPI. Equally, electronic publication of this report would not have been possible without support from the LPI's Center for Computing and Planetary Data Analysis.

*—Allan H. Treiman, Charles Meyer, and Theodor Kostiuk*

# Contents

# 1: Summary of Report

## —Allan Treiman and Charles Meyer

### 1.1. GENERAL OVERVIEW

Although each working group of the Planetary Surface Instruments Workshop approached its topic uniquely, we found general consensus on some important issues.

1. Robotic probes landed on planetary surfaces are critical to exploration of the solar system. Instruments landed on planetary surfaces can answer a different set of scientific questions than can instruments in orbit or instruments on Earth (including analyses of returned samples). Landed instruments should not be seen as competitors to orbital or sample return science, but rather as providing complementary data.

2. Some highly desirable measurements from planetary surfaces are not possible with available technology. On the one hand, these measurements are obvious targets for technology improvements. On the other hand, the scientific questions behind the measurements may need to be reformulated. For instance, analyses of basalts for Ir at the parts-per-billion level is a critical constraint in understanding core formation and mantle-crust interactions, but remote robotic analyses of Ir at this level are impossible at present. However, it might be possible to gain similar constraints on planetary processes by analyses of other elements, such as Fe, Ni, Co, etc.

3. Unambiguous answers to scientific questions will commonly require more than one measurement or analytical technique. Thus, flight instruments must be designed to permit synergy with other instrument systems; for instance, a mineral identification method must permit visual imagery of the sample to be analyzed. An apt analogy from Chapter 7 is that a ". . . spacecraft should not just carry a collection of individual instruments each playing its own tune, but must be an orchestra." In an era of simpler spacecraft, this would seem to imply a few highly specific instruments ("duets" or "trios") cooperating to address tightly focused objectives.

4. A key instrument system in need of development is a microscopic imaging system capable of multispectral or hyperspectral analyses. The need for, and value of, a microscopic imaging system are discussed in Chapter 6 (Mineralogy), Chapter 7 (Carbon-based Compounds and Exobiology), Chapter 8 (Regoliths in 3-D), and Chapter 9 (Field Geology/Processes).

5. Many superb instruments and instrument concepts are available for landed planetary surface missions. The conceivers and builders of these new instruments need to be encouraged to talk with each other and with spaceflight agencies to form a new community of dedicated planetary surface explorers and to advocate development of planetary surface instruments.

### 1.2. PRECISE CHEMICAL ANALYSIS OF SOLIDS

The chemistry group evaluated critical science issues, analytical strategies, and instruments available for landers on small asteroids (fragments from primitive and differentiated planetesimals), small satellites, and large differentiated planetary surfaces. They identified the critical elements and element ratios that should be analyzed to answer the questions identified in the COMPLEX report and in briefings from the various science working groups (SWGs). Many of these answers will require two chemically sensitive instruments, one to analyze the outermost layer (to determine weathering effects) and the second to analyze the subsurface volume of material (to determine the composition of unaltered material). This duo of measurements will have the added bonus of calibrating orbital and remote Earth-based spectral observations of other areas on the surface of planetary bodies.

The chemistry group concluded that in many cases the scientific issues defined by COMPLEX and the SWGs can only be fully addressed with combined packages of instruments that would supplement the chemical data with mineralogical and visual information.

### 1.3. ISOTOPES AND EVOLVED GAS ANALYSES

The isotopes group reports that new varieties of lightweight low-power mass spectrometers are being developed, but none has yet reached the stage where its performance can match current space-qualified mass spectrometers. For poorly studied planetary bodies, the reduced masses of these new instruments outweigh their shortcomings in performance. For the better-studied planetary bodies (Moon, Mars), significant gains in performance will be needed to replace current instruments.

Probably the single most important isotopic measurement would be an absolute age determination, an analysis that has never been done with an *in situ* instrument. Two new techniques (acid dissolution K-Ar dating and laser ablation Pb-Pb or U-Pb dating) were proposed and evaluated at this workshop. Without further development, it is impossible to tell whether or not these techniques could work at a remote location. Interpretation of such an age determination could be equally problematic in the absence of control on samples or opportunity to experiment.

### 1.4. PLANETARY INTERIORS

The planetary interiors group emphasized the importance of geophysical measurements as a window to the internal structures of planetary bodies. Seismic measurements are the most revealing of a planet's interior structure; a network of seismometers would provide the maximum data, but a single seismometer could still provide important data. Measurement of heat flow, even at a single site, will provide an important constraint on thermal forcing of internal planetary processes. However, long-term climatic variations (as inferred for Mars) may strongly perturb the measured heat flow from its long-term average. Measurement of magnetic field orientation and strength from a lander are most useful as an EM sounder, using variations in the solar magnetic field as probes of the planet's interior. Suitable magnetometers are currently available and can be adapted for planetary surfaces, but need to be deployed far from the magnetic "noise" of a lander and protected from temperature extremes. Finally, geodetic measurements can be used in understanding the dynamics and crustal strains in a planet.

Penetrators seem to be ideal delivery vehicles for most of these geophysical instruments. Emplacement by penetrator would provide strong mechanical coupling to rock, isolation from noise (mechanical and EM), and insulation from diurnal temperature variations. However, the use of penetrators raises questions of instrument survivability and determining instrument orientation in the absence of a dipole magnetic field. Geodetic measurements could be readily obtained from any lander as an augmentation to the navigation function. However, it would be important for the benefits of geodetic science return to be factored into the design of navigation systems and hardware.

Specific needs for planetary interiors studies include (1) longevity of spacecraft systems to permit data collection for longer than a year, (2) development of a space-qualified 24-bit A-D converter for seismometers, (3) development of data compression schemes that will extract from a massive data stream (1 Gbit/day) the critical data for seismology, (4) development of electronics that can operate at extreme temperatures, and (5) validation of penetrator technology.

## 1.5. ATMOSPHERES FROM WITHIN

Lander instruments provide a view of planetary atmospheres that cannot be obtained from orbit. First, they can provide chemical analyses for minor and trace constituents, undetectable by remote spectroscopy. Second, lander instruments can provide data on atmosphere-surface interactions, which are unobtainable from orbit because of the difficulty in distinguishing atmosphere and surface in nadir or even limb-viewing geometry. Measurements at the surface can include temperature, gas velocities, compositions, particulate loading, identification of condensates/sublimates, etc. These data are critical in understanding atmosphere chemistry and for a boundary value system for studies of atmosphere dynamics. Third, a lander with some longevity can provide critical data on diurnal, seasonal, and interannual variations in the atmosphere. Finally, measurements from the surface complement measurements from orbit; for example, the lower bound of Mars' ionosphere is inaccessible from orbit.

The atmospheres working group found many instruments qualified for spaceflight or in development, including UV-NIR cameras, microwave/far-IR spectrometers, aerosol/dust analyzers, and atmospheric EM sounders. Not specifically considered, but under development elsewhere, are thermometers, anemometers, and barometers. The group considered that magnetic or thermal sensors can be severely compromised by improper deployment. They also recommend that atmospheric measurements from a lander be performed on a long time base to recover diurnal, seasonal, and interannual variations; be supplemented with entry probe data; be derived from a network of stations, including multiple landers; and be coordinated with orbital measurements.

## 1.6. MINERALOGY

Mineralogy is a critical tool in characterizing planetary surfaces. Minerals tend to be stable only over limited ranges of pressure, temperature, and ambient chemistry (PTX), and so the presence of a particular mineral or assemblage of minerals can permit the characterization of current or past physical and chemical conditions. Mineralogy is an essential tool for use in carbon-based compounds and exobiology, regolith studies, and in field geology. In addition, a knowledge of mineralogy can contribute significantly to understanding chemical and isotopic analyses of planetary surface materials, especially including radiometric age dates. The mineralogy group considered the many mineralogic identification techniques in two ways: in a systematic survey of available methods and in a discussion of analysis methods most suitable to different types of planetary bodies.

For primitive bodies (asteroids, comets, and Kuiper belt objects), the key mineralogic issue is recognizing the different primitive component materials (interstellar, nebular, and protoplanetary) and their secondary products from metamorphism and aqueous alteration in ancient planetesimals. For differentiated bodies without atmospheres (Moon, Mercury, and some asteroids), the key mineralogic questions include the high-temperature mineralogy and oxidation states of their surfaces, evidence for aqueous alteration, and a search for deep crustal and mantle material. For differentiated bodies with atmospheres (Venus and Mars), the critical mineralogic issues center on the products of atmosphere-surface interactions and the conditions required to produce them.

## 1.7. CARBON-BASED COMPOUNDS AND EXOBIOLOGY

The ultimate objective of the exobiology working group was the search for evidence of life and prebiotic chemistry throughout the solar system. Emphasis was placed first on

Mars as an exploration target, then on comets, and lastly on asteroids and satellites of the giant planets. For Mars, the search focuses first on evidence for the action of liquid water: hydrated phases and minerals diagnostic of aqueous and biological processes. For comets and asteroids, the search focuses first on characterizing their organic and related (CHON) constituents with respect to composition, bonding, and isotope signatures.

Many of the instrumentation needs here are duplicated in other groups: chemical composition, isotope and evolved gas analysis, atmospheres from within, mineralogy, and field geology/processes. Most mineralogical, chemical, isotopic, and geological analyses do have implications for life and prebiotic chemistry. The working group echoes "An Exobiological Strategy for Mars Exploration" in calling for instrumentation that addresses surface mineralogy, the chemical environment, and characterization of organic matter. Analytical methods most specific to this group include aqueous chemistry, mass spectrometric methods optimized for organics, and chromatographic and electrophoretic methods optimized for biogenic species. Significant improvement may be possible for all these methods. Finally, the group emphasized that a single instrument is never adequate on its own for analyses in a complex environment. Instrument hybrids or arrays are needed to yield unambiguous results, and the individual instruments must be chosen with care to form "an orchestra." Also implicit in their discussion is the need for significant mobility to seek out the best, ideal, rare, or hidden samples that may retain evidence of life or prebiotic chemistry.

## 1.8. REGOLITH IN 3-D

The regolith group saw the need to recognize and distinguish two groups of science objectives and measurement goals: One group that will lead to better understanding of the evolution of a planetary body and a second group that might be specific to regolith evolution and the ability of the regolith to serve as a "tape recorder" for endogenic and exogenic processes. Given the highly variable state of knowledge regarding the character of regoliths on various solar system bodies, a phased approach of exploration is suggested. This type of approach will provide needed flexibility for evaluating the highly variable regolith properties.

The highly variable level of understanding of regolith properties also requires that sampling strategies be "smarter" in order to ensure the success of the regolith investigation. Samplers need to be able to assess near-surface properties *in situ* and adjust accordingly. For example, a sampler might begin its deployment with a soft push, then evolve to a rotary drill or percussion pile driver.

## 1.9. FIELD GEOLOGY / PROCESSES

The field geology group found four basic requirements for a robotic field geologist: geological context, surface vision, mobility, and sample manipulation. Geologic context requires a combination of orbital (1000–100-m resolution) and descent (10 m) imaging. Surface vision requirements includes range (100 m), resolution (1 mrad, meters to 10 µm), stereo, and VIS-IR multispectral imaging. The minimum mobility for useful field geology is 1–10 km, or 10 pixels of orbital imagery. The sample manipulation requirement includes exposing unweathered surfaces and bringing samples to analytical instruments. In this context, mobility implies that a rover of some sort is critical to an adequate understanding of the geologic field relations and processes in a target area.

Many of the instrumentation needs specific to field geology/processes center on imaging systems. The group called on hyperspectral or multispectral imagery and microscopy as tools for mapping and mineral identification. The remote operation of multispectral sensors will require computer-aided classification of spectra and spectral patterns and decision-making based on the classifications, i.e., artificial intelligence. Fuzzy-logic rule-based systems seem an attractive starting point, but considerable development and testing will be required.

A critical problem for a remote field geologist is seeing fresh, unweathered material. Surface coatings or patinas can develop from many processes, and would obscure the underlying material. Some kind of rock-chipping machine would be needed to ensure that fresh material is exposed for analysis and possible sampling. The group also saw a significant need for a rover-based preliminary analysis system, e.g., a combined X-ray diffraction/X-ray fluorescence instrument, for rapid mineralogical and bulk chemical analyses to assist in sample selection.

# 2: Precise Chemical Analyses of Planetary Surfaces

***—David Kring, Jeffrey Schweitzer, Charles Meyer, Jacob Trombka, Friedemann Freund, Thanasis Economou, Albert Yen, Soon Sam Kim, Allan Treiman, David Blake, and Carey Lisse***

**Abstract.** We identify the chemical elements and element ratios that should be analyzed to address many of the issues defined by COMPLEX. We determined that most of these issues require two chemically sensitive instruments to analyze the necessary complement of elements. In addition, it is useful in many cases to use one instrument to analyze the outermost planetary surface (e.g., to determine weathering effects), while a second is used to analyze a subsurface volume of material (e.g., to determine the composition of unaltered planetary surface material). This dual approach to chemical analyses will also facilitate the calibration of orbital and/or Earth-based spectral observations of the planetary body. We determined that in many cases the scientific issues defined by COMPLEX can only be fully addressed with combined packages of instruments that would supplement the chemical data with mineralogic or visual information.

## 2.1. INTRODUCTION

The Space Studies Board of the National Research Council has outlined four scientific goals for solar system exploration (*COMPLEX*, 1994): (1) to "understand how physical and chemical processes determine the main characteristics of the planets, thereby illuminating the workings of Earth"; (2) to "learn how planetary systems originate and evolve"; (3) to "determine how life developed in the solar system and in what ways life modifies planetary environments"; and (4) to "discover how the simple, basic laws of physics and chemistry can lead to the diverse phenomena observed in complex systems."

These goals and the specific scientific questions they represent can be addressed by analyzing the chemical compositions of planetary surfaces, because these compositions are the direct results of major solar system processes: the accretion of interstellar material into planetesimals and then planetary bodies; initial heating and thermal metamorphism of small planetary bodies; planetary differentiation in both small and large planetary bodies; local geologic processes that build and/or modify planetary surfaces (e.g., volcanism, impact cratering, or sedimentation); the interaction of solid materials with liquids (such as water), either on or beneath the surface; the interaction of the solid surface with any atmosphere(s) that may exist now or in the past; and the interaction of the solid surface with biologic activity.

Because planetary surfaces are the most accessible portions of any solar system body, they are the logical targets of future spacecraft missions and planetary surface instruments. As the fourth goal suggests, however, the nature of the scientific issues or the evidence of the respective processes may not be equally represented on the surface of each planetary body. We will therefore present separate discussions for primitive asteroids, comets, differentiated asteroids, outer solar system satellites and Pluto, and differentiated terrestrial planets. We will then describe current flight instruments capable of making the necessary measurements and outline the analytical strategies that can be used. To fully address many critical scientific issues, the chemical analyses discussed here will often need to be supplemented with some other type of measurement (e.g., imaging or characterization of the mineralogy). We will identify these items and refer to the appropriate accompanying chapters.

We note that to justify planetary surface landers and *in situ* analyses, the critical scientific issues should be unresolvable from orbit (the cheaper and global strategy) or resolved much more cheaply *in situ* than by sample return missions (which can rely on the full capabilities of terrestrial laboratories). One impetus might be complex geology (with more sample varieties than are possible to return, and too heterogeneous for orbital techniques). In this way, landers are ideal for *in situ* analyses on large differentiated planets with complex surface processes (e.g., Mars); complex rubble pile or differentiated asteroids; and comets, which may have heterogeneous ice and rock structures or have surface compositions that change with orbital position or with depth. Small-body missions will be dominated initially by classification issues, to correlate asteroid spectra with meteorite types and to assess the origin of near-Earth asteroid populations (from the Moon, Mars, or the main asteroid belt?). Large-body missions must be more sophisticated because they will involve planetary surfaces that are macroscopically complex. In all cases, the chemical composition of the surface will be used to infer conditions in the planetary interior.

## 2.2. CHEMICAL ANALYSES NEEDED TO ADDRESS IMPORTANT SCIENTIFIC ISSUES

### 2.2.1. Small, Relatively Primitive Bodies

*In situ* analyses of asteroids and comets are needed to determine their elemental, molecular, isotopic, and mineralogic compositions (*COMPLEX*, 1994). Related questions include identifying the sources of extraterrestrial materials that collide with Earth (or will in the future), determining if there are correlations between asteroids and comets, determining the surface geology of these objects, determining the types of carbonaceous materials in cometary nuclei, and determining the range of activity on comets. While asteroids and comets both represent relatively primitive material, we will discuss the analyses needed to address them separately because these objects have different origins, volatile contents, and evolutionary histories.

*Asteroids.* Samples of primitive asteroids are available on Earth as chondritic meteorites and have been analyzed with the best analytical instruments available. These samples, of which ~15,000 are known, provide a good baseline of information for construction of advanced mission designs. Unfortunately, it has been impossible (so far) to correlate these meteorites with specific asteroids or groups of asteroids. Consequently, to fully leverage this database, the principal goal of any *in situ* analysis will be to determine whether or not the object has a composition similar to known meteoritic materials and, if so, which class of materials.

Primitive meteorites are classified as carbonaceous, ordinary, or enstatite chondrites, with many subcategories. The classic discriminators among the chondritic meteorite groups and subgroups include (1) the ratio of metallic Fe to total Fe in bulk analyses (*Van Schmus and Wood*, 1967); (2) the weight percent ratio of total Fe to total $SiO_2$ in bulk analyses (*Urey and Craig*, 1953); (3) the weight percent ratio of total $SiO_2$ to the total MgO in bulk analyses (*Ahrens*, 1964, 1965); and (4) the ratio of FeO/(FeO + MgO) in olivine and pyroxene in the chondrites (*Mason*, 1963). As described below (section 2.3), many of the instruments used to measure the chemical composition of a planetary surface are unable to distinguish metallic from oxidized Fe, rendering discriminator 1 problematic for *in situ* analyses. Similarly, because many of the instruments determine bulk compositions rather than individual mineral compositions, discriminant 4 may not be useful. On the other hand, discriminants 2 and 3 are, in principal, useful with most categories of instruments, because most of the Si in any targeted asteroid should be in the form of $SiO_2$ (there is relatively little metallic Si, even in enstatite chondrites), and all the Mg should be in the form of MgO. Unfortunately, when one considers the errors inherent in analyses by spacecraft hardware (e.g., an APX analysis, as described below), it may not be possible to distinguish among carbonaceous, ordinary, and enstatite chondrite asteroids based on only these two ratios. Other elemental ratios that are likely to be discriminating *and* measurable include Al/Si, Ca/Si, Fe/Mn, Fe/Sc, Fe/(Fe + Mg), and K/La (or proxy K/Sm and K/Gd). For our discussion (and the planning of future missions), we have compiled these ratios in Table 2.1. Because the absolute concentration of an element may also be a useful discriminator, the abundances of several important elements are listed in Table 2.2.

While analyses of an asteroid's elemental composition are sufficient for classification, we note that several other types of measurements can also address this issue. For example, one could measure $Fe^0/Fe^T$ (method 1, above) using Electron Paramagnetic Resonance (EPR) techniques (section 2.3.7 and Chapter 3) or Mössbauer techniques (Chapter 5). In addition, O isotopic compositions have proven to be a very useful classification tool among meteorites and could be used on an asteroid if sufficient precision is obtainable (see Chapter 7).

In addition to determining the relationship between meteorites and a particular asteroid surface, it is also important to correlate the chemical composition of the asteroid with observed asteroid spectra. Earth-based observations of hundreds of asteroids have yielded a large library of reflectance spectra, but these spectra have not been correlated with meteorites or their compositions, frustrating attempts to address many of the issues outlined by COMPLEX. Consequently, a second analytical goal will be to coordinate the chemical analyses described above with spectral analyses of the surface, either from the lander (see Chapter 5), by the spacecraft during the approach phase of the mission, or from Earth-based telescopes. Analytical and flight strategies for asteroid analyses are discussed further in section 2.4.

TABLE 2.1. Element ratios (by weight) that can be used to classify primitive material in the solar systems; where more than two good analyses exist, the mean ± standard deviation is listed.

| | Al/Si | Ca/Si | Fe/Si | Mg/Si | Fe/(Fe + Mg) |
|---|---|---|---|---|---|
| CV | 10.7 | 11.8 | 1.49 | 0.93 | 0.61 |
| CO | — | — | — | — | — |
| CM | 8.5 | 10.0 | 1.60 | 0.89 | 0.64 |
| CI | 8.5 | 9.2 | 1.78 | — | — |
| LL | 6.2 ± 0.3 | 7.2 ± 0.5 | 1.03 ± 0.04 | 0.80 ± 0.01 | 0.56 ± 0.04 |
| L | 6.4 ± 0.4 | 7.1 ± 0.4 | 1.18 ± 0.06 | 0.80 ± 0.01 | 0.59 ± 0.05 |
| H | 6.6 ± 0.5 | 7.3 ± 0.3 | 1.60 ± 0.06 | 0.82 ± 0.01 | 0.66 ± 0.04 |
| EL | 5.5 | 2.7 | 1.15 | 0.71 | 0.62 |
| EH | 5.7 | 5.4 | 1.83 | 0.66 | 0.73 |
| Reference | 1 | 1 | 1 | 1 | 1 |

| | Fe/Mn | Fe/Sc (÷ 1000) | K/La |
|---|---|---|---|
| CV | 162 ± 10 | 21 ± 1 | 674 ± 108 |
| CO | 149 ± 11 | 26 ± 2 | 884 ± 159 |
| CM | 122 ± 12 | 25 ± 3 | 1309 ± 186 |
| CI | 93 ± 5 | 31 ± 2 | 2447 ± 306 |
| LL | 72 ± 7 | — | — |
| L | 83 ± 8 | — | — |
| H | 114 ± 11 | — | — |
| EL | 107 | — | — |
| EH | 146 | — | — |
| Reference | 1,2 | 2 | 2 |

References: [1] *Jarosewich* (1990); [2] *Kallemeyn and Wasson* (1981).

TABLE 2.2. Atomic percents of characteristic elements in chondrites; where more than two good analyses exist, the mean ± standard deviation is listed.

| | Si | Fe | Mg | Al | Ca | K |
|---|---|---|---|---|---|---|
| CV | 15.89 | 23.60 | 14.82 | 1.70 | 1.87 | 0.04 |
| CM | 13.54 | 21.64 | 11.99 | 1.15 | 1.35 | 0.05 |
| LL | 18.98 ± 0.25 | 19.63 ± 0.68 | 15.21 ± 0.27 | 1.19 ± 0.04 | 1.37 ± 0.08 | 0.08 ± 0.02 |
| L | 18.57 ± 0.26 | 21.93 ± 0.80 | 14.91 ± 0.25 | 1.19 ± 0.08 | 1.32 ± 0.07 | 0.09 ± 0.01 |
| H | 17.11 ± 0.26 | 27.45 ± 0.84 | 14.03 ± 0.23 | 1.13 ± 0.08 | 1.24 ± 0.06 | 0.07 ± 0.01 |
| EL | 20.18 | 23.19 | 14.42 | 1.12 | 0.54 | 0.07 |
| EH | 16.69 | 30.60 | 11.06 | 0.95 | 0.90 | 0.06 |

Atomic % of each element was calculated from oxide abundances reported by *Jarosewich* (1990). CV = 2 falls (Allende and Bali); CM = 2 falls (Banten and Murchison); LL = 12 falls; L = 54 falls; H = 26 falls; EL = Eagle (EL6); EH = ALHA 77295 (EH4).

*Comets.* Comets, like asteroids, are important because their primitive materials may contain clues to physical and chemical conditions in the early solar system, such as pressure, temperature, and mixing of chemical and isotopic precursors (*COMPLEX*, 1994). Comets are unique, however, in containing both the rock-forming elements of asteroids and a large proportion of volatiles and organics. The last is particularly important for its implication about primordial life. Thus, it is important to measure the abundances of the rock-forming elements and any volatile and organic constituents. Defining the analytical requirements for a landed comet mission is more difficult than for a landed asteroid mission because there are no macroscopic (meteorite) samples of comets. The only cometary materials available for study thus far are interplanetary dust particles (IDPs). Based on analyses of these particles and current models of comet evolution, it is usually assumed that comets are composed of chondritic material (like CI chondrites) plus additional carbonaceous and icy material. Consequently, a lander on a comet should (like a lander on an asteroid) be able to discriminate among chondritic materials (e.g., Table 2.1 and Table 2.2) and should be able to measure the elemental (and, ideally, isotopic) abundances of C, H, O, and N. Fortunately, some instruments designed to analyze rock-forming elements can also analyze C, H, O, and N (e.g., the γ-ray spectrometer, section 2.3.2). Other useful instruments, designed to specifically analyze volatile constituents, are discussed in Chapters 5 and 7.

Because the surface of a comet is likely to be a heterogeneous mixture of rock and ice, chemical analyses should probably be done in conjunction with surface imaging so that any analyzed volume of material can be identified. Also, since comets experience different periods of activity, it is important for any lander to determine how surface compositions change with time and orbital position and, very possibly, with depth. Analyses of a comet's elemental composition should also be supplemented with analyses of the O and H isotope compositions of solids and ices on the comet (Chapter 7).

### 2.2.2. Small Differentiated Bodies, Rocky or Metallic

Many planetesimals in the solar system differentiated to produce metal and sulfide cores within shells of less dense silicate and oxide material. Because many (if not most) of these differentiated asteroids have been heavily cratered or disrupted, all these differentiated components may be accessible to surface landers. As outlined by *COMPLEX* (1994), it is important to determine the thermal evolution and geochemical processes that produced the differentiated bodies by analyzing the compositions of the components in these heterogeneous bodies or the asteroid fragments of them. In particular, it is hoped that we can identify the heat source(s) responsible for differentiation. Candidate sources include radionuclide decay, which is directly dependent on the chemical composition of the bodies (e.g., the abundances of Al, Fe, K, Th, and U), and induction heating, which is indirectly dependent on the chemical composition of the bodies (i.e., the abundance of electrical conductors like elemental Fe and C).

TABLE 2.3. Element ratios (by weight) in some of the known types of achondritic material in the solar system.

| | Al/Si (× 100) | Ca/Si (× 100) | Fe/Si | Mg/Si | Refs. |
|---|---|---|---|---|---|
| HOW | 23.5 | 24.3 | 0.61 | 0.32 | [1] |
| EUC | 29.0 | 32.5 | 0.66 | 0.19 | [1,2] |
| DIOG | 3.2 | 4.2 | 0.51 | 0.64 | [1] |
| AUB | 2 ± 2 | — | 0.1 ± 0.1 | — | [2] |
| ANG* | 23–40 | 41–84 | 0.36–1.1 | 0.23–0.62 | [3,4] |
| URE* | <0.28–1.0 | 3.6–7.9 | 0.29–0.87 | 1.0–1.3 | [1] |
| URE | — | — | 0.87 ± 0.07 | — | [2] |
| WIN | 6.44 | 4.83 | 0.85 | 0.84 | [1] |
| ACAP | 6.72 | — | 1.48 | 0.90 | [5] |
| MESO* | 13.8–23.0 | 14.9–21.1 | 1.5–5.5 | 0.34–0.50 | [1] |

| | Fe/ (Fe + Mg) | Fe/Mn | Fe/Sc (÷ 1000) | K/La (÷ 1000) | K/U | Refs. |
|---|---|---|---|---|---|---|
| HOW | 0.66 | 35 ± 10 | 6.3 ± 3.1 | — | — | [1] |
| EUC | 0.78 | 37 ± 13 | 5.5 ± 2.6 | — | — | [1,2] |
| DIOG | 0.46 | — | — | — | — | [1] |
| AUB | — | 19 ± 26 | 4.2 ± 5.1 | — | — | [2] |
| ANG* | 0.53–0.77 | — | — | — | — | [3,4] |
| URE* | 0.20–0.46 | — | — | — | — | [1] |
| URE | — | 58 ± 5 | 21 ± 4 | — | — | [2] |
| WIN | 0.50 | 99 | — | — | — | [1] |
| ACAP | 0.62–0.66 | 88 | 34 | 460–610 | 3.8 | [5] |
| MESO* | 0.81–0.94 | — | — | — | — | [1] |

HOW, EUC, and DIOG refer to howardites, eucrites, and diogenites. AUB = aubrites; ANG = angrites; URE = ureilites; WIN = Winona; ACAP = acapulcoites; and MESO = mesosiderites. References: [1] *Jarosewich* (1990); [2] *Schmitt et al.* (1972); [3] *Warren and Kallemeyn* (1989a); [4] *Yanai* (1994); [5] *Palme et al.* (1981).

* Range of values given because these groups of meteorites are not chemically homogeneous.

It is also important to correlate differentiated asteroids with meteorite samples. For silicate achondrites, this requires an instrument that can analyze many of the same rock-forming elements used to classify primitive asteroids (Table 2.3). Fortuitously, one of the best element ratios to use for the purposes of classifying these objects (K/U) also addresses the issue of radionuclide heating. Other useful ratios include Fe/Mn, Fe/Sc, and K/La (Fig. 2.1).

For metal-rich asteroids, it may be impossible to correlate them (by chemical composition) with individual meteorites or meteorite groups. Metal-rich meteorites are commonly classified according to their abundances of the trace elements Ga, Ge, Ir, and Ni. Of these, only Ni could reasonably be analyzed with available *in situ* instrumentation; the first three elements are analyzed on Earth by radiochemical neutron activation, a labor-intensive technique involving intense irradiation with neutrons, wet-chemical separations, and γ-ray spectrometry. On the other hand, landers may be able to

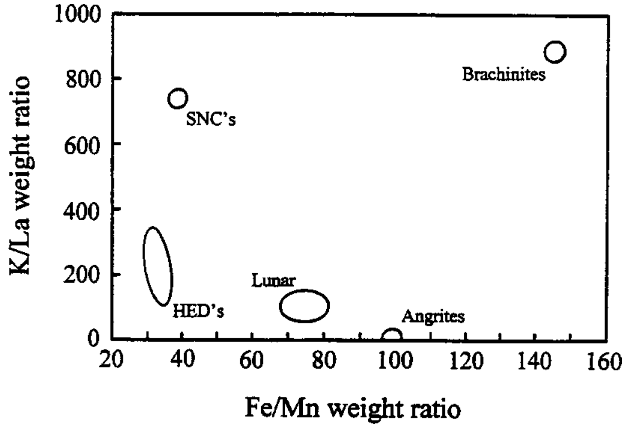

**Fig. 2.1.** K/La vs. Fe/Mn in several types of achondritic material in the solar system. The SNC samples may represent material on Mars and the HED samples may represent material on Vesta.

identify the specific class(es) of carbonaceous and hydrous material that sometimes affect the spectra of M-class asteroids.

As with relatively primitive asteroids, chemical compositions of materials from differentiated small bodies must be correlated with the objects' reflectance spectra, although the spectra need not be collected by a lander. The importance of this type of information is clear from the results obtained after the correlation between Vesta and HED meteorites was discovered.

We also note that differentiated asteroids are sufficiently complex that any chemical analyses need to be supplemented with an imager to identify the geologic context of the sample being analyzed. The lack of geologic context is one of the principal reasons why the igneous evolution of these types of planetesimals has not been resolved from studies of meteorites. Did our meteorites come from lava flows? Did they come from large magma chambers or narrow sills? Did they cool quickly because they were extruded or because they were quenched against the margin of a dike? It has also been difficult because we have had to extrapolate what we know of igneous processes on Earth to bodies with much less gravity and a much shorter thermal history. Consequently, while we may be able to begin to model the igneous evolution of small bodies, images of structures and lithologic contacts on these bodies will probably be needed to resolve these geologic processes. It would be immensely useful, for example, to find remnant lava flows and see to what extent chemical and mineralogical fractionation occurred within the flow (i.e., is crystal fractionation a greater function of shear than gravity on small bodies?) or to determine the extent that volatiles were important when magmas were emplaced (i.e., are there vesicles throughout the lava flow or concentrated only near the top?). Not only will coordinated imaging and chemical analyses help us resolve geologic issues on the specific body being sampled, but by analogy we can better interpret the evolution of all achondrites.

### 2.2.3. Resource Potentials of Small Bodies

Another significant goal for missions to asteroids and comets is to determine their potential as resources for the human exploration and development of space. Asteroids and comets, particularly those with perihelia near the Earth ("near-Earth objects") could be sources of economic materials, including metals, water, and rocket propellant (e.g., C-rich compounds). As above, the meteoritic sampling of asteroids is not useful in evaluating the resource potential of a specific asteroid or comet, as we cannot now correlate specific samples with specific asteroid or comet types. Analyses of these objects for their resource potential must include both chemical analyses (to see if potential resources are available in commercial abundances) and mineralogic and textural analyses (see Chapters 6, 8, and 9) to determine the proper beneficiation and refining methods.

### 2.2.4. Outer Solar System Satellites and Pluto

As outlined by *COMPLEX* (1994), it is important to characterize the surface chemistry of planetary satellites in the outer solar system and to determine their volatile inventories. In general, the principal measurements envisioned are bulk chemical analyses of ices, possibly hydrocarbons, and, in a few cases, rock-forming elements.

The surface of Europa, for example, appears to be almost pure ice, in which case instruments that can measure C, H, O, and N are needed. Some of the instruments described below (section 2.3) can do so, but better packages of instruments designed specifically for ices should probably be considered (see Chapters 5 and 7). Many of the smaller saturnian satellites, also dominated by icy surfaces, fall into this same category.

In contrast, Io is believed to be covered with basaltic lavas and can thus be analyzed with the same types of instruments (and same capabilities) needed to analyze differentiated asteroids. In addition, since Io is partially covered with S-rich deposits, an instrument that can analyze S should also be available.

The surfaces of Ganymede and Callisto are dominated by (water) ice, but they also contain a dark phase that may be carbonaceous and/or silicate material. Consequently, instruments that can analyze rock-forming elements (section 2.3) and/or organics (Chapter 8) are appropriate. Similarly, the surface of Rhea, one of the smaller saturnian satellites, and the surfaces of the uranian satellites should be analyzed with an instrument capable of analyzing rock-forming elements because they appear to contain small amounts of carbonaceous (or some other dark) material mixed with ice.

The remaining saturnian satellite, Titan, is the first target of an attempted landing among the icy satellites. The landing will be attempted by the Huygens probe, which will be launched from the Cassini spacecraft. The probe is not designed to analyze the chemical composition of the surface (only the atmosphere during descent), but the imagery it provides (along with pressure, temperature, and atmosphere composition data) should provide strong constraints on the chemical composition of Titan's surface materials. It is not yet clear how long the probe can survive on the surface (if at all), which is a problem that will need to be resolved if there are any future attempts to send landers.

Finally, *COMPLEX* (1994) has decided that it is important to know the composition and location of ices on Pluto and Neptune's satellite Triton, and to determine the relationship of the ices to the tectonic and volcanic evolution of both bodies. Equally important is an understanding of the evolution of organic matter on these bodies and of the long-term motion of volatiles in and above them (e.g., volatile exchange between the surface and atmosphere). Triton, for example, has a complex seasonal cycle, so it will be important to monitor the compositions over an extended baseline to determine how they may change over time. Also, because these planetary surfaces may have been affected by tectonic, impact cratering, and/or volcanic processes, any chemical analyses should be accompanied by imaging so that the geologic context is clear. The principal target of the analyses are C, H, O, and N and their molecular and isotopic forms (Chapter 7).

### 2.2.5. Differentiated Terrestrial Planets

The large terrestrial planets have complex surfaces that reflect the extended actions of endogenic processes. While the Moon, Mercury, Venus, and Mars are all possible targets of future missions, we focus on Mars because it is the most likely target of missions in the near future (*SSES*, 1994). Mars also presents a good example of the range of issues that can be addressed by chemical analyses of surface materials. Spacecraft instruments have already provided *in situ* chemical analyses of all these bodies except Mercury; these *in situ* data have been augmented significantly by analyses of meteorites from the Moon and particularly the "SNC" meteorites from Mars.

Studies of the terrestrial planets are aimed at understanding the internal structure and dynamics of at least one convecting terrestrial planet other than the Earth; studying the crust-mantle structure of this body; determining the geochemistry of surface units, morphological and stratigraphic relationships, and absolute ages for all solid planets; and determining how chemical and physical processes (impact cratering, surface weathering, etc.) affect planetary surfaces (*COMPLEX*, 1994). These goals and some of the key questions they represent can be directly or indirectly addressed with chemical analyses of surface units. Some of these key questions (cast in terms of Mars) and the analyses they require are:

*What was the thermal state of Mars during differentiation and how has it evolved?*

- What are the absolute and relative abundances of K, Th, and U?
- How has the Mg/(Mg + Fe) ratio in magmas changed with time?

*Does Mars have a different bulk composition than Earth? What is the density of the mantle? What is the size of the core? Did Mars have a magma ocean?*

- What are the Mg/Si and Mg/(Mg + Fe) ratios in ultramafic and mafic igneous lithologies?
- What are the abundances of siderophile elements in these same lithologies?
- What are the abundances of P, Mo, or W in these same lithologies?

*What is Mars' internal chemical structure?*

- What are the absolute and relative abundances of the rock-forming elements, and how are these distributed between different lithologies (for example, lherzolites, basalts, andesites, and gabbros)?
- Are some elements (such as Ca, Al, Th, and U) concentrated in the crust? What is the ratio of incompatible and refractory elements?
- What are the Mg/(Mg + Fe) ratios in magmas?
- What are the absolute and relative abundances of the rare earth elements (REE) in magmas or any other crustal reservoirs?
- What is the oxidation state of the surface?

*Are the heavily cratered (old) uplands of Mars a remnant of an early primary crust or a reworked crustal component?*

- Is the Mg/(Mg + Fe) ratio in lavas in the uplands higher, lower, or the same as it is elsewhere?
- How do the relative and absolute abundances of the REE in lavas in the uplands compare with those in lavas from elsewhere?
- Similarly, how do these elemental components compare in impact melts (which represent bulk crustal melts) from both types of regions?

*What type of volcanism modified the surface of the planet? Based on the compositions of the extrusions, what can we infer about parent (mantle) compositions, magmatic temperatures, and volatile content? Did the magmas change with time or are they correlated with specific types of terranes, and, if so, what can we then infer about the mineralogical, chemical, and physical properties of the interior of the planet and how they have changed with time?*

- What are the abundances of the rock-forming elements?
- How much $SiO_2$ is in the magmas?
- What are the Na/Ca and Mg/Fe ratios in the basalts or in lavas that have different ages (where the ages are determined stratigraphically, by crater counts, or radiometrically)?
- Within a single volcanic province, how has the $(Na_2O + K_2O)/SiO_2$ ratio changed with time?

*Where are the volatiles on Mars and how have these reservoirs evolved with time? Did a reservoir of prebiotic organic compounds ever exist and is there any evidence that might indicate that organic matter underwent prebiotic chemical evolution?*

- What is the distribution of $H_2O$?

- What are the $Fe^{2+}/Fe^{3+}$ and/or $Fe^{2+}/Fe^0$ ratios in fresh lavas, fresh impact melts, dust, and obviously altered surface components?
- How is C distributed in the crust?

*Did life emerge on Mars? What was the form of this life? Does life exist in any form on Mars today?* The types of chemical analyses one expects of the initial robotic surveyors will not answer these questions directly. However, in preparation of future missions, one would want to determine whether or not carbonates, phosphates, cherts, and/or evaporites were deposited.

- What are the abundances of Si, Mg, Fe, Ca, S, P, and C (or $CO_2$) in surface lithologies?
- Are there any C-rich organic deposits?

*What are/were the chemical interactions between Mars' surface and its atmosphere?*

- What are the Mg/(Mg + Fe), $Fe^{2+}/Fe^{3+}$, and/or $Fe^{2+}/Fe^0$ ratios in lavas and weathered products?
- What are the abundances of the rock-forming elements in the dust?
- What is the distribution of $H_2O$? Are there any aqueously altered lithologies?
- Do bulk-element analyses of the rock-forming elements indicate there are chemically fractionated units that may correspond to fluvial sedimentation?
- What are the distributions of S, Cl, Fe, P, C (or $CO_2$)? Are there evaporite deposits, salts, banded iron formations, phosphates, and/or carbonates?

*Are SNC meteorites really from Mars and can we really use them to infer the origin and evolution of that planet?*

- What are the Fe/Mn, K/U, and K/La ratios in mafic and ultramafic igneous rocks on the planetary surface?
- What are the O isotopic compositions of those same rocks?
- What are the Ca/Na and Mg/(Mg + Fe) ratios in basalts and how do they compare with those in shergottites?

## 2.3. ANALYTICAL CAPABILITIES OF SPACECRAFT INSTRUMENTS

There are several categories of elements that can be analyzed with available instruments. Many major and minor rock-forming elements, for example, can be measured with an α-proton-X-ray spectrometer (APX), a γ-ray spectrometer (GRS), an X-ray diffraction and X-ray fluorescence spectrometer system (XRD and XRF), and an X-ray stimulated photon spectrometer (XPS). Analyses of volatiles are also possible with an APX (C, N, O, and S), a GRS (H, C, N, O, and S), an XRD/XRF (C and S), and an XPS (C, O, N, and S). These instruments and their analytical capabilities are described below. Some related instruments are described in those chapters discussing isotopic, mineralogic, or organic compositions (Chapters 3, 6, and 7, respectively).

### 2.3.1. Alpha-Proton-X-Ray Instrument (APX)

The α-proton-X-ray instrument (APX) has evolved from the simpler α-particle instrument that was used to conduct the first chemical analyses of the lunar surface during the Surveyor program. In its original form, the target was irradiated with α particles from a source like $^{242}$Cm. The energies of backscattered α particles were then used to analyze light elements (except H) and the energies of protons produced by (α,p) nuclear reactions were used to analyze slightly heavier elements (Z = 9–14), including the rock-forming elements Na, Mg, Al, and Si, in the outermost few micrometers of the sample. These types of analyses can now be augmented with an additional mode that utilizes the X-rays produced in the sample by the same α particle source (e.g., *Economou and Turkevich*, 1976; *Turkevich and Economou*, 1993). This mode is comparable to X-ray fluorescence (see section 2.3.3) and can approach a sensitivity of parts per million for heavier elements. Examples of the accuracies and sensitivities expected for some major, minor, and trace elements are listed in Table 2.4 and Table 2.5.

Because the APX system has such an extensive heritage, the errors associated with the technique are understood relatively well. Consequently, we will use it as an example of how to determine the capabilities of an instrument relative to the goals of a particular planetary surface mission. Consider, for example, a mission to a primitive asteroid. As outlined above, the classic criteria for identifying and classifying chondritic materials are the ratios $Fe^0/Fe^T$, $Fe^T/SiO_2$ (or Fe/Si), and $SiO_2/MgO$ (or Mg/Si) in bulk samples, and FeO/(FeO + MgO) in olivine and pyroxene. The first ratio will not be useful because an APX cannot distinguish metallic Fe from oxidized forms; neither will the fourth ratio be useful, because an APX determines bulk compositions rather than individual mineral compositions. On the other hand, the second and third ratios can, in principal, be used. However, when one considers the error inherent in an APX analysis (Table 2.6), it is clear that one may not be able to distinguish between carbonaceous, ordinary, and possibly enstatite chondrite materials. To illustrate this point, let us assume that the APX was dropped on an H-chondrite body and we were trying to

TABLE 2.4. The expected accuracies (at 90% confidence limit) for the principal chemical elements analyzed with an APX (*Economou and Turkevich*, 1976).

| | α + p + X-ray modes | |
|---|---|---|
| | Weight % | Atom % |
| C | ± 0.2 | ± 0.4 |
| O | ± 0.7 | ± 1.0 |
| Na | ± 0.2 | ± 0.2 |
| Mg | ± 0.8 | ± 0.7 |
| Al | ± 0.4 | ± 0.3 |
| Si | ± 1.2 | ± 0.9 |
| K | ± 0.2 | ± 0.1 |
| Ca | ± 0.2 | ± 0.1 |
| Ti | ± 0.15 | ± 0.07 |
| Fe | ± 0.4 | ± 0.2 |

TABLE 2.5. Examples of expected sensitivities for minor elements evaluated for a basalt matrix using an APX (*Economou and Turkevich*, 1976).

| | α + p + X-ray modes | |
|---|---|---|
| | Weight % | Atom % |
| N | 0.2 | 0.3 |
| F | 0.05 | 0.06 |
| P | 0.2 | 0.14 |
| S | 0.1 | 0.07 |
| Cl | 0.1 | 0.06 |
| K* | 0.07 | 0.04 |
| V | 0.03 | 0.013 |
| Cr | 0.02 | 0.008 |
| Mn | 0.03 | 0.012 |
| Ni | 0.02 | 0.008 |
| Cu | 0.02 | 0.007 |
| Zn | 0.02 | 0.007 |
| Rb | 0.001 | 0.0003 |
| Sr | 0.001 | 0.0003 |
| Y | 0.0005 | 0.0001 |
| Zr | 0.0005 | 0.0001 |
| Ba | 0.001 | 0.00017 |
| La | 0.001 | 0.00016 |
| Ce | 0.0008 | 0.00013 |
| Nd | 0.0008 | 0.00012 |
| Sm | 0.0005 | 0.00007 |
| Pb | 0.005 | 0.0005 |
| Th | 0.005 | 0.0005 |
| U | 0.005 | 0.0005 |

* Sensitivity of K expected in the presence of a few weight percent Ca.

identify it as such. In this case, an APX analysis might indicate an Mg/Si ratio of 0.82 ± 0.08, which could be interpreted to represent H-chondrite material, but it could also represent L-, LL-, or CM-chondrite material. The other classic ratio, Fe/Si, may be similarly ambiguous; if the same APX analysis indicated an Fe/Si ratio of 1.60 ± 0.10, the body could still consist of either H or CM material. Fortunately, ratios of other elements help clarify the issue. In this case, Ca/Si is particularly useful, because an analyzed ratio of 0.073 ± 0.010 would clearly correspond to H-chondrite material rather than CM-chondrite material. Also, the absolute concentrations of individual elements may help. In the case of an H-chondrite body, the atomic percent Fe is substantially greater than that in a CM body (27.45 vs. 21.64; Table 2.2), even though both have the same Fe/Si value. The difference between these values is large enough that it should not be blurred by the errors associated with an APX analysis (±0.2 atom% for Fe).

TABLE 2.6. Major-element ratios often used to classify primitive material in the solar system and the errors predicted to occur with APX analyses.

| | Al/Si (× 100) | Ca/Si (× 100) | Fe/Si | Mg/Si | Fe/ (Fe + Mg) |
|---|---|---|---|---|---|
| CV* | 10.7 (8.6–13.4) | 11.8 (10.6–13.2) | 1.49 (1.39–1.59) | 0.93 (0.84–1.04) | 0.61 |
| CO | | | | | |
| CM* | 8.5 (5.9–11.5) | 10.0 (8.7–11.5) | 1.60 (1.48–1.73) | 0.89 (0.78–1.00) | 0.64 |
| CI† | 8.5 | 9.2 | 1.78 | | |
| LL* | 6.3 (4.5–8.2) | 7.2 (6.4–8.1) | 1.03 (0.98–1.10) | 0.80 (0.73–0.88) | 0.56 |
| L* | 6.4 (4.6–8.4) | 7.1 (6.3–8.1) | 1.18 (1.12–1.25) | 0.80 (0.73–0.88) | 0.59 |
| H* | 6.6 (4.6–8.8) | 7.3 (6.4–8.3) | 1.60 (1.51–1.71) | 0.82 (0.74–0.91) | 0.66 |
| EL* | 5.5 (3.9–7.4) | 2.7 (2.1–3.3) | 1.15 (1.09–1.21) | 0.71 (0.65–0.78) | 0.62 |
| EH* | 5.7 (3.7–7.9) | 5.4 (4.6–6.3) | 1.83 (1.73–1.95) | 0.66 (0.59–0.74) | 0.73 |

* Data from *Jarosewich* (1990); parenthetical ranges correspond to APX analytical errors predicted by *Economou and Turkevich* (1976).

† Data from *Kallemeyn and Wasson* (1981).

This exercise indicates that unambiguous identification of the target may not be as straightforward using an APX analysis (or other planetary surface instruments) as it would be analyzing a meteorite using methods typically available in terrestrial laboratories. Nonetheless, it appears that combinations of element concentrations and element/element ratios can be used in many cases to successfully determine the nature of the target asteroid surface.

Similarly, an APX can be used to analyze a series of lithologies on the surfaces of differentiated asteroids or planets, as illustrated in Table 2.7, which shows a series of analyses for igneous rocks, a carbonate, and a tektite under simulated martian conditions. As these sample analyses illustrate, an APX can provide absolute abundances of elements rather than just relative abundances.

### 2.3.2. Gamma-Ray Spectrometer (GRS)

Gamma-ray spectroscopy (GRS) is a well-established technique (e.g., *Evans et al.*, 1993; *Boynton et al.*, 1993) for determining the elemental compositions of planetary bodies. Such measurements can be performed from orbit or on the surface. Previous missions have all used the ambient cosmic-ray flux to produce neutron-induced reactions on elements in the planetary surface, which in turn produce the characteristic $\gamma$ rays that are used to determine the elemental concentrations. The last spacecraft GRS was built for Mars Observer (*Boynton et al.*, 1992) and was designed to operate from orbit and provide information on the global surface elemental concentrations and their variations over large spatial regions. Extending these measurements to a surface lander is important because they can provide a direct analysis without having to compensate for atmospheric effects or contributions. Thus, surface measurements can verify and extend the interpretation of orbital measurements and provide a better estimate of the variance that can be assigned to orbital measurements. A surface GRS can also identify specific lithologies and thus enable one to evaluate local heterogeneities and perform detailed mapping, perhaps from a rover-based system. In addition, a surface GRS can provide information about diurnal and seasonal variations of constituents like those that might be produced in a region with permafrost. Typical GRS systems are capable of detecting essentially all major rock-forming elements, as well as volatile components such as H, C, O, and S (see Table 2.8 for a comparison of APX and GRS analyses of a model comet). It should also be noted that a GRS measurement can be integrated with a penetrator, where such an approach is desired for determining the true intrinsic planetary body composition by analyzing material beneath any disturbed surface, whether it be distillation product on a comet (*Evans et al.*, 1986), a weathering patina on an asteroid, or an evaporitic crust on a terrestrial planet.

TABLE 2.7. Analyses of USGS rock standards using a Mars preprototype α-particle instrument under simulated martian conditions.

| Element | Mass Range | Peridotite (PCC-1) α | Peridotite (PCC-1) Conventional Analysis | Basalt (W-1) α | Basalt (W-1) Conventional Analysis | Basalt (BCR-1) α | Basalt (BCR-1) Conventional Analysis | Carbonate (Type 4) α | Carbonate (Type 4) Conventional Analysis |
|---|---|---|---|---|---|---|---|---|---|
| C | 12 | 0.00 | 0.00 | 0.63 | 0.01 | 0.03 | 0.01 | 19.89 | 19.61 |
| O | 16 | 59.32 | 59.71 | 62.04 | 61.37 | 62.24 | 61.77 | 59.39 | 59.97 |
| F | 19 | 0.09 | 0.00 | 0.00 | 0.00 | 0.00 | 0.057 | 0.00 | 0.00 |
| Na | 23 | 0.03 | 0.00 | 2.16 | 1.46 | 2.33 | 2.40 | 0.07 | 0.03 |
| Mg | 24–26 | 21.53 | 22.62 | 2.70 | 3.60 | 1.21 | 1.79 | 0.03 | 0.00 |
| Al | 27 | 0.17 | 0.32 | 6.05 | 6.38 | 6.24 | 5.91 | 0.00 | 0.00 |
| Si | 28–34 | 16.29 | 14.70 | 18.45 | 19.22 | 21.20 | 20.10 | 0.35 | 0.51 |
| "Ca" | 35–44 | 0.45 | 0.15 | 5.16 | 4.58 | 3.08 | 3.54 | 20.16 | 19.62 |
| "Ti" | 45–51 | 0.10 | 0.11 | 0.57 | 0.29 | 0.60 | 0.62 | 0.00 | 0.00 |
| "Fe" | 52–69 | 2.08 | 2.16 | 2.21 | 3.10 | 3.04 | 3.79 | 0.01 | 0.08 |
| "Ba" | 70–∞ | 0.002 | 0.002 | 0.028 | 0.010 | 0.013 | 0.009 | 0.000 | 0.000 |
|  |  | Andesite (AGV-1) |  | Granite (G-1) |  | Granodiorite (GSP-1) |  | Philippinite (Tektite) (PO-300) |  |
| Element | Mass Range | α | Conventional Analysis | α | Conventional Analysis | α | Conventional Analysis | α | Conventional Analysis |
| C | 12 | 0.15 | 0.004 | 0.03 | 0.04 | 0.00 | 0.048 | 0.00 | 0.00 |
| O | 16 | 62.16 | 62.28 | 63.70 | 63.15 | 63.20 | 62.63 | 63.45 | 63.57 |
| F | 19 | 0.07 | 0.05 | 0.06 | 0.00 | 0.42 | 0.43 | 0.00 | 0.00 |
| Na | 23 | 3.29 | 2.95 | 2.38 | 2.22 | 2.08 | 1.89 | 0.49 | 0.90 |
| Mg | 24–26 | 0.35 | 0.79 | 0.00 | 0.21 | 0.44 | 0.51 | 1.69 | 1.22 |
| Al | 27 | 6.96 | 7.24 | 5.90 | 5.72 | 6.26 | 6.32 | 5.48 | 5.49 |
| Si | 28–34 | 21.46 | 21.35 | 24.21 | 25.12 | 22.83 | 23.49 | 24.95 | 25.01 |
| "Ca" | 35–44 | 3.94 | 3.20 | 3.11 | 2.95 | 2.72 | 3.27 | 2.48 | 2.20 |
| "Ti" | 45–51 | 0.03 | 0.28 | 0.13 | 0.07 | 0.06 | 0.17 | 0.33 | 0.21 |
| "Fe" | 52–69 | 1.62 | 1.83 | 0.44 | 0.52 | 0.96 | 1.12 | 1.13 | 1.40 |
| "Ba" | 70–∞ | 0.037 | 0.017 | 0.037 | 0.033 | 0.048 | 0.019 | 0.007 | 0.000 |

The instrument, in this case, did not have an X-ray mode. The results are presented in terms of atomic percent and are normalized to a $H_2O$-free and H-free basis. The quotation marks around heavy-element symbols indicate groups of elements in the mass range shown. See *Economou et al.* (1973) for additional information.

The use of neutron-induced γ-ray production for evaluating elemental content has also been applied to subsurface measurements on the Earth (*Schweitzer*, 1993; *Herron et al.*, 1993). While some measurements make use of natural γ-ray production from K, U, and Th, the most significant multielement analyses are performed with a pulsed neutron generator (PNG). The use of such a generator for surface planetary measurements is practical, as it is a reasonably compact, rugged device with a power requirement that is well within typical power budgets. Current systems use about 20 W during operation (which would typically be no more than 50% of the time during continuous spectroscopic measurements). Systems have been envisioned whose power requirements during operation would be reduced to 1–2 W, although with lower neutron output. The main advantage of such a device is that it produces an ambient neutron flux that is approximately 5 orders of magnitude more intense than that produced by the ambient cosmic-ray flux, a factor that only increases if the planetary body has an atmosphere. This means that if a cosmic-ray-flux-based measurement would take a month to achieve the desired statistical level, the same GRS detector with a PNG could perform the measurements to the same statistical level in about half a minute. This makes it practical to sample many locations or to monitor temporal variations, such as daily or seasonal variations in volatile components in, e.g., a martian permafrost layer. A further advantage of a PNG is that timing of spectral acquisition relative to the neutron production permits a separation of γ

TABLE 2.8. Anticipated accuracies of an APX and two types of GRS instruments if they were able to fly on the Champollion lander of the Rosetta mission.

| Element | Concentration | APX Instrument 1-σ uncertainty (%) | High-resolution GRS Instrument 1-σ uncertainty (%) | Low-resolution GRS Instrument 1-σ uncertainty (%) |
|---|---|---|---|---|
|  | 3.9% | n.d. | 0.8 | 0.5 |
| C | 10% | 2 | 10 | 15 |
| N | 3.2% | 6 | 45 | 100 |
| O | 59% | 1 | 5 | 5 |
| Mg | 4.8% | 11 | 8 | 20 |
| Al | 0.43% | 60 | n.d. | n.d. |
| Si | 5.3% | 14 | 7 | 20 |
| S | 2.7% | 4 | 10 | n.d. |
| Cl | 170 ppm | n.d. | 40 | n.d. |
| K | 300 ppm | n.d. | 5 | 15 |
| Ca | 0.4% | 28 | 75 | n.d. |
| Mn | 0.1% | 30 | 60 | n.d. |
| Fe | 9.2% | 3 | 4 | 3 |
| Ni | 0.5% | 4 | 15 | n.d. |
| Th | 15 ppb | n.d. | 100 | n.d. |

The analyzed composition is a model comet. The listed uncertainties for each element are the 1-σ values as a percentage of the model concentration (by weight) for each element; n.d. means there is no data with which to estimate uncertainty. See the Rosetta Champollion Proposal Information Package ( March 1, 1995) for more information.

rays produced by different types of reactions, all of which are combined when the ambient cosmic-ray flux is used as a source. This timing capability significantly increases the signal-to-noise content of the detected spectra, improving the sensitivity for detecting elemental concentrations for the same neutron flux and $\gamma$-ray detector system.

A further development that has improved the potential utility of GRS measurements is the growth in viable materials, both scintillators and semiconductors, that can be used for $\gamma$-ray detectors. Unique properties of these new materials can improve the signal-to-noise content of a spectrum, reduce the weight of a system without sacrificing spectral information, reduce the sensitivity to varying ambient conditions, or make possible a measurement that would be impractical with traditional detector materials. An example is the design of a spectrometer using a PNG with a $\gamma$-ray detector using Ce-doped Gd-oxyorthosilicate (*Bradley et al.*, 1995) that has been proposed as a GRS for measurements on the surface of Venus.

Surface GRS instruments are intrinsically portable and are thus ideally suited for rover applications. A GRS system on a planetary surface or within a planetary body has a typical measurement volume of about 1000 cm$^3$ and can thus determine a reasonable site-average composition without being affected by small-scale heterogeneities. Important performance parameters of a GRS include energy resolution, detector efficiency, insensitivity to radiation damage, and ability to extract $\gamma$-ray-induced detector signal into an electronic pulse that can be reliably processed. For orbital measurements, the use of anti-Compton shielding, of the same or a different detector material, appreciably improves the quality of the spectra by rejecting $\gamma$-rays that do not come from the planetary surface and from cosmic-ray interactions in the detector material or the spacecraft. When a neutron generator is used on the planetary surface, the significant weight of this shielding can generally be eliminated, as the direct counting rate far exceeds the counting rate from background events.

As an illustration of the sensitivities that can be achieved with a GRS on a lander, we consider a model of the martian surface (*Boynton et al.*, 1993; see also *Boynton et al.*, 1992) that was developed to test the analytical capabilities of orbital measurements designed to determine elemental concentrations to a relative precision of 10%. The calculated sensitivities obtained in the study of an orbiter (using only the cosmic-ray flux) are here divided by a factor of 2 to allow for the improvement for placing the GRS on the surface. These improved sensitivities are then compared with what the same GRS would achieve on the surface when coupled with a neutron generator. In Table 2.9, the final column illustrates the improvement in measurement time to be expected with a neutron generator producing about 10$^8$ neutrons/s. The values for K, Th, and U are not included in the table since their detection sensitivity does not depend on the neutron source intensity. It is clear from the results in the last column that all the listed elements can be determined to 10% precision with a neutron generator in under an hour, with the exception of Ni. This is quite sensible with regard to the expected mode of operation of a rover. Where it is necessary to achieve higher levels of precision, an approximately 10-hr measurement would attain a precision for these concentrations of 1%.

TABLE 2.9. Comparison of analysis times for 10% precision in elemental concentrations for the martian model composition, using a GRS system with and without a pulsed neutron generator (PNG).

| Element | Model Composition | Analysis Time (hr) without PNG | Analysis Time (hr) with PNG |
|---|---|---|---|
| H | 0.11% | 150 | 0.0015 |
| C | 0.60% | 6500 | 0.065 |
| N | 2.8% | 7500 | 0.075 |
| O | 46.6% | 3 | 0.00003 |
| Na | 0.81% | 365 | 0.00365 |
| Mg | 3.7% | 10 | 0.0001 |
| Al | 4.1% | 500 | 0.005 |
| Si | 21.5% | 0.6 | 0.000006 |
| S | 3.0% | 105 | 0.001 |
| Cl | 0.70% | 7.5 | 0.000075 |
| Ca | 4.4% | 220 | 0.0022 |
| Ti | 0.38% | 495 | 0.005 |
| Cr | 0.15% | 6500 | 0.065 |
| Mn | 0.34% | 550 | 0.0055 |
| Fe | 13.5% | 20 | 0.00002 |
| Ni | 52 ppm | 125000 | 1.15 |
| Gd | 2.2 ppm | 34500 | 0.35 |

There are a number of developments that would enhance the current capabilities of GRS systems. Neutron generator development needs to be the final step to proving space worthiness. Current systems are rugged and operate stably over a wide temperature range. However, final layout of the high voltage supply and controlling electronics for satellite configuration needs to be completed. In addition, a smaller, lighter, lower-power version has been envisioned that would be appropriate where only a few watts of power are available. This version is anticipated to produce about 2 or 3 orders of magnitude more flux than is provided by cosmic rays. New semiconductor and scintillator materials can significantly improve GRS performance. However, many of these materials need to be more carefully evaluated for radiation damage effects and to establish the packaging requirements for space worthiness. In addition, for scintillators, recent developments in compact photosensing devices need to be pursued to provide the optimum spectral response characteristics and to provide low-background, nonabsorbing material in their design.

### 2.3.3. X-Ray Fluorescence (XRF)

X-ray fluorescence (XRF) is a powerful and well-established method of chemical analysis for geological materials; XRF instruments have a venerable spaceflight heritage, having operated on the surfaces of Mars (Viking; *Clark et al.*, 1977) and Venus (Vega and Venera; *Zurkov et al.*, 1986; *Barsukov*, 1992). In XRF, the target sample is irradiated with relatively hard (high-energy) X-rays, which (among other processes) ionize atoms in the target by removing inner shell electrons. The resulting inner shell vacancies are filled by electrons from outer shells of the same sample atom, and the difference in energy between the two electron orbitals appears as an X-ray photon (a secondary X-ray). The energies of secondary X-rays are characteristic of the elements from which they are emitted and the electronic transitions involved, and the number of X-rays and their energies can be translated into major-, minor-, and trace-element abundances.

Secondary X-rays can be excited by any high-energy incident radiation: $\alpha$ particles (as in APX, see above), protons (as in PIXE analysis), electrons (as in electron microprobe), and primary X-rays, as in XRF analysis. In laboratory XRF, primary X-rays are produced by electron tubes, in which high-energy electrons impinge on metal targets, usually Cu, Mo, or Fe. Tube sources tend to be massive and require considerable power at high voltage, but new designs are reducing both of these drawbacks. Primary X-rays can also come from radioactive decay of selected radioisotopes. The Viking XRF instrument was of this sort, and used $^{55}$Fe and $^{109}$Cd to produce primary X-rays (*Clark et al.*, 1977); the Venera probes used $^{55}$Fe and $^{238}$U (*Surkov et al.*, 1986). Isotopic sources tend to produce X-rays of narrow energy ranges, but with limited intensities.

Secondary X-rays of different energies (different elements) can be discriminated by a diffractometer (wavelength dispersion) or by semiconductor sensor (energy dispersion). The former is favored for laboratory use because of its excellent resolution, and is usually implemented with a moving scintillator/photomultiplier to detect X-rays. A diffraction geometry could also be implemented without a moving X-ray detector by using CCD arrays in the instrument's focal circle. Semiconductor X-ray sensors are common in SEM and TEM instruments on Earth, and have been used in spacecraft instruments because of their small mass and mechanical simplicity.

X-ray fluorescence can be sensitive to all elements except H and He, but is rarely used for elements lighter than F or N. Detection limits are in the parts per million range for heavier elements. XRF is a bulk analytical method, as secondary X-rays readily penetrate hundreds of micrometers of silicate material. Thus, the analyzed sample volume is relatively large; for the Viking XRF experiment sample volumes were ~25 cm$^3$ (*Clark et al.*, 1977).

It is important to note that XRF instrumentation need not stand alone. XRF is readily implemented with other techniques that involve X-ray sources, such as X-ray diffraction and Mössbauer spectroscopy. Two XRD/XRF instruments intended for remote planetary applications are currently under development, and are described in Chapter 6. One prototype instrument is designed for analysis of rock surfaces (at NASA Ames). Another prototype is matchbox-sized and designed for analysis of particles approximately 100 µm diameter (at NASA Ames). The APX instrument described above relies on similar principles and utilizes similar detectors.

### 2.3.4. Scanning Electron Microscope and Particle Analyzer (SEMPA)

This instrument is designed to image important textures and analyze microscopic components in a target. The basic design of the instrument has been described by *Albee and Bradley* (1987). A preliminary version weighs 11.9 kg, requires 22 W of power, can analyze all elements of $Z > 11$ (Na) with concentrations >0.2% by weight, and carries imaging and X-ray standards on board. The instrument was designed to collect dust particles in the tail of a comet (CRAF), and should probably be considered as at the breadboard stage of development. If the SEMPA were to be flown on missions that land on planetary surfaces, then sampling mechanics would have to be redesigned to accommodate surface samples. The instrument would also have to be tested to determine if it could withstand a hard landing.

### 2.3.5. X-Ray Stimulated Photon Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)

The XPS technique, also known as electron spectroscopy for chemical analysis (ESCA), uses a monochromatic X-ray source in conjunction with an electron energy analyzer to determine the chemical composition and chemical state (or oxidation state; e.g., $S^{2-}$, $S^0$, $S^{4+}O_3$, or $S^{6+}O_4$) of the topmost (50–100-µm-thick) surface layer of solid samples (*Bubeck and Holtkamp*, 1991; *Barr*, 1991; *Ebel and Ebel*, 1990; *Perry*, 1986). In principle, any monochromatic X-ray source can be used, though most laboratory studies have utilized Mg or Al K ($\alpha$) radiation (*Perry*, 1986; *Henrich*, 1987). Such Mg and Al K ($\alpha$) sources have a typical power requirement of several watts and need water cooling. For space applications, alternative X-ray sources may have to be considered. XPS analyzes all elements except H, and its underlying physical principle is as follows: Monoenergetic X-rays impinge on the sample surface and cause electrons from core levels of the target atoms to be ejected. To first approximation, the energy of these photoelectrons is determined by the energy of the impinging X-rays minus the binding energy of the electrons to the atomic nuclei (plus a correction term for the work function of the instrument). To second approximation, the energy of the photoelectrons is also influenced by the electron density in the outer (valence) shell and therefore reflects changes in the oxidation and ligands of the target atoms. XPS data correlate with theoretically calculated chemical shifts (*Maksic and Supek*, 1989). Besides the oxidation states of S, which are often quoted as "textbook examples," XPS is widely used to determine the bonding and oxidation state of C in C-bearing compounds (*Bubeck and Holtkamp*, 1991). With respect to other geological problems, XPS can potentially be used to determine $Fe^{3+}$ and $Fe^{2+}$, the oxidation states of other transition metal cations, and some limited information about the proportions of $O^{2-}$, $O^-$, $OH^-$, and $H_2O$.

A technique that is related to XPS is auger electron spectroscopy (AES) (*Chambers et al.*, 1994). AES is based on the measured energy of electrons emitted from the target by an internal photoeffect. This photoeffect is produced by the same primary process that gives rise to XPS, or by irradiation with high energy, typically 10–30-kV electrons, such as in an electron microscope. This produces an electron hole in a core level that is then filled with an electron from a higher level. The energy produced by this internal process is transferred to another electron within the same atom, which is then emitted as an auger electron, carrying information about the element from which it emerges. AES and XPS have similar surface sensitivities (*Bubeck and Holtkamp*, 1991), but AES does not contain information about the oxidation state or ligands of the target atom.

Typical XPS and AES laboratory instruments require ultrahigh vacuum, both to minimize surface contamination that may otherwise mask the chemistry of the underlying sample, and to avoid electron-gas collisions in the long path through the electron energy analyzers. By making the electron energy analyzer small and reducing the path length for the electrons to a few millimeters, the vacuum requirements for electron-gas scattering can be somewhat relaxed, e.g., on Mars where the ambient atmospheric pressure is low. On airless bodies like an asteroid or inactive comet, the issue disappears and both XPS and AES would be suitable.

XPS laboratory instruments have the capacity to focus X-rays into a 100-µm spot. Larger spot sizes may be used on a lander instrument, perhaps several square millimeters. AES laboratory instruments typically do not use X-rays for excitation, but rather electron beams that have much better spatial resolution.

AES has a higher quantum yield than XPS and therefore provides stronger signals. AES also has a significantly higher quantum yield than XRF for relatively light elements ($Z <$ Na). AES would compete well with XRF as a chemical analysis tool, in particular for low-Z elements, were it not limited by its extreme surface sensitivity, which makes any AES analysis strongly dependent on surface contamination. In cases of even moderate levels of surface contamination, of the order of a monolayer, it is impossible to obtain reliable information about the composition of the underlying bulk sample.

While XPS suffers from similar surface sensitivity, this apparent disadvantage may instead be used as an advantage. XPS is unique among spectroscopic techniques because it provides information about the presence and nature of C-bearing compounds spread over the surfaces of mineral grains, even at a monolayer level. XPS is therefore a technique that might be able to address issues related to the Exobiology Program (see also Chapter 8).

Dust particles and soil grains are obvious candidate samples for XPS (and AES). If the samples have to be introduced into a high-vacuum system for analysis, then robotic sample selection and handling requirements are severe. One possibility that lends itself to fine-grained soil samples is the use of sticky tapes or grids. Even though such collection devices will probably use organic "glue" that could interfere with the search for *in situ* organics, they can be "overloaded" with sample material so as to mask any chemical signature from the underlying tape or grid. Larger solid rock or ice samples with relatively smooth surfaces could be studied directly, if the appropriate robotic handling capacity is available to position them inside the XPS (or AES) instrument.

### 2.3.6. Charge Distribution Analysis (CDA)

CDA is a technique that is still very new to planetary sciences, but it has unique capabilities that cannot be provided by any other analytical method *(Freund et al.*, 1993, 1994a; *M. M. Freund et al.*, 1989). Currently under development at the NASA Ames Research Center and in industry, CDA determines the dielectric polarization of solids at the 0-Hz limit. It does so by measuring the force in an electric field gradient of reversible polarity. The measurements are typically carried out as a function of temperature (ambient to 800 K) or of UV flux. CDA provides two parameters that are of interest to minerals and planetary materials: (1) bulk polarization and (2) sign and magnitude of a surface charge.

The scientific rationale for CDA is based on the recognition that "water" dissolved as $OH^-$ in nominally anhydrous magmatic (olivine, pyroxene, feldspar, etc.) or metamorphic (garnet, quartz, feldspar, etc.) minerals (*Bell and Rossman*, 1992; *Aines and Rossman*, 1984) undergoes, at least in part, a particular internal redox reaction by which $OH^-$ pairs convert into $H_2$ molecules (reduced) plus peroxy entities (oxidized) such as peroxy anions, $O_2^{2-}$, or peroxy links, X/OO\Y with X, Y = Si, Al, etc. (*F. Freund et al.*, 1989; *Freund and Oberheuser*, 1986; *King and Freund*, 1984). The significance of this is that minerals that have crystallized or recrystallized in an $H_2O$-laden environment, especially at high pressures, will always contain some "impurity" $OH^-$. If these dissolved $OH^-$ undergo redox conversion, the infrared spectroscopic signature for dissolved "water" may disappear completely or nearly completely. Even in terrestrial laboratory studies such minerals would then appear free of $OH^-$ and would likely be (wrongly) classified as having formed under anhydrous conditions. As a result of the redox conversion of $OH^-$, the minerals contain peroxy entities that represent electronic defects in the $O^{2-}$ sublattice. As long as the $O^-$ are spin-paired and diamagnetic, they are dormant and undetectable. Upon heating or UV irradiation, however, the $O–O^-$ bond dissociates into paramagnetic $O^-$, equivalent to defect electrons or "positive holes" (*Freund et al.*, 1994a).

The $O^-$ are of dual interest: (1) They are electronic charge carriers that propagate through the $O^{2-}$ sublattice with little interference from the cation sublattice, even if the latter contains transition metal cations in low oxidation states (*Freund et al.*, 1993); and (2) they are highly oxidizing radicals (*Freund et al.*, 1990). While propagating through the mineral lattice, the $O^-$ cause an increase in the electric conductivity that is very hard to measure (*Freund et al.*, 1993), but also a diagnostic increase in the dielectric polarization that can easily be determined by CDA. When trapped at a surface, the $O^-$ cause this surface to acquire a positive charge that can be detected by CDA. Concomitantly, trapped surface $O^-$ represent a powerful oxidant that can oxidize $H_2$ to $H_2O$

or subtract an H atom from $CH_4$ to produce $CH_3$ radicals (*Yamamoto et al.*, 1993; *Lunsford et al.*, 1988). The latter issue is relevant to the exploration of Mars and the characterization of the still-enigmatic martian soil oxidant. The currently prevailing opinion is that the soil oxidant consists of a physisorbed layer of $H_2O_2$ molecules formed photochemically from traces of water vapor in the martian atmosphere and frosted into the soil. Thus, CDA can determine (1) whether or not a mineral formed in a $H_2O$-laden environment and (2) whether the martian soil oxidant consisted of an $H_2O_2$ frost formed from traces of water vapor in the martian atmosphere or consisted of a layer of trapped surface $O^-$ radicals photodissociated in the bulk of peroxy-bearing mineral grains and trapped on the mineral surfaces.

Given that CDA is a new technique, an instrument suitable for planetary exploration is only in the design stage (*Freund et al.*, 1994b). The core device is a miniaturized atomic-force-microscope-type force sensor (license AT&T Bell Laboratories) (*Griffith and Griggs*, 1995) with a tip carrying a special electrode to which the positive and negative bias voltages are applied. The tip has to be brought into proximity (0.1–1 mm) of the sample to be studied. The sample will typically consist of a small grain (1–3 mm) and it has to be heated to temperatures up to 800 K. Robotic operation requires a manipulator to select, grab, and accurately (±0.1 mm) position a sample grain.

### 2.3.7. Electron Paramagnetic Resonance (EPR)

This technique, which is also referred to as electron spin resonance (ESR), uses a microwave (~9 GHz) source and magnetic field for characterization and quantification of paramagnetic transition metal ions, radicals, and defect centers (created by high-energy radiation) in minerals. The EPR spectra usually show species-specific signatures such as splitting factors (*g* values), hyperfine splittings, and spectral line shapes that can be used for characterization. The technique is for molecular characterization as well as for determining the oxidation states of transition metal ions. It cannot, however, detect Fe metal. The technique is also limited by the total amount of Fe in the sample; it will not work, for example, if there is more than 10% FeO in olivine. Consequently, while it may be a very good technique when analyzing anorthosites and gabbros, it may not be useful with some primitive materials.

This is a well-established technique in terrestrial laboratories and has a typical sensitivity at the parts-per-billion level. For flight instruments, it is estimated that sensitivities at parts-per-million level can be obtained. An EPR spectrometer for a prototype flight instrument is being developed at JPL. It has a mass of ~300 g and a power requirement of <5 W. Mössbauer is a competing technique (see Chapter 5).

### 2.3.8. Nuclear Magnetic Resonance (NMR)

This technique uses a radio frequency (~13 MHz) source and magnetic field (3 Kgauss) for detection and quantitative measurement of various forms of water: adsorbed and chemically bound $H_2O$, -OH, H, etc. Other nuclei with nuclear spins are detectable with appropriate RF ranges.

This, too, is a well-established technique in terrestrial laboratories. A NMR flight instrument prototype in a penetrator configuration is being built at JPL. The instrument mass is ~150 g and requires <5 W power.

## 2.4. ANALYTICAL AND FLIGHT STRATEGIES

In many mission scenarios, the scientific issues require two chemically sensitive instruments to analyze the necessary complement of elements (e.g., rock-forming elements plus volatile elements and their isotopes). Two chemically sensitive instruments are also needed in many cases so that one can analyze the outermost planetary surface (e.g., to determine weathering effects), while a second can analyze a subsurface volume of material (e.g., to determine the composition of unalterd planetary material). It is also necessary sometimes to coordinate the chemical analyses with measurements designed to determine other properties (such as the mineralogy of the surface). Examples of these requirements are outlined below in the context of the issues that pertain to specific types of planetary bodies.

### 2.4.1. Small, Relatively Primitive Bodies

Asteroids are airless bodies and thus do not have the protective shield of an atmosphere. Consequently, micrometeoritic and solar particle damage could have significantly altered the near-surface environment. To ensure that an analysis of unaltered material is obtained, a technique that analyzes the subsurface (>1 cm deep?) is preferred. This could involve devices that dig trenches, drill cores, or bury instrument packages in penetrators. Alternatively, an instrument that analyzes a large volume of material, like a GRS, could be employed. To quantify the chemical effects of any surface modifications, one could use a GRS in conjunction with a surface-sensitive instrument, such as an XPS or APX. Because asteroids are likely to be rubble piles of material with different chemical or petrologic properties, any chemical analyses should probably be coordinated with an imaging system. In some cases, bulk chemical analyses will need to be supplemented with individual mineral analyses (see Chapter 5). Similarly, because impact processes are constantly modifying the surfaces of asteroids, and there are hints that these processes juxtapose material with different spectral properties (e.g., Galileo's observations of Ida), the chemical analyses should be supplemented with reflectance spectra. Depending on the capabilities of spectral systems, this task could be conducted during approach, from orbit, or from the lander. This task is particularly important if one is ever going to be able to link the meteoritic database with the library of asteroid spectra. Comets have a lot more activity occurring on their surfaces than asteroids, and thus it will be important to design systems that can measure compositional variations over an extended period of time (as the orbit evolves) and to determine if the surface activity has produced a layered structure in the surface materials. To obtain vertical compositional profiles, devices that dig trenches, drill cores, or bury an instrument package in penetrators should be considered. In the case of comets, instruments must be selected that can analyze both the rock-forming elements and volatile constituents. A GRS is a good candidate because it analyzes many of the rock-forming elements plus H, C, O, N, and S. However, instruments that are designed specifically to analyze volatiles and organics should also be included (see Chapters 5, 7, and 8). For comparison of IDPs with particles on the comet surface or in the surrounding coma, instruments like the XPS or SEMPA should be considered. In all cases, the heterogeneity of the target, plus the expected activity, suggest that any chemical analyses could best be interpreted if they were integrated with an imaging technique.

### 2.4.2. Small, Rocky, or Metallic Differentiated Bodies

Geologic context is the watchword here. These bodies will probably have very complicated surfaces, produced first by the volcanic, tectonic, and impact cratering processes that affect geologically active planetary surfaces, and then modified by an extended period (>4 b.y.) of collisional evolution that has either cratered or disrupted the bodies. For that reason, it is imperative that good imaging systems be utilized in conjunction with any chemical analyses. Because these surfaces are likely to be heterogeneous, mobile systems are also required. Possible candidates include rovers or hoppers, both of which are compatible with most of the instruments described above. The chemical analyses should be governed by the same criteria used to examine primitive asteroids and, to again link the meteoritic database with the library of asteroid spectra, any chemical analyses should be conducted in regions where the reflectance spectra is also being determined.

### 2.4.3. Outer Solar System Satellites and Pluto

Because many of the bodies have surfaces dominated by ices, the best package of instruments and analytical strategy are described in Chapters 5 and 7. In those cases where silicate or carbonaceous material is present (like Ganymede, Callisto, and Rhea), one or more of the instruments described in section 2.3 should also be on board. In the case of Io, instruments that analyze the rock-forming elements should take priority. Because Io still has active volcanism, analyses should be coordinated with a high-quality imaging survey to identify lava flows and other morphological features. If possible, the imaging systems (see Chapter 6) should also be able to constrain the mineralogy of the lithologies being analyzed. Because Io has a S-rich surface, this element is a particularly important analytical target. It may also be necessary to have an analytical system that can measure material below a surficial blanket of S.

### 2.4.4. Differentiated Terrestrial Planets

The surfaces of these types of planetary bodies are complex and may require more than one analytical instrument for chemical analyses. Sometimes, for example, it is useful to compare and contrast the composition of the outermost surface layer and the underlying volume of rock (e.g., to determine the interaction of the surface with the atmosphere via weathering). This approach was illustrated on the USSR's Vega 2 mission to Venus, which carried both a GRS and an XRF (*Barsukov*, 1992). The GRS, which analyzed the deepest and largest volume of material, measured 0.4 ± 0.2 wt% K. In contrast, the XRF, which measured the outermost surface material, measured 0.08 ± 0.07 wt% K. One interpretation of this differerence in analyzed K contents is that the uppermost surface of Venus is depleted in K relative to deeper material. If so, the true crustal K abundance requires a method like the GRS technique. On the other hand, if one wants to study processes that affect the surface of Venus, techniques like GRS and XRF are both critical. The utility of a coupled GRS-XRF package has also been discussed in the context of a mission to Mars (*Yin et al.*, 1988). In a feasibility study for the proposed Lunar Geoscience Observer (LGO) mission, a GRS combined with an X-ray spectrometer (XGRS) was found to be capable of properly distinguishing at least 14 different lithologies on the Moon (*LGO-SWM*, 1986). While this instrument couplet was designed for an orbiter, it illustrates the utility of this approach, which can also be implemented in a configuration suitable for a lander.

This two-instrument concept is attractive on Mars where weathering processes seem likely (e.g., a crust was observed in Viking images). Instead of a GRS-XRF system, one could utilize a GRS-APX system (Fig. 2.2). This system can be used passively, without any modification of the planetary surface. Alternatively, one could send a single instrument if trenching or some other mechanical method is used to expose successively deeper layers of the planetary surface.

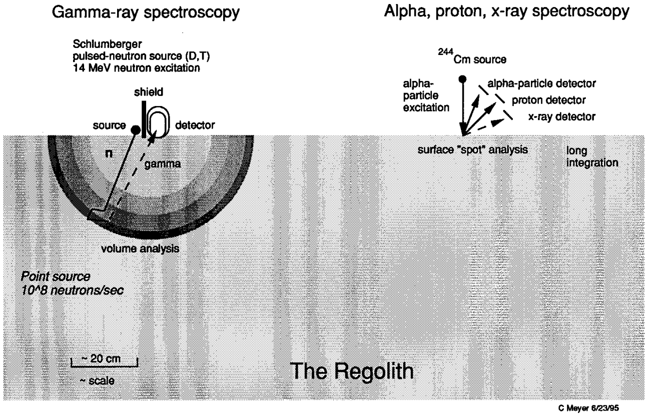

Fig. 2.2.

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# 3: Isotopic Analysis and Evolved Gases

***—Timothy D. Swindle, William V. Boynton, Ara Chutjian, John H. Hoffman, Jim L. Jordan, Jeffrey S. Kargel, Richard W. McEntire, and Larry Nyquist***

## 3.1. INTRODUCTION

Precise measurement of the chemical, elemental, and isotopic composition of surface material and gases, and observed variations in these compositions, can contribute significantly to our knowledge of the ultimate source(s), ages, and evolution of solar system material. This chapter deals with isotopic analysis and evolved gases. These analyses are mostly, but not exclusively, made by mass spectrometers or some other type of mass analyzer, and can address three broad areas of interest:

1. Atmospheric composition: isotopic, elemental, and molecular. Mass spectrometers have measured the atmospheres of most of the terrestrial planets, and are beginning to be applied to the outer planets and primitive objects (see Table 3.1).

These are the easiest measurements to make, since the material to be analyzed is already in the gas phase. Since the reconnaissance of the solar system's major atmospheres is nearly complete, the next generation of atmospheric mass spectrometers will have to be able to outperform previous experiments to be scientifically useful. Specific measurement goals are discussed below.

2. Gases evolved from solids. Usually, this involves releasing volatile elements from near-surface samples by heating, acid dissolution, or other selective process, followed by mass analysis. Laser ablation extraction also produces a gas (actually, a plasma), but differs from other techniques in that it is more selective spatially (spot sizes in the 100-µm range) but less selective chemically (ionizing virtually every atom within a small volume). Lack of chemical sensitivity is a problem in isotopic analyses of trace constituents, but is an advantage in determining the abundances of various elements. Evolved gas analyzers have not been flown on any spacecraft, with the exception of the LIMA-D and DION experiments (*Sagdeev et al.,* 1986) on the ill-fated Phobos mission.

TABLE 3.1. Missions on which mass spectrometers have been flown.

| Location/Mission | Type of Mass | Principal Spectrometer | Mission Status Constituents |
|---|---|---|---|
| *Moon/Apollo 17* | Single-focusing sector | Ar, Ne, H | Operated successfully for 10 lunations. |
| *Mars/Viking* | | | |
| Atmospheric | Mattauch-Herzog double-focusing sector | $CO_2$, $N_2$, Ar | Operated successfully on surface. |
| GC-MS | Nier-Johnson double-focusing sector | | Operated successfully on surface. |
| *Venus/Pioneer Venus* | | | |
| Large probe | Single-focusing sector | $CO_2$, $N_2$, Ar | Operated successfully through entire atmosphere. |
| Bus | Mattauch-Herzog double-focusing sector | | Operated successfully until loss of signal in upper atmosphere. |
| *Comet* | | | |
| P/Halley/Giotto | Nonstandard double-focusing energy analyzer | $H_2O$, CO, $CO_2$, $NH_3$, $CH_4$ | Operated successfully until 1000 km from comet when spacecraft hit "wall" of dust. |
| Jupiter/Galileo | Quadrupole | | In flight. |
| Saturn/Cassini | Time of flight | | In preparation. |

3. Solids. On many bodies, analyses of solids may have the greatest scientific payoff because radiometric dating of rocks (finding ages using the abundances of radioactive isotopes and their decay products) is the most precise and reliable way to determine quantitative planetary chronology. In addition, isotopic composition of nonradioactive isotopes can be diagnostic of the origin and evolution of planets. These analyses are the most difficult considered because the elements with the largest and most interesting isotopic variations are often rare, and isotopic shifts in the common elements are often subtle. The only successful analysis of solids *in situ* by a spacecraft was the PUMA analysis of dust from Comet P/Halley (*Jessberger and Kissel,* 1991). However, we have abundant and precise information on the isotopic composition of solids from Mars (in the form of martian meteorites; *McSween,* 1994) and the Moon (both lunar meteorites and the returned Apollo samples; *Warren,* 1994).

Current isotopic data on nine elements where information is available (mostly from *in situ* analysis, but also from meteorites and telescopic observations) are summarized in Fig. 3.1. This figure emphasizes the dynamic range required for meaningful isotopic studies—ratios of $10^2$ or $10^3$ are common, and He and H isotopes often have even larger abundance ratios. The figures also show that, for many elements, isotopic variations from one body to another are small—the size of the points on the plot corresponds to 5–10% uncertainties, comparable to the precision of most spacecraft measurements. However, isotopic variations are commonly even smaller. The extreme example is O, where studies of meteorites have shown that there is a tremendous amount of genetic information in the isotopic ratios, but only if they can be measured to 0.1% accuracy or better (*Clayton et al.,* 1991, and references therein).The next section of this chapter is a discussion of the scientific problems that could be addressed by evolved gas and isotopic analysis. This is followed by a discussion of the types of instruments that might be considered. Finally, there is a discussion of some specific technical problems that need to be solved to address some of the specific scientific questions.

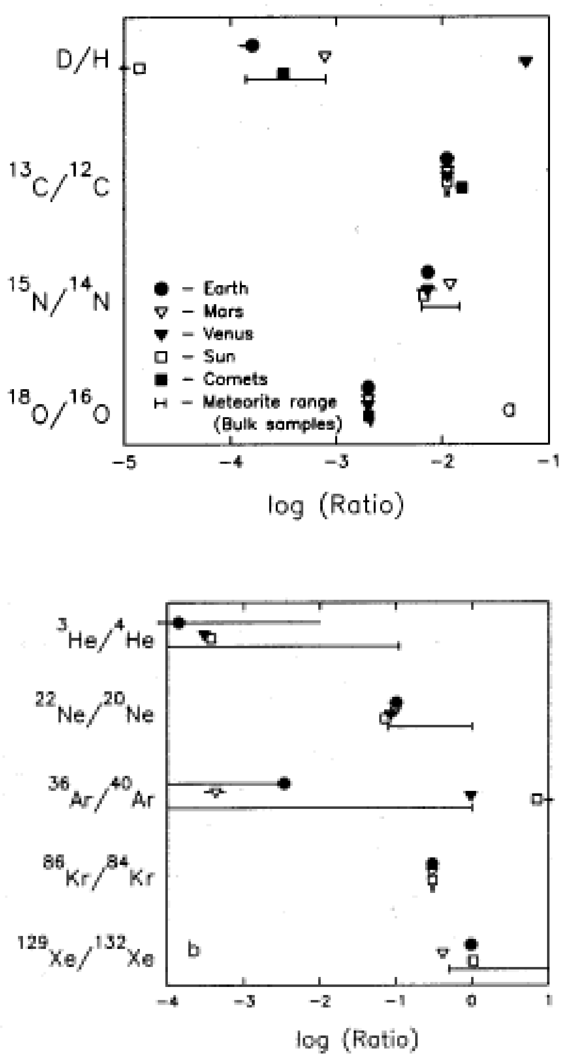

**Fig. 3.1.** Isotopic ratios of the major isotopes of **(a)** the reactive elements H, C, N, and O and **(b)** the noble gases. For Earth, the lines extending from the atmospheric point are the ranges observed in terrestrial rocks. Points with arrows are those where the ratio is off scale. Data from *Faure* (1986), *Epstein and Taylor* (1972), *Pepin and Carr* (1992), *Swindle* (1988), *Göbel et al.* (1978), *Eberhardt et al.* (1995), *Hoffman et al.* (1980), and *Schultz and Kruse* (1989).

We spend considerable effort on the question of whether any *in situ* technique can give a scientifically useful age of a rock. The usual assumption is that ages can only be determined on returned samples because the sample preparation and measurement precision needed are beyond the reach of spacecraft instruments (*Drake et al.*, 1987). This claim appears to be true with current instrumentation. However, we concur with *COMPLEX* (1994, p. 63) that "determination of even relatively imprecise ages can be very valuable in some cases. The flexibility, affordability, and feasibility of achieving many . . . goals would be greatly enhanced by development of even crude dating techniques that could be placed aboard landed science packages."

## 3.2. SCIENCE ISSUES

In this section we briefly review the science questions that can be addressed by evolved gas and isotopic analysis. We rely heavily on *COMPLEX* (1994) for our selection of the important questions addressable by these techniques for each object. We will work our way through the solar system roughly in order of ease of access to objects.

### 3.2.1. Moon

Practically all elements and their isotopes have been measured in returned lunar samples (*Heiken et al.*, 1991). Volatile gas analysis of the lunar regolith materials returned by Apollo missions have revealed a unique isotopic composition for implanted solar wind gases and solar cosmic ray products compared to other objects in the solar system. How can *in situ* measurements improve the knowledge brought by these measurements? We discuss three specific questions, all of which are put in more context by *LExSWG* (1992).

*Lunar water.* The existence of lunar $H_2O$ remains an issue of debate. The potential for the existence of water ice in permanently shadowed craters in lunar polar regions has long been argued (e.g., *Ingersoll et al.*, 1992, and references therein). If water ice is present in the polar regions, it could potentially be an important resource, as well as being scientifically interesting. In addition, it appears that under conditions at the lunar surface, solar H should reduce silicates to form $H_2O$, either through direct implantation or through mixing of regolith with hot gas generated in large meteorite impacts. In early D/H and $^{18}O/^{16}O$ studies of lunar soils, terrestrial contamination could not be ruled out. In fact, *Epstein and Taylor* (1972) concluded (from $\delta D$ and $\delta^{18}O$ values) that the "lunar water" extracted from returned lunar samples was primarily of terrestrial origin, probably from the Apollo spacecraft and astronauts. To find water in the regolith would require that technology be found to assist in avoiding or eliminating terrestrial contamination by water in instruments landed at the lunar surface. To complement earlier laboratory determinations, *in situ* instrumentation must be capable of measuring with something approaching the 1% accuracy specified by *COMPLEX* (1994).

*Characterization of the ancient solar wind.* Since the Moon's surface may be regarded as a passive collector of solar radiation for most of its history, attempts to determine secular variations in solar activity by examining the record in regolith materials have long been a part of lunar sample studies (*Pepin et al.*, 1980). Correlations have been sought between isotopic measurements of gases, such as D/H and $^{4}He/^{3}He$, and other time-dependent parameters. These efforts have suffered from the inherent lack of precise knowledge of the regolith history of the examined samples. Most returned lunar samples, including cores of lunar regolith, do not testify to a well-defined lunar stratigraphy, which would be required for development of a relative timescale. Local stratification for the lunar regolith, which has preserved a true sequence of meteoritic bombardment, may yet be discovered through robotic geology. Such a discovery followed by *in situ* measurements of solar wind elements and their isotopes may provide valuable information on early solar history. These measurements should be made with the same precision (a few percent or better) as previous laboratory measurements.

*Characterization of the lunar atmosphere.* Although the lunar atmosphere is extremely tenuous, its behavior can help account for the distribution and redistribution of volatile gases at the lunar surface. Diurnal temperature variations influence the release and condensation of the gases from the regolith. *In situ* measurements during Apollo (*Hoffman et al.*, 1973) detected $H_2$, $^{4}$He, $^{20}$Ne, $^{36}$Ar, and $^{40}$Ar at night, but only $^{4}$He in the daytime, when backgrounds from anthropogenic input were high. $O_2$ and $CO_2$ were not detected, nor were Na and K, which have been observed telescopically. Although increased sensitivity could lead to some improvement over Apollo measurements, the greatest gain could come from having less activity at the site of the instrument.

### 3.2.2. Mars

Many of the most critical questions about Mars addressable in the near future revolve around the history of water. When was there water on the surface and what happened to it? Has a portion of the atmosphere been lost, and if so, when? Isotopic and evolved gas analysis can provide important information. In particular, only through isotopic measurements can the question of "when" be definitively answered. Most of our present knowledge of Mars (*Kieffer et al.*, 1992) comes from two sources: the Viking mission, which included two orbiters and two landers; and the SNC meteorites, 11 rocks that are believed to come from Mars. Detailed relative chronologies of martian surfaces have been determined from Viking images, and accurate crystallization ages of some of the SNC meteorites have been determined, but the relationship of the two cannot be determined. Absolute chronologies based on extrapolation of the lunar cratering flux give ages that vary by as much as $2 \times 10^9$ yr for some surfaces (Table II of *Tanaka et al.*, 1992). Thus surface ages, even if uncertain by as much as 10–20%, would be significant. Several different kinds of surface ages might be adequate. Crystallization ages of lava flows on terrains of known relative age could be used to calibrate the crater-based age scales, but cosmic-ray exposure ages (based on $^{3}$He or $^{21}$Ne) of young ($<10^9$ yr) surfaces might be as useful. Alternatively, it might be possible to determine directly the ages of aqueous alteration products. The problems involved with various approaches to such ages will be discussed in section 3.4.

Mass spectrometers on the Viking landers measured the abundances of eight elements, including the isotopic abundances for most of them (to precisions of 5–50%) . The $^{15}$N/$^{14}$N and D/H ratios are much higher than terrestrial, indicating mass-dependent atmospheric loss processes. The radiogenic noble gas isotopes $^{40}$Ar and $^{129}$Xe are also enriched relative to $^{36}$Ar and $^{132}$Xe respectively, although the exact ratios are only known to the 20% level for Ar and 50% level for Xe. The isotopic composition of C, O, and Ne were reported to be within 5% of terrestrial. Much more precise measurements are available from gas trapped in glassy inclusions in the SNC meteorite EET 79001. The relative elemental and isotopic ratios for N and the noble gases match the less-precise Viking measurements over 10 orders of magnitude in gas abundance, providing the strongest argument that these meteorites are indeed from Mars. The elemental abundance of He and the isotopic composition of O have been measured telescopically, but the O measurement is only marginally consistent with the Viking measurement (they differ by 10%, but each has 5% quoted precisions). Additional measurements of the atmospheric composition would have to be considerably more precise than Viking to be valuable. Percent-level measurement of $^{18}$O/$^{16}$O would be helpful in determining the interaction of the atmosphere with the polar caps and surface, and more accurate noble gas measurements would allow for more refined models of atmospheric evolution.

Measurements of the molecular composition of evolved gases, both from martian regolith or from martian polar caps, would be helpful in constraining current interactions between these samples in terrestrial laboratories, including many that would be difficult or impossible to apply *in situ*. One of characteristic features of the SNC meteorites is their O isotopic composition, but is only diagnostic if abundance ratios of all three O isotopes ($^{16}$O, $^{17}$O, and $^{18}$O) can be measured to better than 0.1% precision (preferably 0.01%). However, 1% level accuracy of the $^{38}$Ar/$^{36}$Ar or $^{129}$Xe/$^{132}$Xe ratios would be nearly as good.

### 3.2.3. Comets

Comets are very small (less than 10 km radius) bodies that contain ices of various types. They are thought to have remained in a very cold state since their time of formation and thus may be samples of the most primitive materials known in the solar system. As a result, comets are considered crucial for understanding the origin of the solar system and of life (*COMPLEX*, 1994, p. 188).

Comets contain molecular species more volatile than water ice, whose overall composition may reflect that of grains derived from the parent molecular cloud that was the solar system's progenitor. Comparison of a complete sample of molecular species, coupled with a determination of the mechanisms by which they are bound into the water ice and organic phases, will provide a dataset of extraordinary value in characterizing the nature of the forming solar system. Further, it will provide a strong set of constraints on the concept that comets or related outer solar system objects supplied much of the volatile inventory of the terrestrial planets early in the solar system's history.

Analyses of gases in cometary comae have been made both from groundbased observations and from spacecraft at Comet P/Halley. In order to constrain the origin of the cometary grains, however, it is necessary to determine the phase from which the gases are evolved. For example, we know that comets contain CO, but it is critically important to understand if the CO is present as a pure ice phase, is trapped in a clathrate hydrate, or is absorbed on amorphous water ice. Each of these possibilities puts different constraints on the temperature and pressure environment in which the cometary grains formed. By knowing the temperature at which these gases are evolved from the comet, it is possible to determine the host of the $CO_2$. This important scientific objective of understanding the pristine ice phases requires a lander-based instrument that can collect the pristine ices from beneath the surface and determine both the composition of the evolved gases and their release temperature.

In addition to understanding which gaseous compounds are associated with which phases in the comet, it is important to determine their isotopic composition. Meteorites are known to have an isotopic composition of light elements, H, C, N, and O, that differs substantially from normal terrestrial values and in fact differs between different phases in the same meteorites. It is very important to determine the isotopic composition of these elements in comets and especially to determine the isotopes both in different compounds and in the same compounds from different hosts. For example, we want to know if the $^{13}C/^{12}C$ ratio in CO associated with amorphous ice is different from that of CO associated with clathrate hydrate or of $CH_4$ associated with clathrate hydrate.

### 3.2.4. Asteroids

The asteroids are a diverse set of objects, all less than 1000 km in diameter, ranging from primitive asteroids that are believed to contain ices to differentiated bodies (*Binzel et al.,* 1989). We believe we have samples of many asteroids in our collections of meteorites, but, with few exceptions, we don't know which meteorites sample which asteroids (*Wetherill and Chapman,* 1988). Hence, one of the most crucial questions about asteroids is that of the connection between meteorites and asteroids, and that is not readily amenable to isotopic analysis—the precision needed to measure isotopic ratios definitively (e.g., all three isotopes of O to 0.01%, *Clayton et al.,* 1991) can probably only be obtained by returning a sample, which may not be prohibitively expensive anyway for these low-gravity objects. On the other hand, there are some types of asteroids that apparently contain hydrated minerals, although these types are not common near the Earth and may not be well represented in meteorite collections. These asteroids might very profitably be studied by some of the techniques used for studying comets, especially evolved gas analysis, which could determine the abundance of water and other volatiles, which are of both scientific and resource interest.

### 3.2.5. Venus

*Surface.* The venusian surface has been studied by seven successful Soviet landing craft, three American and several Soviet atmospheric probes, and the Magellan synthetic aperture radar, among other projects. Each lander succumbed to the harsh conditions on Venus after roughly an hour of operation, which was enough time to transmit television images, engineering data on the surface rocks, and X-ray-fluorescence and $\gamma$-ray spectrometer analyses of surface rocks. The surface (at least in the lowlands) is dominated by mafic volcanic rocks (*Barsukov et al.,* 1986). The surface is much too hot to allow aqueous weathering or the existence of most common types of terrestrial hydrated minerals on Venus, but surface-atmosphere chemical interactions (weathering) does occur, with the production of minerals such as calcite and anhydrite, which appear to be abundant on Venus (*Barsukov et al.,* 1986; *Fegley et al.,* 1992; *Kargel et al.,* 1993). Some version of evolved gas analysis would be the most effective way to determine the actual weathering products present, and isotopic analysis would constrain some of the details.

Cratering statistics indicate that Venus may have experienced global volcanic resurfacing around 300 m.y. ago, and that it has been relatively quiescent ever since. This inference carries broad implications for the nature of mantle convective dynamics in Venus and perhaps in the other terrestrial planets (*Schaber et al.,* 1992). Testing this hypothesis is one of the key scientific objectives for Venus (*COMPLEX,* 1994, p. 96).

Ages for carefully selected volcanic rocks from perhaps five terrains, even if only accurate to 10%, could readily test the global resurfacing model. Aside from the serious engineering hurdles that would have to be passed to have a spacecraft survive on the surface, the success of any attempts to produce isotopic ages or useful stable isotopic measurements for venusian rocks depends on the degree to which certain minerals on Venus may have been closed to significant isotopic exchange and reequilibration. The high surface temperatures and the occurrence of carbonate-sulfate weathering might tend to cause some elements in some susceptible minerals to be unreliable for useful isotopic work. Unfortunately, Ar can diffuse out of virtually every mineral (*Head and Swindle,* 1995), and cosmic-ray exposure ages will not be applicable because of the shielding from the atmosphere. The behavior of isotopic systems under metamorphic conditions on Earth suggest that many other parent and daughter elements widely used in radiometric dating methods (U, Pb, Lu, Hf, Sm, Nd, La, Ba, Re, and Os) are probably fairly immobile on Venus even in the face of high temperatures and severe chemical weathering, but these will only help if techniques to precisely measure their isotopes can be developed. To get a rough idea of the magnitude of changes in isotopic ratios expected on Venus due to radiogenic growth and the accuracy with which isotopic measurements would have to be made to provide scientifically useful results, we have calculated radiogenic growths for three isotopic clocks, using trace-element abundances typical of terrestrial samples analogous to two model rock compositions expected on Venus, olivine leucitite (Venera 13) and mid-ocean ridge basalt (Vega 2). In 300 Ma (*Schaber et al.,* 1992), the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios would increase by less than 0.1%, while the $^{206}$Pb/$^{204}$Pb ratio would increase by a few percent. Measurement precisions would have to be an order of magnitude better than the size of these increases to get 10% precision on ages.

*Atmosphere.* Venus' atmosphere has been studied by several spacecraft, most notably the armada of four spacecraft from two different space agencies (Pioneer Venus Orbiter and Multiprobe and Veneras 11 and 12) that arrived in December 1978, each carrying a mass spectrometer and gas chromatograph. This unique complement of highly sophisticated instruments has provided a wealth of information on the composition of the Venus' atmosphere (*Hoffman et al.,* 1980).

Isotopic compositions obtained by various instruments are included in Fig. 3.1. It was not a surprise that $CO_2$ is by far the dominant constituent, but the $^{40}$Ar/$^{36}$Ar ratio (300× lower than Earth and >2000× lower than Mars) and D/H ratio (100× higher than Earth) were surprises. In general, much is known about the composition and isotopic ratios of the Venus atmosphere, but the error bars in many cases are quite large (±50%) and there remain some disagreements between the results from the various instruments. Future studies of the Venus atmosphere need to address the precision of the measurements, verify that the D/H ratio is indeed 2 orders of magnitude different from Earth, and determine some of the ratios of rarer isotopes that could be diagnostic of the origin and evolution of the atmosphere, including $^{20}$Ne/$^{22}$Ne, $^{38}$Ar/$^{36}$Ar, and the major isotopes of Kr and Xe. In addition, we need to measure the oxidation state (i.e., $O_2$ abundance or CO/$CO_2$ ratio) in the lowest part of the atmosphere, and obtain more definitive data on the interactions between surface materials and S- and Cl-bearing compounds in the lower atmosphere.

### 3.2.6. Mercury

Mercury is the least well known of the terrestrial planets, with only Earth-based observations and the Mariner 10 flybys (*Vilas et al.,* 1988). Mariner 10 did not carry any mass spectrometers, so no isotopic information is available. Mariner 10's airglow spectrometer did identify H, He, and O in the tenuous mercurian atmosphere, and Na and K have been identified telescopically. If further flybys or a rendezvous mission precede any surface missions, the questions addressable by isotopic and evolved gas analysis can be more finely honed. For the moment, there are some obvious fundamental questions that can be addressed.

The foremost question at the moment is the composition and origin of the radar-bright polar caps. Analysis of gases evolved by heating of a sample from a polar region could address the elemental and molecular composition of the polar cap, and provide isotopic information (for example, D/H ratio of water ice) that could constrain the mode of origin.

The age of the mercurian surface is completely unknown, although it is believed to be quite old. Since it is the innermost planet, determining the ages of surfaces by determining the crystallization ages of rocks would provide a calibration point for cratering rates throughout the inner solar system. In addition, determining the ages of rocks from the youngest surfaces would determine how recently volcanic activity occurred, which in turn is crucial for understanding the evolution of the interior.

Mercury's atmosphere is most similar to that of the Moon, and measurement of the elemental and isotopic composition of the mercurian atmosphere could address the same sort of questions: What is the source of the atmosphere? Is some of it degassed from the interior? How does it vary through the mercurian day?

### 3.2.7. Icy Satellites and Pluto

Some of the most important questions about the solar system's origin can only be answered with studies of icy satellites of the gas giants, and some of these questions will require isotopic investigations of ices by landed spacecraft. We do not anticipate these types of missions being launched any time in the next decade, but the technology to conduct these sorts of missions seems not much more than some combination of the technologies developed for the Galileo and Cassini orbital tours, *in situ* comet analyses, and, if they can be developed, Mars missions involving *in situ* isotopic dating.

Investigations of stable isotopes in undifferentiated primitive icy satellites and their planets' atmospheres could teach us a great deal about compositional fractionations and other formational processes in the circumplanetary nebulae and about the differentiation of the gas giants and their massive atmospheres. Similarly, analysis of the elemental and isotopic composition of the atmospheres of those bodies with tenuous atmospheres, such as Triton and Pluto, could reveal much about the origin and evolution of those atmospheres and their parent bodies. Other problems addressable by isotopic analysis have more restricted pertinence to the icy satellites themselves. Many of these studies are of a reconnaissance nature, so they could produce useful data with lower precisions than that required for instruments flying to planets for which we already have some knowledge.

Given the much greater distances and the double energy penalty that would be involved for a sample return mission, the chronology of outer planets and their satellites may be best addressed by isotopic measurements from a robotic lander. Models require anything from millions to hundreds of millions (or even billions) of years for formation of giant planets and their satellite systems. Convincing evidence of the duration of accretion of primitive icy satellites would provide an important constraint on solar system formation. Similarly, absolute calibration of cratering ages on even a single icy satellite would have similar value in providing absolute calibration in the inner solar system, since the relationship of the various impacting populations is not definitively known. *Kargel* (1992) has shown that some cryovolcanic flows could contain enough K and Rb to permit radiometric dating, if appropriate techniques can be developed.

Perhaps the most significant use of isotopic and evolved gas analyses in the outer solar system might be investigations of organic chemistry on Titan. These investigations could have broad implications for prebiotic chemistry on Earth and elsewhere in the universe, one of the key concepts developed by *COMPLEX* (1994). The Cassini mission and comet missions discussed above will lay the groundwork for any future Titan missions.

## 3.3. POTENTIAL INSTRUMENTS

In this section, we review many of the instruments that could potentially be used to answer the questions listed in the previous section. We begin by discussing a variety of mass analyzers, and then some of the more promising techniques for getting ions to the mass analyzer. In this chapter, we emphasize techniques leading to mass analysis, although we recognize that, for some evolved gas analyses, a mass analyzer is not required.

### 3.3.1. Mass Analyzers

Table 3.1 lists the mass analyzers that have been or are planned to be flown to study planetary atmospheres. The U.S. has never flown a mass analyzer for solids, although the European Giotto mission (PUMA) analyzed dust particles from Comet P/Halley, and the Russian Phobos mission had analyzers (LIMA-D and DION) scheduled to be used on the surface. These and other mass analyzers are described below; Table 3.2 lists the principal advantage of each.

TABLE 3.2. Principal advantages of each type of mass spectrometer.

| Instrument | Principal Strengths |
|---|---|
| Magnetic, single-focusing | Simple operation, no RF voltages.<br>Very good mass resolution with proper ion sources.<br>Simultaneous collection of 2–3 mass peaks.<br>Very high sensitivity. |
| Magnetic, double-focusing mass spectrograph | Excellent mass resolution.<br>More complex operation.<br>Very high mass-rejection ratio.<br>Simultaneous collection of a wide range of mass peaks. |
| Quadrupole, linear | Good mass range.<br>Accepts positive or negative ions in same instrument.<br>No magnetic field.<br>Highly efficient in ion transmission, but at a fairly low mass resolution.<br>Ion energy independent. |
| Quadrupole ion trap | Very compact and low mass.<br>Very high mass resolution.<br>Very high sensitivity.<br>Large mass range.<br>Very rapid analysis.<br>Possible to do mass analysis on specific mass species (MS-MS technique). |
| Time of flight | Wide acceptance angle.<br>Very rapid analysis.<br>High sensitivity. |
| Wien filter | Simultaneous collection of range of mass peaks.<br>No RF voltages. |

*Magnetic sector-field.* Magnetic sector-field mass spectrometers have been the mainstay for analyses of planetary atmospheres (Table 3.1). They typically consist of an ion source, a magnetic momentum analyzer, and a detector, which usually consists of channeltron electron multipliers or microchannel plates (Fig. 3.2). Pulse counting circuits accumulate the data and store them for transmittal to a data handling system. Ions are formed by electron bombardment of the source. The resulting sensitivity at 250 µA emission current is of the order of $10^{-5}$ to $10^{-6}$ amps/torr, consistent with the detection and signal processing dynamic range. Electron energy can be varied (e.g., from 15 to 70eV) to assist in determining molecular and atomic composition by changing the resulting cracking patterns and charge states. Ions are accelerated from the source by voltage ($V_s$) and collimated into a beam. The beam then traverses a magnetic field (strength B) that bends it through a suitable angle (usually usually 90° or more), and is focused onto a collector slit. The acceleration, a, of an ion of charge q and mass m in the magnetic field is

$$a = [q(v \times B)]/m \qquad (3.1)$$

where $v$ is the velocity, which is in a plane perpendicular to the magnetic field. Since the acceleration for a radius of curvature $r$ is

$$a = v_2/r \qquad (3.2)$$

the mass-to-charge ratio of ions that successfully traverse the curved path of the mass spectrometer flight tube is a function of the magnetic field strength and the ion momentum, the latter being varied with time to scan the mass spectrum. Most spacecraft mass spectrometers have used multiple collectors, e.g., ion beams with three different path radii focused simultaneously on three collector slits, to cover a wide mass range with a fairly narrow voltage sweep range. This way, multiple mass peaks (three, in the example) may be monitored simultaneously.

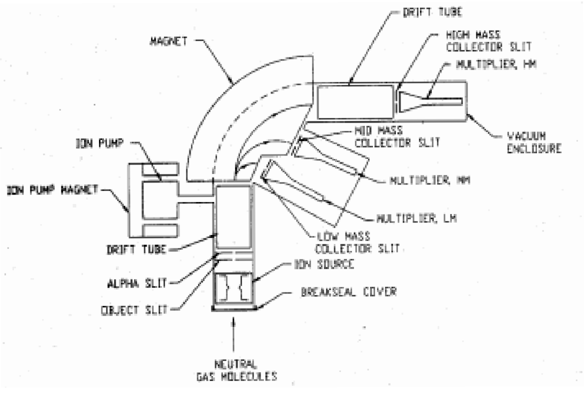

**Fig. 3.2.** Single focusing mass spectrometer, with collectors for simultaneous analysis of three masses.

Behind each slit is a high-counting-rate channeltron electron multiplier that monitors the mass spectrum as the ion beams are scanned across the collector slits. When counting rates are plotted as a function of $V_s$, equivalent to ion mass, a mass spectrum is produced depending on the form of $V_s$. One typical operating mode is to step from peak top to peak top, which results in an efficient use of both telemetry band width and spectral scan time. Magnetic mass spectrometers may employ an electrostatic analyzer in tandem with the magnetic analyzer. Such a configuration (Fig. 3.3) has double-focusing properties (both angle and energy focusing). These will generally exhibit higher mass resolution than single focusing magnetic analyzers but are more complex to operate. Focal plane detectors, such as microchannel plates, may be used to simultaneously collect many ion peaks, thus making the instrument a spectrograph.

*Quadrupole mass filters.* Strictly speaking, the quadrupole is a mass filter rather than an analyzer because it transmits ions having only a small range of m/z values, and there is no mass dispersion or focusing as in magnetic analyzers. Thus, it is analogous to a narrow-bandpass electrical filter that transmits signals within a finite frequency bandwidth, and a trade-off is made between transmission and resolution. The conventional quadrupole mass analyzer (Fig. 3.4) utilizes four parallel cylindrical or hyperbolically shaped rods. The rods are long relative to the inner "kissing circle" diameter, to minimize fringing fields on the active length of the rods. A quadrupolar potential is established by applying a time-varying potential +Φ and –Φ on alternate rods (at the four locations ±x and ±y), where

$$\Phi = (U_o + V_o \cos \Omega\, t)[(x^2 - y^2)/r_o^2] \qquad (3.3)$$

(*Paul et al.,* 1958) for a dc component $U_o$, and an rf component $V_o$ of frequency Ω. The ions are injected (in the z direction) into the central "flip-flopping" saddle-potential region, and only those ions having the correct mass are transmitted to the exit aperture without sliding into one of the rods. The ion trajectories in the x and y directions are governed by the Mathieu equations

$$x^2 + (a - 2q) \cos 2\xi\, x = 0 \qquad (3.4)$$

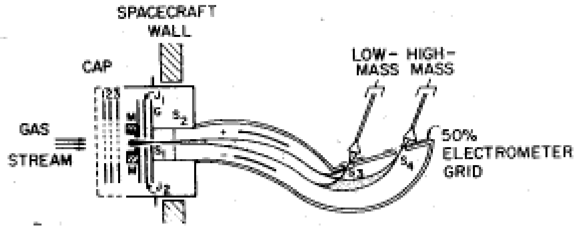

**Fig 3.3.** Schematic drawing of a Mattauch Herzog double-focusing mass spectrometer (*Nier et al.,* 1973). The cap shown by the dotted line is ejected in orbit, exposing the ionizing region to the gas stream. Two detectors are shown, but the focal plane could be covered by a microchannel plate detector.

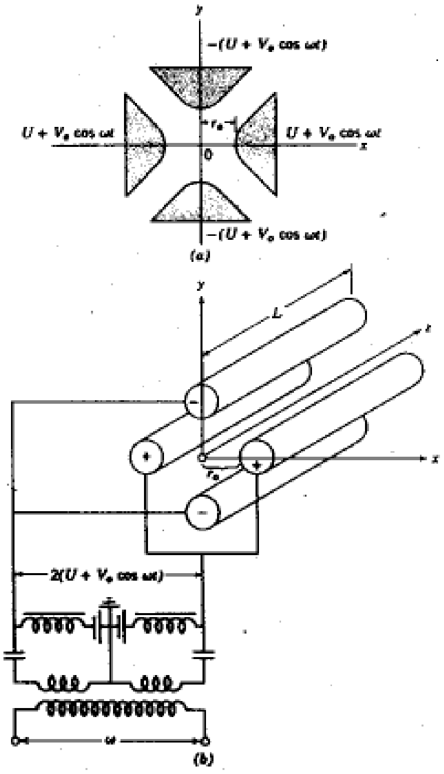

**Fig. 3.4.** The quadrupole mass filter (*White and Wood,* 1986) showing idealized electrode configuration and cylindrical rod assembly. An ion source is placed in front of the rods and a channeltron electron multiplier usually follows the rods.

where the parameters a and q determine the region of stable solutions to equation (3.4).

A mass spectrum is obtained by sweeping $U_o$ and $V_o$ linearly (at a fixed Ω), and detecting the transmitted masses (one at a time) at the exit plane with a Faraday cup or particle multiplier. The resolution of the device depends on the rod geometry $r_o$, frequency Ω, rod length, and axial and radial ion injection energies. In the original publication (*Paul et al.,* 1958), resolutions m/(δm) = 1500 were reported, sufficient to resolve $^{16}O$ (15.9949 dalton) and $^{12}ClH_4$ (16.0313 dalton). NASA flight mass spectrometers for planetary aeronomy are of the quadrupole type with hyperbolic rods. The resolution is approximately 0.3 dalton, with narrow wings on each peak so that two adjacent masses can be resolved if their intensity ratio is $10^4$–$10^5$ (*Spencer et al.,* 1985; Niemann, Cassini penetrator mass spectrometer). This is vital for exploring the full density range of trace ions and neutrals present in a complex planetary atmosphere. A miniature quadrupole array, with sixteen 25-mm-long rods, weighs less than 30 g (including ionizer and detector). The advantages of a well-designed quadrupole analyzer are sensitivity, good mass range and resolution, dynamic range ($10^6$ or better), and mass rejection ($10^4$ or better for adjacent masses). Disadvantages are that the transmission is mass dependent, and is a strong function of desired resolution.

*Time-of-flight analyzer.* A conventional time-of-flight (TOF) mass spectrometer consists of an ion source, a long field-free flight tube, and particle detector (*White,* 1968). Timing gates (akin to traffic lights on a boulevard) are placed at each end of the flight tube. Ions from the source have a relatively narrow energy distribution, usually of width 0.5–1.0 eV. For high resolution a narrower energy distribution is needed. This may be done by use of an energy "predisperser" such as a Bessel box or an electrostatic analyzer. The ions are accelerated (usually to 10–1000 eV) toward the first gate, which is opened for a short time "δ" by a square pulse, and a packet of ions enters the tube. Ions with different masses have different velocities and traverse the tube with different flight times T. The opening time of the second gate (traffic light is "green") fixes the mass of the ions transmitted and detected. The relation between the flight time T, length of tube L, and injection energy E is just

$$m = 2E\,(T/L)^2 \qquad (3.5)$$

where T/L is (particle velocity)$^{-1}$.

Advantages of the TOF method are its large mass range, sensitivity (no limiting slits), and relative simplicity of construction. The principal disadvantage is that the duty cycle D, the product of the cycle repetition time and the time (δ) that the gate-opening pulse is "on," is usually less than 1%. One is limited in the pulsing frequency by mass-aliasing effects: A faster particle from a later pulse can catch up with a slower particle from an earlier one. To obviate this, one may install a third traffic light in the tube, so that ions must have traversed two timed gates after the opening gate. This arrangement eliminates aliasing velocities to an order sufficient to disallow expected overlapping velocities in the sampled plasma. One may accommodate many pulses in the flight tube, and hence D can be increased to about 10% (*Martus et al.*, 1993). Another smaller disadvantage is the need for faster risetimes and narrower pulsewidths if one needs to go to shorter flight tubes to miniaturize the TOF instrument.

*Laser ablation mass spectrometers.* In laser ablation mass spectrometers, a tiny spot on the surface of a sample is ablated by a short laser pulse. Surface material is converted into a low-energy plasma, and some of the resulting ions, expanding away from the ablation point, travel through an electrostatic "reflectron" and impact a microchannel plate detector (MCP). The electrostatic fields in the reflectron (Fig. 3.5) are designed to cancel energy dispersion of the ions over a broad energy range covering the peak of the ion distribution, resulting in ion time-of-flight (TOF) from the point of ablation to the MCP that is independent of ion energy, and proportional to the square root of ion mass. For typical compact laboratory instruments, the TOF ranges from a few microseconds (for H) to <100 µs (for >200 amu), and thus the MCP current as a function of time after the laser pulse provides a mass spectrum of the surface material. This current can be digitized with high accuracy and time resolution, providing isotopic mass resolution for every element. A laser ablation mass spectrometer was flown on the Phobos mission (LIMA-D). Modern instruments are small, low power, and low mass (a few kilograms), well suited for mission to small bodies in the solar system, and provide quantitative analysis for all elements and isotopes present in a sample down to levels below 100 ppm.

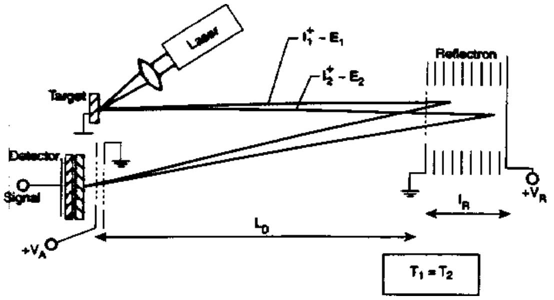

**Fig. 3.5.** Schematic diagram of a laser ablation time-of-flight (TOF) mass spectrometer. A pulsed (<10 ns) laser ablates a 10–30-µm spot on the target, creating energetic plasma ions, some of which follow trajectories such as those for ions labeled I1 and I2. Ions of the same mass but different energies (for energies between VA and VR) experience TOF dispersion in the free-flight region LD that is compensated within the reflectron region LR; TOF then depends only on the mass. Multistage reflectrons are frequently used, and many configurations of the instrument are possible.

*Quadrupole ion trap.* The quadrupole ion trap analyzer (QTA) is a form of quadrupole mass analyzer that employs three electrodes, two of them end-caps that are normally at ground potential and between them a ring electrode to which DC and RF voltages are applied (Fig. 3.6). After ionization, ions are trapped in orbit in the RF field until measurement is desired. The RF voltage, which has a frequency of the order

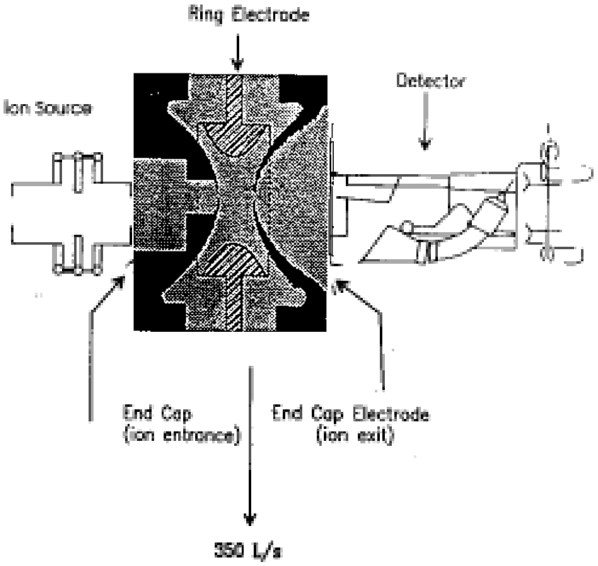

**Fig. 3.6.** Schematic of a quadrupole trap analyzer (QTA). The ring electrode and end caps are cylindrically symmetric about a horizontal line from the ion source to the detector.

of 1 MHz, causes the ions to undergo stable oscillations between the electrodes, provided their mass-to-charge ratio falls within appropriate limits. Otherwise, their motion is unbounded and they quickly leave the trap. To extract the ions, the amplitude of the RF voltage is increased, causing ions of successively increasing mass to be ejected through one of the end caps into an electron multiplier. The signal from the electron multiplier, typically a channeltron, forms a mass spectrum from which the identification and relative abundances of the gases that were sampled by the QTA are determined. The design of the ion trap analyzer allows for an unprecedented reduction in the weight of the mass spectrometer. A prototype of the analyzer, which fits in the palm of a hand, weighs <100 g, which is less than 10% the weight of a conventional analyzer. The trap function, in addition, provides an unparalleled increase in sensitivity and mass resolution.The QTA has not yet been flown in space but at least two groups are trying to develop it in the near future.

*The Wien filter.* The Wien filter is based on the principle of an ion of the correct velocity traversing a region of crossed electric and magnetic fields, the ion's injection velocity being perpendicular to the crossed fields. At the tuned velocity, the electrical force $q\mathcal{E}$ will just match the magnetic deflection $qv \times B$, and the ion will pass undeflected. All other ion velocities will be deflected in a plane defined by the incident ion direction and the direction of $\mathcal{E}$. This tuned velocity is simply given by, for fixed particle injection energies E,

$$v^2 = (\mathcal{E}/B)^2 = 2E/m \tag{3.6a}$$

or

$$m = 2E(B/\mathcal{E})^2 \tag{3.6b}$$

A spatially extended detector (microchannel plate strip, charged-couple device, or multianode detector) may be used at the exit to detect groups of masses simultaneously. Good homogeneity of the magnetic field is required. Any single-particle detector must be shielded (to less than about the 0.005 tesla level) from the B field of the filter.

Advantages of the Wien filter are its mass multiplexing (10 masses, say, detected simultaneously). Disadvantages are the need to have accurately aligned and homogeneous $\mathcal{E}$ and B fields, and to use a shielded particle detector without disturbing the field homogeneity at the detection plane. Peak broadening effects, such as beam shear in the $\mathcal{E}$ field, have not been characterized yet.

### 3.3.2. Extraction and Inlet Systems

Evolved gas analysis via gas chromatography (GC) is a technique that has been used for years in the laboratory to analyze gaseous mixtures. There are two aspects of the technique: separation and detection.

*Separation.* The separation of the compounds in the gas is based on the principle of establishing an equilibrium between a mobile phase (the gas) and a stationary phase (a solid or liquid). The gas flows through a column that is either packed with, or has its walls coated with, the stationary phase. An inert carrier gas, often N or He, constantly flows through the column. When a gas mixture is to be analyzed, a small amount (relative to the volume of the column) is introduced at the head of the column and the carrier gas forces the gas mixture through the column. Compounds that are strongly adsorbed by the stationary phase are removed from the gas mixture, while those that are not adsorbed pass directly through the column. The gases that are adsorbed are then released back to the pure carrier gas that follows the gas-mixture spike. These gases are again adsorbed a little further down the column and released a short time later as more pure carrier gas flows past. This process repeats itself many times as the strongly adsorbed gases make their way down the column. At the end of the column the gases exit, separated by the degree to which they were adsorbed; the first gases out are those that were not adsorbed, followed by those with progressively greater affinity for the stationary phase.

It should be obvious that one stationary phase is not suitable for separating all compounds since the nonadsorbed compounds are not separated; they move through the column as if it were an inert pipe. Depending on the compounds of interest, several columns are generally used. For example, one might be used for polar compounds, e.g., water and ammonia, another for nonpolar compounds, e.g., hydrocarbons, and a third for the "permanent" gases, e.g., N, O, and CO.

Old technology columns were typically several millimeters in diameter and took about 5–10 min to process a gas sample. This time requirement implies that one could not monitor gases that were changing rapidly with time. Newer columns are a fraction of a millimeter in diameter and can process a mixture in tens of seconds.

*Detection.* The detectors used to determine the time of elution and amount of the compound fall into two categories: specific and nonspecific. For mixtures of simple compounds, a nonspecific sensor is adequate; the time of elution is diagnostic for the compound. For more complex compounds, several different compounds can have similar elution times. In this case, a specific detector, usually a mass spectrometer, is used. The combination of a GC and a MS is useful for complex mixtures, as GC spectra with a nonspecific detector are difficult to interpret, and the mass spectrum of a non-separated mixture may also be too complicated to interpret. A disadvantage of coupling an MS to a GC, especially with high-performance columns, is that the elution peak of a compound of interest will be very narrow (fraction of a second), and there may not be sufficient time to get adequate statistics to determine isotopic ratios. A common nonspecific sensor relies on differences in thermal conductivity between the eluting gases and the carrier gas. Thermal conductivity can be measured with a hot thermistor, and changes in conductivity are proportional to the concentration of elutant. Another nonspecific sensor relies on differences in electrical conductivity of the gas when ionized. An example of this detector is the metastable ionization detector (MID). In the MID, a low-energy β-emitting radioisotope inside the detector activates the He carrier gas to an excited state. The eluted molecules become ionized via collisions with the activated He, and the current in the detector is proportional to the concentration of the eluted compound. The latter detector is more sensitive, but the electronics are more complex.

*Evolved-gas analysis of nonseparated gases via compound-specific detectors.* For very simple mixtures, or for applications where concentrations of only a few species are needed, it is possible to include specific chemical sensors for each compound of interest. For example, to determine the composition of breakdown products of clay minerals and carbonates such as might be expected on Mars, it is possible to simply include only a sensor for water and one for $CO_2$. Most compound-specific detectors are designed so the compound of interest sets up an electrochemical potential across suitable electrodes, much like in a pH meter. Most compound-specific electrodes are also sensitive to other compounds (to varying degrees), and sensors for a number of specific compounds may be required to yield unambiguous analyses. For water, other types of sensors can measure relative humidity or dew point. These devices are much simpler than a GC, but require that one know beforehand (and without doubt) the nature of the solids to be analyzed.

*Lasers as a means of extraction.* Lasers produce a very stable power density ($W/cm^2$) and may operate during day or night. The average and peak power requirements must be determined along with the duty cycle. The selection of the laser must be based on (at least) the following criteria: (1) absorption of laser radiation by the material, (2) a thermal model, and (3) characterization of the laser.

Using these absorption properties as criteria for selection, lasers for potential use as a means of extraction from silicate surfaces include ion lasers like Ar and Kr (UV), $CO_2$ (10.6 mm, IR), and the fourth harmonic of the Nd:YAG (266 nm, UV). The ion lasers are more expensive and less efficient.The laser characteristics determine the spot size that can be heated to a required temperature, and also whether the laser is continuous or pulsed. The spot size is determined by the divergence of the beam and can be calculated. With the laser at a distance of 10–100 cm from the sample, and typical laser beam parameters, a spot size of 4–7 mm can be achieved without lenses, and a spot size of 400–8000 mm can be achieved with a single lens. Larger beam diameters can be achieved by using beam expansion techniques.

*Laser ablation.* Pulsed lasers, such as the Nd:YAG, deliver an extremely high power density, $>10^9$ $W/cm^2$, for a short duration, 5–10 ns, to the sampled spot. This creates a plasma ball of ionized target material at the focused spot. Mass spectrometers may detect the ablated elements at a distance of up to several tens of meters. The release of ionized elements by this laser is rather indiscriminant with regard to siting of an element within the lattice region being ablated. Thus major elements would be expected to dominate the release spectrum. Laser ablation techniques have been incorporated in planetary surface instrument designs in combination with spectroscopy (LIBS, *Blacic et al.*, 1993) and mass spectrometry (LIMA-D, *Sagdeev et al.*, 1986; and *DeYoung and Situ*, 1993). A pulse repetition rate of 0.1–0.2 Hz may be reasonable. Typical parameters are summarized in Table 3.3.

TABLE 3.3. Laser extraction systems.

| | Ablation | Desorption |
|---|---|---|
| Maximum range | Several tens of meters for major elements | <1 m |
| Laser type | Nd:YAG<br>1.06 µm | $CO_2$<br>10.6 µm |
| Power density | $10^9$ $W/cm^2$ | 800 $W/cm^2$ |
| Spot size | 1–2 mm | 400 µm (focused 2–4 mm beam) |

*Laser desorption.* The $CO_2$ continuous wave (CW) laser operating at IR wavelengths imparts its energy over a longer duration, allowing for a controlled heating of the sample. Gases and other elements may be thermally desorbed from solid surfaces under vacuum conditions in this fashion. The desorbed gases may be measured with a mass spectrometer. This approach has the advantage of providing the potential for stepwise release of gases from the sample, allowing for *in situ* component separation. Trace amounts of trapped gases may be released selectively by moderately exciting and expanding the lattice of the target material. Thus, interference from major elements may be avoided, but the mass spectrometry must occur relatively close to the target to detect the trace amounts of released gases.Thermal model calculations suggest that small lasers with only small peak power consumption (~10 W) may be adequate for *in situ* heating of silicate materials. To heat a 1-$mm^3$ spot on quartz to a temperature of ~950°C within 1 s requires a power density of 160 $W/cm^2$. Taking into account heat loss and other considerations, a laser that can deliver several hundred Watts per square centimeter should be sufficient. A 10-W CW laser with a 4-mm beam has an unfocused power density of about 80 $W/cm^2$ or, when focused to a 400-mm spot, about 8000 $W/cm^2$. This is a theoretical calculation based on ideal conditions. In practice, however, the achievable power density at the focused spot could be down by a factor of 2–4. Also, in order to calculate the actual energy transfer to the sample, the losses at surfaces of the focusing lens and the sample itself have to be accounted for. This will introduce another loss of a factor of about 5. The practical transferred power density will therefore be about 800 $W/cm^2$, sufficient to carry out heating experiments.

The duty cycle and/or repetition rate determines the average power delivered to the sample and the "off" time. The 10–20-W peak power requirement would be excessive if continuous operation were required. The duty cycle, however, need not be continuous. Periodic "zaps" with durations of only a few seconds may be sufficient for surveys. Thus, the average power required could be significantly lower than the peak power, with the appropriate choice for the period. The operation of pulsed lasers normally gives high peak power, but a low average power. Assuming a 10-ns pulse and a 0.1-Hz repetition rate, the pulsed Nd:YAG laser used for LIBS can deliver 180–1000 mJ of energy for an average power of 0.3–1.5 W (*Blacic et al.,* 1993). The duty cycle of the continuous $CO_2$ laser can mimic pulsed operation through power modulation. The "pulses" are longer (>1 s) due to the time required to ramp the power. From the thermal model discussed above, a focused continuous 10-W $CO_2$ laser could deliver enough heat energy to 1 $mm^3$ of quartz in a 3-s "pulse" to reach 950°C, using an average power of 2–3 W and a 0.1-Hz pulse rate frequency during operation.

*Chemical dissolution.* In terrestrial laboratories, extensive chemical procedures are performed on much of the material slated to undergo isotopic analysis. Most of these procedures may be too complex for robotic probes to planetary surfaces, but it is possible that chemical dissolution, simply dissolving some readily attacked portion of a rock, might work. For example, halite can be dissolved in water or, at a slower rate, in methanol. On a robotic surface probe, this could be followed by mass spectrometric analysis of the gases released (e.g., Ar) and chemical analysis of the elements in the solution (e.g., K). *Wampler and Weaver* (1987, reported in abstracts by *Wampler and Hassanipak,* 1986, 1988) successfully used methanol to dissolve halite and stratigraphically obtain ages by the K-Ar method (see discussion in section 3.4.1). One of the few extraterrestrial bodies where salts might be expected is Mars, but if there are salts (e.g., evaporites) on Mars, their ages and composition would be of great interest. In terrestrial laboratories, chemical dissolution using HF has also been applied to U,Th-Pb dating of zircons (*Mattinson,* 1994), but the stronger acids and longer dissolution times required for silicates would make them more difficult to analyze *in situ*.

*Inlet systems.* A common problem of mass-spectrometer-based systems is interfacing the high vacuum of the ionizer-analyzer-detector portion ($10^{-3}$–$10^{-4}$ torr in the ionizer, and $10^{-6}$ torr at the analyzer and detector) with a higher-pressure external atmosphere (to 760 torr). Common methods for dropping the pressure, and retaining the analyte sample, are (1) use of a variable-diameter (low-conductance) pinhole aperture; (2) use of a gas-chromatographic column with variable-conductance inlet valve, dropping the pressure as well as effecting a temporal separation of the analyte (*Carr,* 1984; *McFadden,* 1973; *Holland et al.,* 1994); (3) use of analyte diffusion through a hollow-fiber membrane (membrane-extraction mass spectrometry, MEMS) (*LaPack et al.,* 1991); (4) a molecular jet separator by which the pressure is dropped, and higher molecular-weight analytes are separated from the lighter carrier gas, which may be, for example, the $CO_2$ on Mars or $N_2$ on Titan *(McFadden,* 1973; *Grayson and Wolf,* 1967; *de la Mora and Rosell-Llompart,* 1989; *Darrach and Chutjian,* 1995); and (5) use of a new type of "volcano" field-emission ionizer array in which the small opening of the volcano tip provides a low-conductance entry to the ionizer region, as well as acts as a sharp tip for field-ionization of the analyte-carrier gas mixture (*Spindt,* 1992).

In (4) the jet focusing and separation are most efficient when the ratio of analyte molecular weight to carrier-gas molecular weight is greater than or equal to about 10. Furthermore, a forepump is required to pump the intermediate nozzle-skimmer region. The devices in (2) and (5) are interesting in that they have been fabricated in miniaturized forms (micro-gas-chromatographic columns, and the microvolcanoes) for "matching" to future miniaturized quadrupole, ion-trap, Wien-filter, magnetic-sector, etc., analyzers.

## 3.4. AVENUES FOR FUTURE DEVELOPMENT

Having laid out the questions to be answered, and the general techniques that might be applied, what specifically could be done to improve our chances of answering those questions? One of the most intriguing possibilities is that a reliable technique to determine ages could be developed. We present discussions of four techniques that show varying degrees of promise, though none of the four has yet been developed sufficiently. In addition, we consider some instrumental requirements, those of precision, miniaturization, and survivability. Finally, we present some ideas about sample selection that need to be considered in any development effort.

### 3.4.1. Ages

One of the greatest scientific accomplishments of the Apollo program was to turn the study of the Moon's chronology into a quantitative discussion. Although geochemical clues to the Moon's evolution were available in the data from the Surveyors, ages were only determined because samples were returned. Nearly 30 years later, there is still not a single reasonably well determined absolute age from an *in situ* spacecraft measurement, and chronology is one of the chief justifications in arguments for sample return missions (*Drake et al.,* 1987). Given the importance of ages, we will discuss several potential techniques for determining ages with *in situ* instruments. In particular, we will set out the analytical precisions required for any of these techniques to work, as well as the interpretational problems that can be foreseen.

Radiometric dating methods are most powerful when the analyst can divide a sample into subsamples with the different ratios of the radioactive parent isotope to its daughter (*Faure,* 1986). If the parent and daughter elements share a common origin or equilibration time, parent/daughter abundances and ratios for these subsamples will be systematically related and

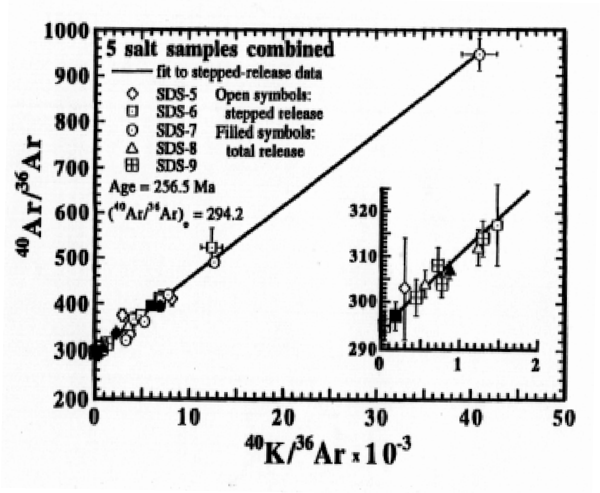

**Fig. 3.7.** Isochron diagram of $^{40}Ar/^{36}Ar$ vs. $^{40}K/^{36}Ar$ determined by K-Ar analysis with stepped dissolution of bedded salts (mainly halite) from the Permian Palo Duro Basin, Texas. Data points represent the Ar and K released by individual dissolution steps; numbers adjacent to the data points give the sequence of dissolution. The age is related to the slope of the isochron, and agrees reasonably well with the stratigraphic age of 266 Ma. The intercept gives the isotopic composition of trapped atmospheric argon. Data from *Wampler and Weaver* (1987).

form an isochron (Fig. 3.7), which defines the age of origin or equilibration. Thus, mineral separates from a single rock sample (i.e., portions of a rock prepared by physical separation of material) or multiple whole-rock samples from a cogenetic suite are commonly used in Rb-Sr, Sm-Nd, U-Pb, and other dating methods. Similarly, $^{40}Ar/^{39}Ar$ dating with stepped heating separates phases by their thermal stability, effectively yielding internal isochrons for rock samples. Potassium-argon dating with stepped dissolution (*Wampler and Weaver,* 1987) provides a similar separation by stability against chemical dissolution.

*Potassium and argon extraction by dissolution.* The chief benefit of K-Ar dating by stepped dissolution, if eventually applied to *in situ* dating of martian or other extraterrestrial samples, is that subsampling and extraction of K and Ar and can be done under ambient conditions with little expenditure of energy (grinding, heating, etc.). Unlike $^{40}Ar/^{39}Ar$ dating, stepped dissolution does not require neutron activation or gas release by heating; unlike some other methods, such as Rb-Sr mineral isochron dating, K-Ar dating with stepped dissolution does not require a mechanical or manual separation of mineral grains. Dissolution also allows all the major soluble components of a sample (the very components that give up their K and radiogenic Ar) to be analyzed; in general this is not possible with incremental release by heating.

In principle, the stepped-dissolution release method is applicable to almost any kind of rock. In practice, it works best for phases that are easily dissolved. Thus, it is most likely to be useful for dating evaporites, salty soil samples (e.g., martian soil), and partly weathered rocks. Analysis of salts (in evaporites and soils) and alteration products in igneous rocks may be the most direct means by which to obtain important constraints on the chronology of hypothesized warm, wet epochs on Mars. Analysis of weathered igneous rocks, whether actually desired or not, may be unavoidable if we are to isotopically date volcanic rocks *in situ* on another planet, because it might prove to be very difficult to obtain unweathered material. Stepped dissolution provides a means to obtain information on the age of alteration (or some type of average age if it was a long drawn out process or occurred in multiple episodes) and the original crystallization age if a large amount of the rock's K is still sited in original unaltered remnants of the rock.

Good isochrons obtained by K-Ar analysis with stepped dissolution of terrestrial evaporitic halite from the Permian Palo Duro Basin has shown that this method can yield accurate results for salts that have been undatable by other radiometric techniques (Fig. 3.7; *Wampler and Weaver,* 1987; *Wampler and Hassanipak,* 1986, 1988). Uranium-lead age determinations using slow-stepped dissolution of zircons in concentrated HF acid have recently produced age information of higher quality than the results of the usual single-release method applied to zircons from the same rock (*Mattinson,* 1994). Potassium-argon dating with stepped dissolution seems ideally applicable to the types of rocks and minerals that were formed by precipitation from aqueous solutions, because the laboratory dissolution would provide a crude reversal of the formation processes, unlike methods that achieve decomposition by heating.

However, interpreting remotely measured K-Ar age data will be fraught with uncertainty. If the primary emphasis is placed on knowing the time of igneous activity on planetary bodies, the K-Ar method has been only partly successful. For lunar samples, its greatest successes have been for mare basalts extruded after the large impacts that formed the major basins on the lunar surface, and in dating the times when the basins formed. Potassium-argon dates of prebasin lunar crustal rocks are often influenced by impact-related Ar outgassing, and apparently crustal rocks from Vesta (eucrite meteorites) are also so influenced (*Bogard,* 1995). Finally, the presence of trapped Ar in shergottites has helped to confuse the interpretation of the ages of these meteorites of putative martian origin. If this is true of rocks that petrographically appear to be good igneous basalts, the problems attendant to interpreting the time of formation of martian evaporites and sedimentary rocks must be anticipated. These problems will be exacerbated by the high $^{40}Ar/^{36}Ar$ ratio in the martian atmosphere, which will increase the difficulty of detecting trapped atmospheric Ar when it occurs.

*Rubidium-strontium.* As discussed above, stepped dissolution has some attractions as a sample extraction method for K-Ar age determinations and could also be useful for Rb-Sr dating. Transfer of dissolved Rb and Sr from solution to ions, whether by thermal ionization, laser ionization, or whatever, could present problems, but has not been studied in detail. Assuming that transfer is possible, what might we learn by applying Rb-Sr dating to dissolution step fractions?

Consider first the analysis of bulk samples. Assuming that we are able to determine both the isotopic ratio $^{87}Sr/^{86}Sr$ and the elemental ratio $^{87}Rb/^{86}Sr$ to "good" precision, what might we learn, and how good would "good" have to be?

The most unambiguous case would occur for rocks of very low Rb/Sr, as might be seen in plagioclase-rich crust like that of the Moon. If multiple sampling and analyses are possible, such a crust would probably yield individual samples of quite low Rb/Sr. For such a rock, $^{87}Rb/^{86}Sr$ values near BABI would suggest a very ancient crust, while higher values would imply late crust formation and complex petrogenetic processes that produced reservoirs enriched in Rb relative to Sr compared to the bulk planet (e.g., the Earth's crust). To make these inferences, however, $^{87}Sr/^{86}Sr$ values would need to be measured to better than 1%, preferably better than 0.1% (see Table 3.4).

Another favorable case is from samples with Rb/Sr ratios that are much higher than Rb/Sr in the bulk planet, e.g., rocks of granitic composition. These samples would also have high concentrations of K, and thus could be detected from orbit by their high natural radioactivity. Although areas of planetary surfaces with granitic compositions might be quite limited, determining the ages of such areas, in a geological context, could be important for calibrating methods that determine relative age, such as crater count ages.

The ages here are Rb-Sr model ages, calculated from measured $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ of bulk samples, and an assumed value of initial $^{87}Sr/^{86}Sr$ ratio, usually BABI. Among the returned lunar samples, there are some instances in which Rb-Sr model ages are close approximations to igneous ages (Table 3.4). As seen from Table 3.4, comparison between the model and crystallization ages can be rather good if one is willing to accept age uncertainties (errors) of as much as ±20%, with the rationale that an uncertain age is better than no age at all. To achieve this level of uncertainty, $^{87}Sr/^{86}Sr$ must be measured to ~0.1%; for granitic samples, 1% uncertainty would yield reasonable precision on the age. However, this good agreement is to some extent a misleading consequence of the antiquity of all lunar samples, since the "default value" for a Rb-Sr model age is 4.55 Ga. Nevertheless, model ages would imply that the Moon's surface is in general quite "old." The data needed for a model age contains information that can be used for "quality control." That is, when the $^{87}Rb/^{86}Sr$ ratio of a sample is much higher than average, the model age gives a good to excellent approximation to the crystallization age (e.g., granite and KREEP in Table 3.4).

TABLE 3.4. Rb-Sr model ages compared to crystallization ages for lunar surface samples.

| Landing Site | Rock Type | Sr (ppm) | $^{87}Rb/^{86}Sr$ | $\varepsilon_{BABI}$* | Model Age | Cryst. Age | Error (%) |
|---|---|---|---|---|---|---|---|
| *Apollo 11* | Soil | 165 | 0.0461 | 46.2 | 4.56 | | |
| | Hi-K basalt | 165 | 0.0938 | 73.1 | 3.8 | 3.59 | 6% |
| | Lo-K basalt | 180 | 0.0098 | 9.2 | 4.52 | 3.71 | 22% |
| *Apollo 12* | Soil | 127 | 0.144 | 129.5 | 4.37 | | |
| | Basalt | 116 | 0.0283 | 16 | 4.42 | 3.3 | 34% |
| | Granite | 114 | 1.368 | 1242 | 4.42 | 3.99 | 11% |
| *Apollo 14* | Soil | 182 | 0.233 | 217 | 4.54 | | |
| | KREEP | 192 | 0.1824 | 164 | 4.37 | 3.87 | 13% |
| | Granite | 64 | 7.54 | 6340 | 4.11 | 4.13 | 0 |
| *Apollo 15* | Soil | 130 | 0.127 | 119 | 4.59 | | |
| | Basalt | 74 | 0.021 | 15 | 4 | 3.3 | 21% |
| | KREEP | 187 | 0.285 | 249 | 4.25 | 3.94 | 8% |
| *Apollo 16* | Soil | 170 | 0.0447 | 45 | 4.9 | | |
| | Basalt | 180 | 0.0294 | 26 | 4.29 | 3.84 | 12% |
| | KREEP | 162 | 0.163 | 150 | 4.48 | 3.93 | 14% |
| *Apollo 17* | Soil | 168 | 0.0256 | 168 | 4.84 | | |
| | Basalt | 181 | 0.0083 | 10 | 5.5 | 3.82 | 44% |
| | KREEP | 89 | 0.0238 | 210 | 4.32 | 4.07 | 6% |

*Enrichment of $^{87}Sr/^{86}Sr$ in ε units (0.01%) relative to lunar initial $^{87}Sr/^{86}Sr = 0.69898$.

The relatively good agreement between lunar Rb-Sr model ages and crystallization ages cannot be obtained for all planetary samples, for instance the "martian meteorites" (Table 3.5). For the shergottite subgroup of martian meteorites, Rb-Sr model and crystallization ages are distinctly different. This difference could be discounted, however, if the ~180-Ma "crystallization ages" for the shergottites instead reflect impact melting. It should be noted that the current consensus is that the ~180-Ma ages truly reflect igneous crystallization (*McSween,* 1994). For the rest of the martian meteorites, agreement between model and crystallization ages is much better. In this connection it should be pointed out that martian granites are not represented in Table 3.5. A landing strategy that targeted granitic surface areas as identified from orbit could result in instrument placement in a region where at least some of the local rocks would have Rb-Sr model ages that were good approximations of their crystallization ages. Further, it is reasonable to consider whether ages might also be determined by the K-Ca method. The K-Ca method is completely analogous to the Rb-Sr method, and again works best for high K/Ca materials, e.g., granite. However, K-Ca dating requires much higher precision of measurement than does Rb-Sr dating, so K-Ca is unlikely to be useful for landed surface missions. In the lunar granite with an enhancement

TABLE 3.5. Rb-Sr model ages compared to crystallization ages for martian meteors.

| Meteorite | Rock Type | Sr (ppm) | $^{87}Rb/^{86}Sr$ | $\varepsilon_{BABI}$* | Model Age | Cryst. Age | Error |
|---|---|---|---|---|---|---|---|
| Shergotty | Basalt | 51 | 0.397 | 352 | 4.33 | 0.165 | 2500% |
| Zagami | Basalt | 43 | 0.376 | 335 | 4.35 | 0.18 | 2300% |
| EET 79001 | Basalt | 67 | 0.203 | 200 | 4.77 | 0.178 | 2600% |
| ALH 77005 | Lherzolite | 13 | 0.172 | 169 | 4.77 | 0.187 | 2450% |
| Nakhla | Clinopyroxene | 37 | 0.123 | 89 | 3.54 | 1.31 | 169% |
| ALH 84001 | Orthopyroxene | 4 | 0.367 | 360 | 4.77 | 4.50 | 6% |

*Enrichment of $^{87}Sr/^{86}Sr$ in ε units (0.01%) relative to lunar initial $^{87}Sr/^{86}Sr = 0.69898$.

of the $^{87}$Sr/$^{86}$Sr ratio of 63% (6300 ε units, Table 3.4), the enhancement of the $^{40}$Ca/$^{44}$Ca ratio is only 0.5%, or 49 ε units.

*Uranium-thorium-lead.* The U-Th-Pb method of radiometric age determination has received little consideration for use with a landed planetary instrument; the technique as used in terrestrial laboratories employs either extensive chemical preparation of samples or large, high-resolution, ion microprobes with which U-rich phases such as (rare) zircons can be analyzed *in situ*. Recent developments in laser and mass spectrometry technology make it feasible to consider at least the requirements that a laser-based instrument would have to meet in order to yield useful data. The U-Pb data summarized in Table 3.6 for representative extraterrestrial samples are intended to convey the scope of the requirements for such an instrument without being exhaustive in regard to the extraterrestrial sample database.

The U-Pb isotopic system has a well-known advantage relative to other methods of age determination in that model ages can be determined from measurement of the isotopic ratio $^{207}$Pb/$^{206}$Pb alone. The utility of the Pb-Pb model ages is limited by the fact that the initial Pb isotopic composition in the sample in question must be known. Thus, Pb-Pb model ages have found greatest applicability among ancient meteorite samples for which it is reasonable to assume that the initial Pb isotopic composition was the same for each sample and equal to the initial value for Pb in the early solar system as determined from laboratory measurements on meteoritic samples with very low U/Pb ratios. Beyond the zeroth order determination of model ages in the range of ~4.55 Ga for primitive meteorites, the Pb-Pb model ages have found application for ordering the formation ages of the meteorites in a fine-scaled chronology. The latter requires a precision of measurement of the $^{207}$Pb/$^{206}$Pb ratio of ~0.1%, a value that probably will be difficult to achieve in a remotely operated planetary instrument. However, such a value might be set as a goal for instrument development. A further goal might be to achieve this level of precision for samples of relatively undifferentiated solar system material, represented by the Orgueil carbonaceous (CI) chondrite in Table 3.6.

TABLE 3.6. Representative U-Pb data for extraterrestrial samples.

| Body | Sample | Type | $^{238}$U (ppb) | $^{204}$Pb (ppb) | $^{206}$Pb (ppb) | Total Pb (ppb) | $^{207}$Pb/$^{206}$Pb | Refs. |
|---|---|---|---|---|---|---|---|---|
| Undiff. asteroids | Orgueil | Cl | 8 | 48 | 450 | 2434 | 0.595 | [1] |
| Eucrite parent | Ibitira | Basalt | 102 | 0.15 | 93 | 318 | 0.628 | [2] |
| Angrite parent | ADOR | Magmatic | 163 | 0.24 | 151 | 368 | 0.616 | [3] |
| Mars | Shergotty | Basalt | 120 | 6 | 88 | 387 | 0.921 | [4] |
| Moon | 15555 | Lo-Ti basalt | 144 | 0.16 | 98 | 238 | 0.405 | [5] |
| | 75055 | Hi-Ti basalt | 157 | 0.29 | 137 | 342 | 0.577 | [5] |
| | 60025 | Fer. anorth. | 1.8 | 0.05 | 2.1 | 6.7 | 0.718 | [6] |
| | 14310 | KREEP | 3110 | 1.65 | 2475 | 6122 | 0.494 | [7] |
| | 12013 | Granite | 5750 | 3.3 | 4690 | 11430 | 0.534 | [8] |

References: [1] *Tatsumoto et al.* (1976); [2] *Chen and Wasserburg* (1985); [3] *Wasserburg et al.* (1977); [4] *Chen and Wasserburg* (1993); [5] *Tera and Wasserburg* (1974); [6] *Hanan and Tilton* (1987); [7] *Tera and Wasserburg* (1972); [8] *Tatsumoto* (1970).

As an aid to potential instrument developers, Table 3.6 gives typical values of the abundances of $^{238}$U, $^{204}$Pb, and $^{206}$Pb in the samples chosen as representative of different types of "planetary" bodies. Knowledge of the $^{204}$Pb abundances in samples is necessary to correct the measured $^{207}$Pb/$^{206}$Pb ratios for nonradiogenic initial Pb, required even for the Pb-Pb model ages. Determination of the $^{238}$U abundance as well would be very important because it would allow determination of ages using the U-Pb concordia diagram, making the ages so derived much more rigorous. Although Pb isotopic measurements of sufficiently high precision are useful alone for samples of ancient asteroids (and comets?), represented by the first three entries in Table 3.6, useful data for samples of larger planetary bodies such as Mars and the Moon will in general require measurement of U abundances as well. The data in the table imply that precision at least at the percent level for $^{207}$Pb/$^{206}$Pb is required for samples in which the $^{206}$Pb abundances are at the ~100-ppb level. Samples with very low U and Pb abundances, such as lunar crustal anorthosites, will provide the greatest challenge, whereas once again, granitic samples present the most easily achievable target goals. The Pb-Pb model ages of granitic sample 12013 (or at least the granitic portion thereof) are ~3.9–4.0 Ga, the age generally accepted as the crystallization age of this sample.The lunar granite data represent characteristics of U-Pb data necessary to obtain valid crystallization ages from Pb-Pb ages: high relative abundances of both U and Pb. These characteristics may be met by mineral phases within planetary samples, as well as by rocks on planetary surfaces. An *in situ* analysis capability, as might be provided by a sharply focused laser beam, plus a sample scanning capability, would be highly desirable. A spot size on the order of 30 mm seems a good goal, with better focusing capability desirable, and worse focusing capability up to ~100 mm being useful for analyzing individual mineral grains. If such a capability could be achieved, finding and analyzing a high-U phase would be like "hitting the jackpot," whereas simply analyzing two major mineral phases in a single rock would be a significant augmentation of information compared to a "bulk" analysis of the same rock, provided U abundances could be measured as well as Pb. In the latter case, the possibility would exist for determining an isochron on a concordia diagram, and thus a much more rigorous age measurement than otherwise would be the case. The desirability for such a capability is represented by the data for KREEP "basalt" 14310. (Sample 14310 may actually be an impact melt rock of basaltic composition.) Although the bulk U and Pb data for 14310 appear very similar to those for 12013, the Pb-Pb model age of 14310, ~4.28 Ga, is significantly higher than its 3.88-Ga crystallization age. This is because the initial Pb present in this rock had a composition that was significantly more radiogenic than that of "primordial" Pb, used in correcting the measured Pb composition for a nonradiogenic component. Whether or not a ±10% error in age would significantly affect interpretations of planetary evolution based on the age data would depend on the geological context of the sample being analyzed. In any event, analysis of both U and Pb in at least two mineral phases of a sample such as 14310 would be necessary to detect the presence of radiogenic initial Pb.

The above considerations applied to 14310 apply even more forcefully to samples of lower U and Pb concentrations. In particular, this is true of the "martian meteorites." Perhaps because we have no granitic martian meteorites, there are no examples that can be cited for which young Pb-Pb ages can be considered good approximations to the crystallization ages of the samples in question. The Pb-Pb ages of shergottites, for example, are ~4.5 Ga, but the crystallization ages are ~180 Ma. Proper interpretation of the U-Pb data for martian meteorites requires analyses of multiple mineral phases for both U and Pb and interpretation within the framework of the U-Pb concordia diagram.

*Cosmic-ray exposure ages.* Planetary surfaces exposed to galactic cosmic radiation can be expected to contain products of nuclear reactions as a result of spallation reactions on major elements. This occurs primarily at ~50 cm depth. If the surface material remains undisturbed to this depth, then the age of exposure of the surface can be determined from the production rate of the products. Spallation reactions on a given target element generally produce many different products in roughly equal amounts. In practice, measurements of the three isotopes $^{3}$He, $^{21}$Ne, and $^{38}$Ar, normally the least-common isotopes of the three lightest noble gases, have commonly been used to determine exposure ages. Production rates for these isotopes have been determined from target studies in particle accelerators and nuclear reactors. The production rates, which are dependent on the chemistry and geometry of individual target objects, are typically of the order of 1 atom per gram per minute. The accumulation would then be $10^{-11}$ g (or, in the terminology used in noble gas studies, $10^{-8}$ cm$^{3}$ STP) per gram per $10^{6}$ yr. Other, "trapped," components for these isotopes must be separated and subtracted from the measured amounts. At $^{3}$He and $^{38}$Ar, the trapped component sometimes dominates in meteorites and often dominates in lunar samples, leaving $^{21}$Ne as the most reliable noble gas isotope for cosmic-ray exposure age determination. Still, precise isotopic measurements, preferably of $^{21}$Ne/$^{22}$Ne and $^{21}$Ne/$^{20}$Ne, are required for separation of the cosmic-ray-produced $^{21}$Ne from the trapped component.

The validity of the age depends not only on an accurate measurement of the composition and an accurate assessment of the production rate, but also on the assumption that the material has resided undisturbed within a restricted depth for the period of exposure. The lunar surface presents an example of a planetary regolith that has been extensively comminuted to depths greater than 1 m for a few billion years. For this reason, "ages" calculated from the total amount of cosmic-ray-produced $^{21}$Ne in Apollo regolith samples are regarded with caution and sometimes as meaningless. Only well-documented geologic settings allow for age interpretation (*Walton et al.,* 1973). At the martian surface, accumulation of stable cosmic-ray-produced isotopes in solidified lava flows may indeed be useful for assessing the age of the flows. The challenge would be for remote geologic sampling and accurate (1–5% precision) measurement of quantities necessary for determination of the cosmic-ray contribution to the least abundant isotope of Ne, $^{21}$Ne.

*The importance of multiple ages and petrographic context.* It is not obvious that any of the techniques discussed can actually provide ages meaningful enough to address any of the important questions of planetary evolution and history. Even beyond the analytical difficulties of making the measurements (and few, if any, of the required measurements could be made with the required precision using present technology) and the engineering difficulties of acquiring the right samples, it is often not certain that the "age" obtained is really that of the event of interest. The cosmic-ray exposure ages of the lunar regolith provide one example. The spurious ages of terrestrial salts caused by natural dissolution provide another. The high model U-Pb and Rb-Sr ages of most samples other than granites are yet another. And terrestrial geochronologists are hesitant to accept any age determination based on minerals as poorly characterized as would occur for an *in situ* measurement of U-Pb systematics.

Experience has shown that, in general, radiometric ages can be interpreted with confidence only when concordant ages are measured by two or more techniques, and when interpretation can be made within a known petrographic context. It is still true that by far the best response to these conditions can be made for samples returned to terrestrial laboratories for analysis. If *in situ* analysis is going to be attempted, consideration should be given to the possibility for remote age determinations by more than one method. Finally, if only one method is available, sampling strategies must be considered that maximize the probability of detecting geologically based biases in remotely determined ages.

### 3.4.2. Improving the Performance of Instruments

A goal for composition analyzer flight instrument development is to approach as closely as possible with *in situ* measurements the analysis precision now possible only with laboratory instrumentation, and to do so with instruments that are compact, low-mass, and reliable.

*Measurement precision.* For gas analyzers, improvements in traditional techniques (magnetic sector mass analyzers, quadrupole mass analyzers, time-of-flight mass analyzers, ion traps, etc.) are being pursued by a number of groups, and significant advances are possible. The elemental and isotopic composition of solids is measured through sputtering or ablating surface material into a similar range of types of high-precision mass analyzers. To the extent that future small flight instruments will be able to provide precise isotopic measurements at all masses, they will be important contributors to mission science.

*COMPLEX* (1994, p. 123) recommended measuring H, C, N, O, and the noble gases in atmospheres to a minimum accuracy of 10%, and the D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{18}O/^{16}O$ ratios to an accuracy of 1%. These are adequate general guidelines for evolved gases as well as atmospheres, although they might not be sufficient for specific objects. The science questions discussed above for Mars can serve as an example. Viking mass spectrometers measured the abundances and isotopic ratios of the atmospheric constituents on Mars to precisions of 5–50%. The isotopic composition of H and O in water, if known to 1%, would be useful in understanding the current interaction of the atmosphere and surface, and similar benefits would accrue from 1% level C measurements. $^{38}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ ratios would help identify the origin of SNC meteorites as being from Mars, even if measured at 10% levels, but a precision of 1–5% (particularly for $^{38}Ar/^{36}Ar$) would be far better. One of the best tests of the martian origin of SNC meteorites would be from measuring the relative abundances of all three O isotopes, but only if the measurement could be done to a precision of better than 0.1%. Measurement of the $^{20}Ne/^{21}Ne/^{22}Ne$ to a precision of better than 5% would be required to determine cosmic-ray exposure ages. Such measurements (and others such as $^{15}N/^{14}N$, $^{26}Mg/^{25}Mg/^{24}Mg$, etc.) have been made to a much lesser extent for Mars surface materials and for asteroids and comets than they have been for the martian atmosphere. There are many missions in which significant advances can be made with lower-precision isotopic measurements. In addition, comparison of composition over a range of samples (different samples on Mars, different individual comet grains, comet nucleus samples from different depths, diverse asteroid samples, etc.) could show significant and important variations.

Problems encountered in refining the precision of isotopic ratio measurements include overlapping mass numbers of different molecules—mass doublets, e.g., CO and $N_2$ at 28 dalton, and hydrogenated molecules and the heavier isotope mass number, e.g., $^{12}CH$ and $^{13}C$ at 13, or $H_2{}^{16}O$ and $^{18}O$ at 18. To overcome this problem, it would be necessary to have mass resolutions of ~3000 to analyze CO (27.9949) and $N_2$ (28.0061) separately, ~30,000 to analyze $^{40}Ar$ (39.9624) and $^{40}K$ (39.9640) separately, and >500 for the hydrocarbons. The Pioneer Venus Large Probe mass spectrometer did have a resolving power of nearly 500. It might be possible to reach 30,000 in future instrumentation (e.g., ion traps, reflectron time-of-flight analyzers, etc.). To the extent that one of the molecules in the mass doublet is produced by fragmentation of a parent molecule during ionization in the instrument, a possible improvement is to use low electron energy to produce the ions without fragmentation. Ionization efficiency decreases markedly when the electron energy is less than 25 eV, but with enough gas pressure in the ion source, this method becomes feasible. Selective gettering of one species of a mass doublet may also help alleviate the problem in some cases.

For measurements of solids, techniques such as pulsed laser ablation at relatively high energy density can be used to convert surface compounds into their elemental constituents, avoiding many (but probably not all) of the problems of overlapping molecules and isotopes. This technique is well matched to time-of-flight analysis of the resulting ions.

*Dynamic range.* There are many factors in an instrument that affect the dynamic range or range of true signals that can be measured. In any mass spectrometer it is not only the full-width (FW) at half-maximum (HM) that determines useful resolution, but the FW at tenth or even hundredth maximum. With broad wings, two mass peaks one atomic mass unit (u) apart will not be resolved if the intensity of one is $10^4$, say, that of the other. Isotopic ratios this large are not uncommon (see Fig 3.1).

In a quadrupole mass spectrometer, factors that broaden the wings of a peak are fringing at the quadrupole entrance aperture and large acceptance angle. Some relief is usually gained by using a small aperture relative to the "kissing circle" diameter of the poles, but this results in a loss of signal intensity. Other solutions, such as a tube protruding into the quadrupole region or a field-matching entrance cylinder, are used. In the ion trap, dynamic range is also affected by the sheer ion capacity of the trap. If a miniature trap can only hold $10^3$ ions (above which Coulomb collisions cause resolution loss), then frequent fill-sample-dump cycles must be used to measure ion intensities in a ratio of $10^{-4}$ or less. Duty cycle and efficiency of trapping ions in the well then become important. Larger traps, of course, can hold more ions (order of $10^6$) so the problem is less severe. In a Wien filter, beam shear due to the varying energy of the ions across the input ion-beam diameter (caused by the electric field across the plates) smears the output mass spectrum, causing overlapping wings. Small beam diameters are a solution, but signals will again be reduced. In a magnetic sector uniformity of field, magnetic-field fringing at the entrance slit and large input angles will again cause wings.

Occasionally one finds a limit to the dynamic range by a "double-bind" situation. If one is measuring small ion currents on a metal strip, for example, the limit of lower intensities may be electrometer sensitivity or competition from a spurious background (photons, electrons, sputtered or desorbed ions, etc.). The limit of higher intensities (gained by increasing gas pressure or electron-ionizer current) may be ionizer-filament lifetime, detector lifetime, arcing limit of the detector high-voltage, or Paschen breakdown in the ionizer, mass-analyzer, and/or detector.

*Instrument miniaturization and compatibility.* A corollary to NASA's new mantra of "faster, better, cheaper" is "smaller, lighter, lower power." The future appears to include miniaturization of many types of mass, energy, and velocity analyzers, without sacrificing important parameters such as mass range, resolution, rejection (spectral wings), dynamic range, and sensitivity. Proper dimensional and voltage scaling must be followed, and the use of many *parallel arrays* of instruments, miniaturized or micromachined, can compensate for the reduced input-aperture area (*Boumsellek et al.*, 1993). Quadrupoles (*Boumsellek et al.*, unpublished data), ion traps (*Hoffman et al.*, unpublished data), and a "mass spectrometer on a chip" (a Wien filter with an extended metal-strip ion collector at the output plane; *Freidhoff et al.*, unpublished data) of dimensions of tens of millimeters have been made to work in several laboratories. A small magnetic sector is also under construction (*Sinha et al.*, unpublished data). Miniaturization (shortening) of time-of-flight or reflectron instruments depends upon fast (subnanosecond) pulsing circuitry and low capacitances and inductances in the flight instrument. Even smaller (0.1–2 mm dimensionality) analyzers are being designed and developed. One approach uses the LIGA method to achieve submillimeter dimensions, retain the often-needed 0.1% dimensional tolerances (amounting to 1 mm in 1000 mm), and provide mass-production capabilities.

In order to "match" system dimensions one must also shrink such items as gas-chromatographic columns, ionizers, detectors, and vacuum pumps. Little work is being done in the last regard, although small turbopumps (7.5 l/s) have recently become commercially available (Alcatel Vaccum Products, Hingham, Massachusetts).

Another less obvious benefit in miniaturization is that the requirement that the particle mean free path be smaller than instrument dimensions implies that shorter mean free paths (higher operating pressures) can be tolerated in the smaller devices. Operating at millitorr or higher pressures means that pumping requirements can be relaxed. However, matching ionizers and detectors must now be capable of emitting and detecting at the higher pressures.

*Survivability*. An obvious requirement for any instrument to be effective is that it survive long enough to make a sufficient number of measurements. Without meaning to belabor the point, we mention some general problems of survivability, and some problems specific to mass spectrometers and lasers.

General: The extremes of planetary surface temperatures, from a few tens to several hundred degrees Kelvin, will limit the performance and the survival of most electronic instrumentation, including mass spectrometers and lasers. Most "hi-rel" (high reliability) electronic components are designed to survive up to 125°C, but printed circuit cards may become unreliable at that temperature, particularly if they are cycled between extremes, as would happen on a body with no substantial atmosphere. Thermal expansion between the printed wire traces and the boards can cause separation and potential failure.

Dust could also be a hazard in many places, ranging from active comets to the lunar terminator to martian dust storms. Dust is an especially serious hazard for any optical device, such as a laser. Venus might be one of the few places where dust would not be a problem, but its hot, heavy, and corrosive atmosphere has always presented one of the greatest challenges to *in situ* instruments, although several have now been successfully landed.

Mass spectrometers: Gas pressure in the range of 1 torr to $10^{-2}$ torr can cause problems with high voltages. Corona discharges and acing can occur in this pressure region, the problem being exacerbated with increasing voltage. $CO_2$ has a lower breakdown voltage than $N_2$ or $O_2$, so the problem becomes worse on Mars. It is best to contain high voltages either in a reasonable vacuum ($<10^{-4}$ torr) or near Earth's atmospheric pressure.

Laser extraction systems: The environmental pressure may also influence the performance and survival of lasers. Beams should "zap" targets under near-vacuum conditions to distinguish products from the ambient atmosphere. High environmental pressures would require a pumping system for the extraction chamber and the optical path of the laser. Natural UHV environments, such as the Moon or an asteroid, pose no such problem. Gas lasers, in the vacuum of some planetary surface environments, must have vacuum seals capable of preventing performance- and survival-limiting leaks from occurring.

### 3.4.3. Sample Selection and Preparation Issues

Gaining answers to many driving scientific questions depends critically on selecting proper samples for analysis and preparing them correctly. Here we give a brief discussion of some of the issues involved. Of course, some questions don't require careful sample selection: To the extent that a body's atmosphere is in equilibrium, atmospheric measurements from any location carry global information. However, evolved gas analyses and, to an even greater extent, age analyses depend critically on sample considerations.

*Sample selection.* Sample site selection is one of the most crucial aspects of any effort to derive knowledge of a planet's history from its rocks. Each planet or satellite has a unique geology and history, so scientific objectives and site selection criterion will be different for each planetary object. Engineering aspects can seriously constrain target selection, as clearly was the case during the Viking and Mars Pathfinder landing site selection processes. Can the spacecraft deal with a landing on what might be a bouldery volcanic lava flow? Can it reach the poles? Can it survive far from the subsolar latitude? These considerations, in turn, constrain the science that can be done.

If we assume that engineering is not an issue (i.e., one can place a lander where interesting rocks are to be found), the optimum site depends on the scientific objective(s) of the mission. At the lowest level of consideration, this is obvious. For example, if one is interested in obtaining the isotopic age of a volcanic rock, one normally has to go to a volcanic terrain, whereas if one is interested in obtaining the stable isotopic composition of precipitated ices, the polar caps would be the place to go. Commonly, there are several scientific objectives of a mission and tradeoffs are necessary, since some objectives may be difficult to attain simultaneously. For instance, there are no morphologically fresh unambiguous volcanic deposits in immediate environs of the residual polar ice caps on Mars, so a mission with multiple goals of studying polar ices and volcanic rocks would require considerable mobility.

Furthermore, the site selected must contain rocks that can be used to make the required measurements. Many isotopic studies, particularly radiometric dating studies, require *optimal* sampling, and thus a sampling strategy based on considerable prior knowledge. This sampling strategy may dictate mission strategy and even mission sequencing. All radiometric age determination methods depend on the presence of natural radioactivities. The greater the abundance of the natural radioactivities in a given sample, the easier the task of the geochronologist, and the lower the demands on analytical techniques and equipment. Thus, if the highest-priority scientific goal is to determine the radiometric ages of one or more geologic provinces to absolutely calibrate cratering rates on a given planetary body, for example, then one or more areas having the highest levels of natural radioactivity, but meeting the geological criteria, could be selected on the basis of orbital measurements of $\gamma$-ray activity. After landing in an area, there should be some way to select the rocks with the appropriate chemistry (rich in the element of interest) and genesis.

There are additional considerations. For example, a calibration of the cratering rate curve through geologic time on any planet would be difficult with only a single sample. At best, it would be possible to determine one point on the curve (although if that point were judiciously selected it could still be scientifically quite significant). Similarly, the experience analyzing Apollo cores showed that variations in volatile contents in a single core are dominated by local stratigraphy, and the same may be true of cores of polar deposits. Determining isotopic shifts from weathering interactions (e.g., on Mars or Venus) or transport processes (polar volatile deposits of Mercury and perhaps the Moon) is a less daunting task than determining ages. However, it still requires fairly precise measurements and careful selection of rock samples that might show the desired effect.

In some cases it might be possible to gain both global and local information from a single site, if it is possible to find exposed bedrock and globally distributed soil at the same site. This might be especially useful if the ubiquitous martian dust consists of minerals that were formed by hydrogeologic activity and then redistributed by eolian processes that would not disturb isotopic signatures. Similarly, samples of regoliths on small asteroids may be something approaching global, but for some problems (such as surface exposure dating) analyses would be most useful if accompanied by analysis of bedrock.

*Sample preparation.* Sample preparation will have to be a consideration for any analysis of gas extracted from solids (i.e., evolved gas), no matter what technique is used. For example, in the lunar regolith, volatiles are concentrated in a thin (>1 mm) shell at the outer edges of grains, and hence might be susceptible to loss by abrasion. Thus, any experiment on lunar volatiles would have to be careful to neither destroy nor contaminate the surfaces of grains. Weathering products on Venus or Mars, or volatiles in the regolith of an asteroid, would also be expected to be concentrated near surfaces.

One of the key advantages terrestrial chronology studies have over robotic *in situ* measurements is the terrestrial analyst's ability to select subsamples by their mineralogy. One might conceive of a robotic mechanism scheme to perform mineral separations *in situ*, or at least to grind or crush a sample until a vision system could detect mineral enhancements. But the price of such a scheme would be not only complexity, but also weight and hence expense; thus it seems unlikely that any processing-intensive technique will be worth considering. Simpler strategies, such a tools to chip or dust off samples to expose a fresh surface, are more likely to be feasible.

## 3.5. SUMMARY

### 3.5.1. Atmospheric Composition

Mass spectrometers have successfully analyzed several atmospheres, but, as is usually the case in science, have generated as many questions as they have answered. To make further progress, mass analyzers need to be more precise than their predecessors. The *COMPLEX* (1994) goal of 10% precision for the all the noble gases, H, C, O, and N, and 1% precision for the isotopes of H, C, N, and O, is a reasonable target. In addition, these higher-performance mass analyzers need to be miniaturized to a level that will fit on the smaller spacecraft to be expected in coming years.

### 3.5.2. Evolved Gases

Some version of evolved gas analysis, usually involving some volatile element, is a priority at virtually every conceivable target. Little has been done with evolved gases to date, so it seems almost inevitable that any successful measurement will produce interesting science. Analysis of elements or compounds may not need to be of high precision to be useful. However, since the isotopic shifts expected are often much smaller than the difference between atmospheres, it seems prudent to try to detect isotopic ratios with at least the precision recommended for future atmospheric studies.

### 3.5.3. Ages

Several working groups have identified the determination of radiometric ages as among the highest-priority objectives. To determine ages to 10% precision (sufficient to answer current questions for every body except the Moon) would require an uncertainty of less than 10% of the expected shift in the isotopic ratio being measured. From Tables 3.4, 3.5, and 3.6, it can be seen that while 1% measurement precision will suffice in a few cases, precision of 0.1% or better is more commonly needed. If there is an underlying assumption that radiometric ages will be determined remotely on a representative sampling of a given landing site, we consider such aspirations unrealistic. If, however, the goal is one of determining one or a few ages on an optimal sampling of material, we believe the odds of success improve dramatically. Several possible radiometric (and cosmic-ray-based) techniques have been discussed above. A solicitation of interest may well turn up other candidates, after which a funding program could be developed to pursue two or three of the most promising ideas. The alternative, which in many cases demands less extrapolation of technology, is to use *in situ* missions for characterization, and attempt to develop inexpensive sample return missions for detailed chronologic studies.

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# 4: Planetary Interiors

***—W. Bruce Banerdt, Rachel Abercrombie, Susan Keddie, Hitoshi Mizutani, Seiichi Nagihara, Yosio Nakamura, and W. Thomas Pike***

Investigating the composition, structure, and processes of the interior of planets is fundamental to understanding the origin, evolution, and present state of the solar system. Interior measurements provide the basic information about what planets are made of and how they "work." In virtually every science strategy report for exploring the solar system or a single planet, one of the major stated objectives has been to determine interior structure and dynamics of the terrestrial planets. In broadest terms this includes characterization of the core/mantle/crust divisions in terms of depth of boundaries, composition, and mineralogy; the study of mantle/core motions (i.e., convection and magnetism); and determination of the thermal history and state, as well as the closely associated tectonic and volcanic history of a planet.

For example, these objectives have been explicitly enumerated in the latest report of the Committee on Planetary and Lunar Exploration of the National Research Council (*COMPLEX*, 1994). This report identified two main themes to guide planetary science in the next two decades: understanding planetary origins and understanding the constitution and fundamental processes of the planets themselves. Within this latter theme, planetary surfaces and interiors comprised one of the four major components. It proposed four specific goals related to interior measurements for addressing this theme:

1. Understand the internal structure and dynamics of at least one solid body, other than the Earth or the Moon, that is actively convecting.
2. Determine the characteristics of the magnetic fields of Mercury and the outer planets to provide insight into the generation of planetary magnetic fields.
3. Specify the nature and sources of stress that are responsible for the global tectonics of Mars, Venus, and several icy satellites of the outer planets.
4. Advance significantly our understanding of crust-mantle structure . . . for all the solid planets.

These goals can all be addressed to some extent, and in many cases almost exclusively, by measurements made on the surfaces of planetary bodies.

However, this enterprise has unique difficulties, in that even with *in situ* instruments on the surface one is still essentially confined to remote sensing of the region of interest. There are basically four types of measurements that can be made at the surface that are directly relevant to the deep interior: seismic, magnetic, heat flow, and geodetic. We will discuss each of these in turn.

## 4.1. SEISMOLOGY

The importance of seismology in understanding the interior structure and tectonics of a planet cannot be overstated. It is the only tool available that can furnish detailed global and regional information on the compositional structure and physical state of a planetary interior. Whereas gravity, dynamics, and magnetic measurements can supply key information on some aspects of interior structure, they cannot provide a substitute for the precise radial (and, to a lesser extent, lateral) structure information that can be derived from seismic data. Some of the salient questions that could be addressed are described below.

### 4.1.1. Thickness of the Crust

Gravity studies can offer tantalizing suggestions as to the crust's structure, but are essentially ambiguous without additional constraint. The mean crustal thickness has fundamental implication for the degree of differentiation of a planet and for the nature of its magmatic evolution. Crustal thickness also bears directly on the thermal evolution of the planet because of the tendency of incompatible radioactive elements to segregate into the crust. Lateral thickness variations are intimately related to the isostatic state of topography and thus the mode of support of topographic features.

### 4.1.2. Layering Within the Mantle

The accumulation of teleseismic travel-time data, together with normal mode (free oscillation) measurements, will allow the resolution of the radial density structure of the mantle. This structure may be due to chemical stratification or to pressure-induced polymorphic phase transitions. Any such layering would have important implications for the evolution and dynamics of the interior. In addition, the different pressure-temperature conditions of the interior can allow an independent test of models that have been developed to explain the interior structure of the Earth.

### 4.1.3. Size and Nature of the Core

Information derived from relatively large, distant seismic events can be used to unambiguously establish the existence and radius of an iron-rich core, its density (which is determined by the ratio of Fe to lighter alloying elements such as S), and its phase (solid or liquid). Both the nature of the solar nebula from which a planet formed and the subsequent thermal evolution of the planet can be constrained by this single vital measurement.

### 4.1.4. Transmission Properties of the Interior

One of the remarkable contrasts between the Earth and the Moon discovered by the Apollo seismic experiment was the difference in the seismic signal characteristics for the two bodies. Compared to events with similar size and range on the Earth, lunar signals are prolonged, with little coherence between the three components of ground motion. For example, an event that would generate a signal with a length of one minute on the Earth might last for up to several hours on the Moon. This is attributed primarily to the very high *Q* (low seismic attenuation properties) of the outer shell of the Moon and a sharp increase in seismic velocity with depth in the regolith (*Dainty et al.,* 1974). Whereas the outer layers of the Earth have a *Q* of about 200–300, the *Q* of the Moon has been estimated to be about 4000–6000 (*Nakamura and Koyama,* 1982). This contrast has been ascribed to the difference between the Earth and Moon in volatile content, primarily water, with reduced water content resulting in higher *Q*. Seismic attenuation is also sensitive to the temperature of a material relative to its melting point. The *Q* of a planet can thus tell us a great deal about the bulk properties of its interior.

### 4.1.5. Level and Distribution of Seismicity

The level and distribution of seismicity on a planet reveals a great deal about how geologically active it is today and about the state of stress due to tectonic processes and other sources. It can also provide information about the meteoroid flux in the planet's vicinity and the efficiency of its atmosphere (if any) in shielding it from impacts.

An in-depth discussion of the goals and requirements for a particular seismic investigation, that of Mars, is contained in a report by *Solomon et al.* (1991).

### 4.1.6. Instrument Sensitivity

The physical quantity we measure with seismic instruments is normally the displacement of the ground with respect to time (time series) resulting from propagation of seismic waves through the planetary interior. Other quantities associated with seismic wave propagation, such as strain and rotation, may sometimes provide useful information, but are not likely to be the main objects of the measurement in the initial phase of planetary exploration unless specific scientific objectives arise that require these quantities to be measured.

The choice of planetary body and specific measurement objectives dictate to some extent the required response characteristics of a seismometer, e.g., its frequency range, sensitivity, and dynamic range. While instrument sensitivity as high as possible is desired for a planetary body of unknown seismic activity in order to be prepared for a very low level of activity, the local level of ground noise generally limits the usable instrumental sensitivity.

Figure 4.1 shows approximate frequency bands of ground motion observed on the Earth, ranging from solid Earth tides to local body waves, together with the typical level of ground noise that limits terrestrial seismic observations. Also shown on the figure is the largest seismic ground motion ever recorded on the Earth. An ideal seismometer for the Earth would respond to the entire dynamic range between the noise and the largest observed ground motion levels for the entire frequency band. However, this is not achieved even for instruments used on the Earth, and all terrestrial instruments are limited in both frequency and dynamic range to meet a particular objective.

For a planetary body other than the Earth, the appropriate ranges of instrumental response depend on several factors, including size of the planet, expected seismic activity, and expected sources of background noise. For small bodies, such as asteroids, the lowest frequency of interest for certain types

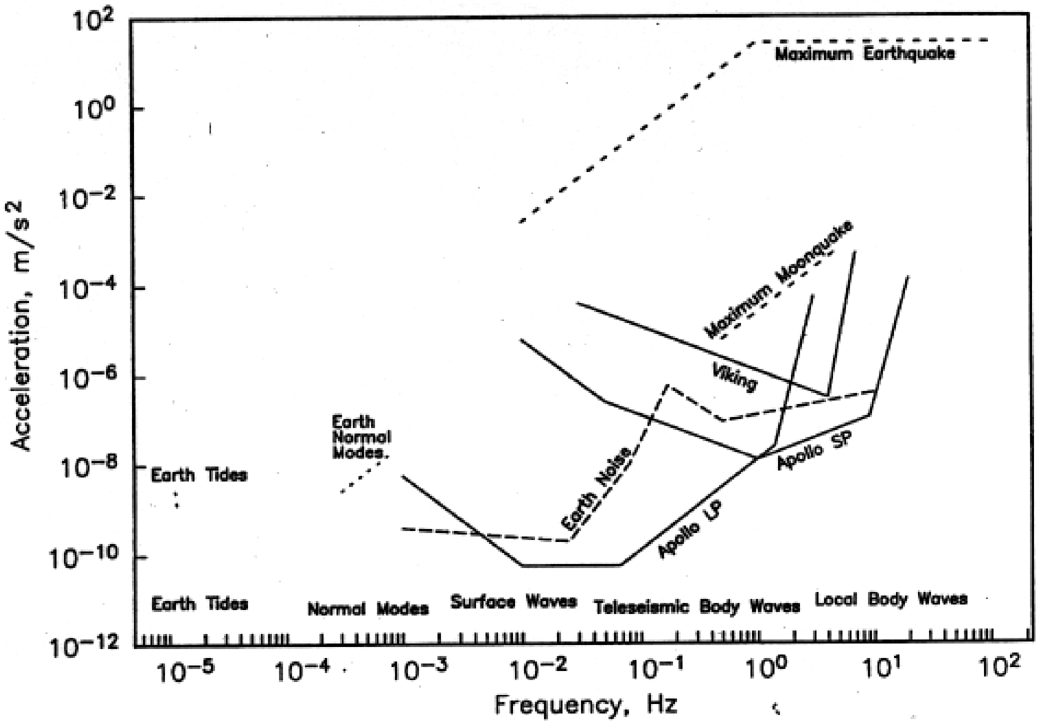

**Fig. 4.1.** Approximate frequency ranges of various types of seismic signals, along with seismic noise levels and sensitivities of previous planetary seismometers.

of seismic waves, such as normal modes and surface waves, will obviously be higher than on Earth. The expected level of seismic activity of a given planetary body is largely unknown until we have some data, and estimates are unreliable at best. Therefore, it is best to try for the highest achievable instrumental sensitivity until at least some real data are acquired to indicate the level of seismic activity on the planetary surface. Another reason why one should aim for the highest sensitivity possible for the initial observation is that the number of seismic events generally increases in proportion to an inverse power of the event size, thus dramatically increasing the number of detected events as one increases the detection sensitivity. Since the background seismic noise on most other planets is expected to be significantly lower than on the Earth, higher sensitivity than is useful on the Earth is desirable.

Also shown on Fig. 4.1 are the sensitivity of the Apollo lunar seismometer and the Viking martian seismometer. Many of the detected seismic events on the Moon were barely above the sensitivity threshold of the Apollo instrument. The background noise level on the Moon was below the instrumental sensitivity except at the times of sunrise and sunset, when thermal disturbances caused large ground noise. The Viking seismometer did not detect any positively identifiable seismic event, quite possibly because its sensitivity was too poor to detect seismic signals, even if they were present. Since the Viking seismometer was installed on the lander instead of directly on the ground, the observed background noise was mostly due to wind shaking the lander.

Expected background noise is extremely low on a planetary body with no atmosphere or ocean. For bodies with atmospheres, some noise due to the ground/atmosphere interaction (wind) is expected. Even then, it is best to start with the highest practical instrumental sensitivity consistent with the expected background noise. Once we obtain some data on actual seismic activity and background noise, then more appropriate ranges of frequency and sensitivity may be adopted to maximize information content of the returned data.

### 4.1.7. Number of Stations

The number and distribution of seismic stations recording simultaneously on a planetary surface greatly influence the quality and quantity of information that can be derived from the acquired data. Generally, the larger the number of stations, the more detailed the information on the planetary interior that can be obtained. Although there is no clear threshold in the number of stations below which no useful information is obtained, at its lower end, each increment in the number of stations significantly increases the usefulness of the acquired data.

To start with, even if we have only one station on a given planet, we can still expect certain useful information. Data from one seismic station will tell us at least (1) the level and other properties of the background noise and (2) the characteristics of the signals that may prove to be from natural seismic events. In the initial stages of exploration of a planet, such information is highly valuable in designing instruments that are to be deployed later to maximize the information return in future missions. In addition, (3) if the internally generated seismic signals can be unambiguously differentiated from noise, the level of seismic activity of the planet can be determined, and (4) if there is a seismic event large enough to excite detectable normal modes, even a single station with a sufficient low-frequency response may also provide deep structural information.

Two seismic stations operating simultaneously on a planetary surface will significantly increase the information content of the acquired data, especially if they are separated by at least a few tens of degrees of arc on the surface. Events detected nearly simultaneously at both stations positively identify them to be from natural sources, not artifacts originating from the landing vehicles themselves. If the types of seismic phases, e.g., P and S arrivals, can be identified based on ground motion recorded on three orthogonal components, an approximate distance and rough direction to the source may be estimated assuming seismic velocities inside the planet.

When the number of stations increases to three, again assuming they are operating simultaneously, the source of observed seismic events can be located for an assumed internal structure. With four stations, for the first time we will start getting information on the seismic velocity structure in the planet from natural sources, assuming that the internal structure is approximately radially symmetrical. An ideal configuration for this array is roughly 60° spacing between each of three of the stations, with the fourth station placed on the opposite side of the planet, near the antipode of the three-station triangle.

The four-station network is probably within the grasp of the current planetary program and would provide extremely valuable information about the interior of a planet. Should the opportunity arise, there is a great deal more that could be learned from more ambitious seismic networks. For a large planetary body, a group of four seismic stations in a regional network, like the Apollo seismic network on the Moon, provides detailed information on only one region of the planet. To obtain a global structure, a few more regional networks are needed. Four networks of four stations each, located roughly at four apexes of a tetrahedron, would give a reasonable global coverage of an entire planet. The networks may also be arranged in such a way that one of the stations is located near the antipode of a known or suspected seismically active region, specifically to obtain information about deep structure. Beyond this number, further deployments of seismic stations would probably be made to satisfy certain specific objectives, such as to determine detailed lateral variations in structure or to investigate tectonic activity in a particular area or region.

### 4.1.8. Duration and Deployment

There is a significant advantage to maximizing the time spent making seismic measurements on a planet. In seismology, the interior structure is determined not from the analysis of a single seismic event, but is arrived at through the accumulation of many such events, each of which contributes statistically to the result. Tens to hundreds of recorded quakes are necessary to make meaningful inferences about the interior. On the Earth, a seismometer at a quiet site can record a globally detectable event roughly every day. On the Moon, only a few dozen large quakes were recorded over the nine-year lifetime of the experiment (although thousands of smaller events were recorded due to the extremely low noise floor, and many of these proved useful for interior studies). Clearly, long durations are required, especially on planets that are relatively tectonically inactive, in order to obtain the full benefits of a seismic investigation. A mission duration of months to a year is strongly recommended. Such long-duration surface missions pose engineering challenges, particularly with regard to power systems and maintaining instrument sensitivity and calibration. On some planets, such as Venus and Mercury, thermal aging is a great concern.

There are three main issues associated with deployment of seismometers on a planetary surface: isolation from noise sources, coupling with the ground, and knowledge of orientation.

The greatest problem with the Viking seismometer measurements stemmed from the fact that the instrument was mounted on the large lander. This lander presented a large cross section, and there was considerable shaking by the wind. Additionally, all other mechanical activities of the lander created acoustic noise that was transferred to the seismometer. On the Moon, the seismometers were deployed tens of meters from the landing stage of the LEM, but even at this distance lander noise is apparent in the records. The smaller size envisioned for future landers will partially alleviate this problem. In addition to lander-induced noise, the sensitivity of unprotected seismometers is, especially in the presence of an atmosphere, severely limited by environmental influences. These include temperature, air pressure, and wind.

Ideally, the seismometer would be buried at a depth exceeding the seasonal thermal skin depth at a distance of perhaps 100 m from the spacecraft, although this is almost certainly impractical within probable mission constraints. A reasonable alternative would be to deploy it from the end of an extendible boom, placing some distance between the seismometer and the lander. Wind and thermal noise can be reduced considerably by covering the instrument with an insulating "tent." Penetrator deployment provides one method of "burying" a seismometer, and provides good isolation from environmental noise.

In order to sense the very small motions of the surface that comprise seismic waves, the detector must be well coupled to the ground. Again, mounting on the deck or interior of a lander is clearly a poor choice. Relatively good coupling can be obtained with three sharp "feet," which will make positive contact with a hard (rock) surface or will penetrate into a soft (soil) surface. Care must be taken that noise isolation techniques (such as thermal insulation) do not screen the desired signals as well. We note that a penetrator deployment offers excellent ground coupling in addition to its environmental noise isolation advantages, although orientation (see below) and a long-term power supply are issues that need to be addressed.

It is critical to know the orientation (in addition to the position) of the seismometer relative to the planetary geodetic grid in order to locate detected seismic events. Although extreme precision is not required at the level of these investigations, it will be necessary to locate sources to within few hundred kilometers or so. This will require knowledge of the orientation of the seismometer to no worse than 5°. The easiest way to accomplish this (in the absence of a strong dipolar magnetic field) is to use a directional Sun sensor. For seismometers deployed on the surface, this should not present a problem. For penetrators, it would seem to require the inclusion of an "aft body" that detaches from the main penetrator and remains at the surface.

### 4.1.9. Present Instrument Technology

Examples of state-of-the-art terrestrial broadband seismometers are the Strekheisen STS-2 and the Guralp CMG-4. These instruments have a peak sensitivity of about $10^{-10}$ m/s$^2$ (generally following the terrestrial ground noise level shown in Fig. 4.1) over a frequency range of $10^{-3}$ to 10 Hz, with decreasing sensitivity outside this range, and a dynamic range of roughly $10^6$.

Two seismometers have been flown on planetary missions (not including the Ranger seismometers, which never operated): the Apollo ALSEP seismometer (e.g., *Latham et al.*, 1971, 1973; *Nakamura et al.*, 1982) and the Viking lander seismometer (*Anderson et al.*, 1972, 1976, 1977). The Apollo missions placed five instruments on the Moon, the first of which failed after several weeks of operation. These seismometers were actually composed of two instruments each, a short-period (SP) and a long-period (LP) seismometer. The sensitivity of these instruments is shown in Fig. 4.1. The peak sensitivity was comparable to terrestrial instruments (when operated under ideal low-noise conditions), although the bandwidth was much narrower. The ALSEP package had a mass of about 9 kg, much too large for current missions. The Viking instrument was extremely constrained in terms of mass, power, and telemetry. As can be seen in Fig. 4.1, it had a much lower sensitivity than terrestrial or lunar instruments, and in fact did not unambiguously detect any natural seismic activity.

Presently envisioned planetary seismometers have taken advantage of 20 years of technological advances in material, fabrication techniques, and electronics to achieve higher performance from designs that are orders of magnitude less

TABLE 4.1. Planetary seismometer parameters.

| | |
|---|---|
| *Apollo* | |
| Mass | 11.5 kg |
| Power consumption | 13.4 W |
| Frequency range | $10^{-3}$–10 Hz |
| Sensitivity | $10^{-10}$ m/s$^2$ |
| *Viking* | |
| Mass | 2.2 kg |
| Power consumption | 3.5 W |
| Frequency range | 0.1–10 Hz |
| Acceleration sensitivity | $5 \times 10^{-7}$ m/s$^2$ |
| *Guralp* | |
| Suspension | Pivoted cantilever with coiled spring |
| Mass | 0.32 kg |
| Power consumption | 280 mW |
| Size | 7.5 cm × 5.0 cm (one component) |
| Frequency range | 0.0027–50 Hz |
| Velocity output | 750 V/m/s |
| *JPL Microseismometer* | |
| Suspension | Micromachined silicon, 10-Hz resonance, $6 \times 10^{-9}$ m/s$^2/\sqrt{\text{Hz}}$ noise floor |
| Transducer | UHF capacitive displacement, $5 \times 10^{-13}$ m/$\sqrt{\text{Hz}}$ sensitivity |
| Configuration | Tetrahedral (three-components of acceleration plus one redundant) |
| Mass | <0.1 kg |
| Power consumption | 100 mW |
| Size | 5 cm on edge |
| Acceleration sensitivity | Better than $10^{-8}$ m/s$^2$ |
| Frequency range | 0.01–100 Hz |
| *OPTIMISM* | |
| Mass | 0.35 kg (one component) |
| Power consumption | 20 mW |
| Size | 9 cm × 9 cm × 9 cm |
| Frequency range | 0.001–8 Hz |
| Velocity output | 750 V/m/s |
| Acceleration sensitivity | $1 \times 10^{-9}$ m/s$^2$ |
| *ISAS Lunar Penetrator Seismometer* | |
| Mass | 0.35 kg (one component) |
| Power consumption | 20 mW |
| Size | 5 cm (diameter) × 5 cm (length) |
| Velocity output | 950 V/m/s |
| Frequency range | 0.5–8 Hz |

demanding in terms of mass and power requirements. Several examples of current designs are described below.

*Guralp planetary seismometer.* Guralp Ltd. (of Reading, U.K.) design and manufacture broadband seismometers that are used worldwide in diverse environments, including boreholes and ocean-bottom installations. They have now put their 20 years of terrestrial experience to bear on designing a prototype seismometer for use on Mars. The specifications of the instrument are given in Table 4.1. It is an accelerometer, similar to those in use on Earth, with promising sensitivity and response. A coiled supporting spring allows considerable size reduction over a more standard leaf spring. The design includes a motor for mass centering, which will allow compensation for diurnal and seasonal temperature variations. It also features a new locking mechanism for isolating the delicate pivots and holding the mass secure during launch and hard landings. The seismometer can operate in any orientation. Thus a single instrument design can be used for detecting both vertical and horizontal motions, and there would be no need to level a three-component instrument. A prototype instrument is scheduled to be built in 1996.

*JPL micromachined seismometers.* Over the last decade micromachining of semiconductor materials using techniques developed in the microelectronics industry has been applied to the production of accelerometers. The resulting structures, compact and robust, meet the requirements for the next generation of planetary seismometry, although in general the high resonant frequencies (kilohertz and above) of the suspension have led to insufficient sensitivity. However, by reducing the resonant frequencies to the range of 10–100 Hz and employing ultrasensitive position transducers, micromachined seismometers can offer performance to rival that of conventional terrestrial seismometers. A program has been established at the Jet Propulsion Laboratory to explore novel approaches to micromachined suspensions and ultrasensitive position transducers. The prototypes are now sufficiently developed for proposal to planetary mission opportunities.

Micromachining, predominantly of single crystal silicon, has a number of advantages over the conventional production of suspensions from metals. Single crystal silicon is a surprisingly strong material with, for example, a yield strength 20× that of steel. Being dislocation-free, and hence relatively immune to creep, it is very stable, not needing the controlled aging of metal springs. It has few energy dissipative modes, and hence very high $Q$s (in this case $Q$ is the dissipation quality factor of the spring) of over 10,000 are possible in vacuum; the thermal noise floor of the suspension can thus be extremely low even with a small (<1 g) proof mass. Micromachining etching processes can give very fine tolerances, to tens of nanometers, greatly facilitating miniaturization. Bonding of components can be achieved almost seamlessly, minimizing long-term mechanical drift and allowing the production of hermetic seals for *in vacuo* suspension packaging. Selective metallization enables the formation of electrodes, wires, and contacts, and the use of silicon allows integration of the mechanical sensor and transducer electronics within one structure.

Micromachined structures lend themselves naturally to capacitive transducer schemes: Plate separations can be highly toleranced and hence very small (<5 µm). Such small separations are essential for acceptable sensitivity from 10- to 100-Hz suspensions. However, even with such geometrical gain factors, it is still necessary to use a very sensitive capacitive transducer. One such, the ultra-high-frequency capacitive (UHFC) transducer, has been developed at JPL for seismometry. The variable capacitance between a suspended moving plate and a fixed plate is made part of a tank (LC) circuit excited at near resonance (of up to 100 MHz). By implementing a highly peaked electronic circuit, the response at the half-power points of resonance can be made highly sensitive to changes in the variable capacitance. The

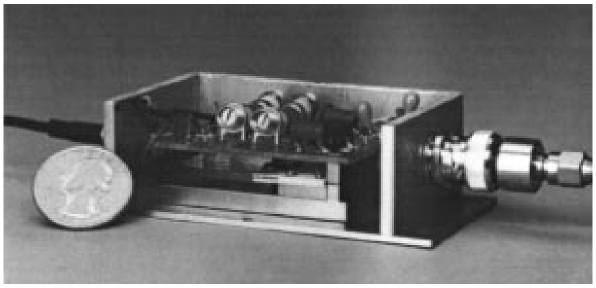

**Fig. 4.2.** Prototype JPL microseismometer.

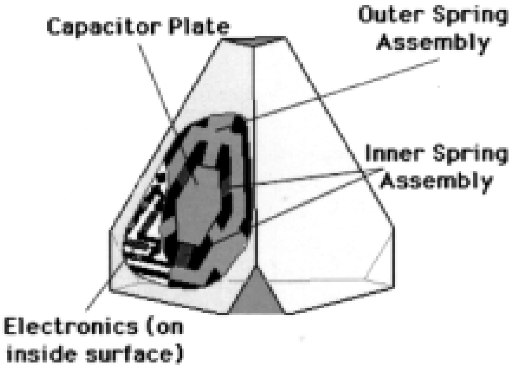

**Fig. 4.3.** Schematic of JPL microseismometer.

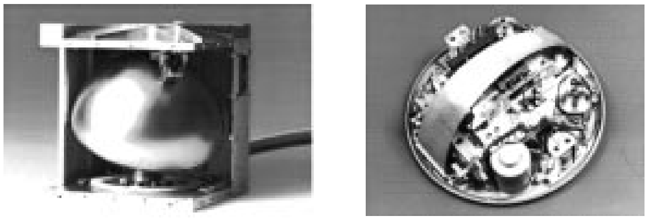

**Fig. 4.4.** Flight model of the OPTIMISM seismometer (left) and detail of the interior of the Ti half-sphere (right).

signal at these frequencies is demodulated from the excitation frequency and compared to the signal from either a fixed capacitance circuit or, more sensitively, the inverted signal from a second opposing fixed plate. Such an approach gives good rejection of frequency and amplitude fluctuations of the excitation signal. Additionally, the UHFC transducer gives a passive voltage gain of about 10, which can obviate the need for a preamplifier at the output of the seismometer. Alternative schemes with the potential for high sensitivity, though without the passive gain, are based on the switched capacitance approach. In this case care must be taken to minimize switching-induced errors and effects of instabilities in the supply voltages.

Figure 4.2 shows a prototype microseismometer using a silicon suspension and a UHFC transducer. Figure 4.3 shows a schematic of an integrated four-axis compact seismometer currently being proposed for Mars and cometary deployment. Specifications for this device are given in Table 4.1.

*OPTIMISM seismometer.* The OPTIMISM seismometer (Fig. 4.4), which has been designed and built by the Institut de Physique du Globe de Paris, the Institut Nationale des Sciences de l'Univers, and the SODERN company of France, will fly on the Russian Mars'96 mission. The OPTIMISM consists of a vertical seismometer, contained in a Ti half-sphere. The sphere can be leveled to within less than 0.2° by a gravity-driven gimbal after landing, and is then locked. The seismometer inside the sphere is a leaf-spring pendulum device, which uses a self-compensated spring alloy and achieves thermal compensation through careful design of the pivot and pendulum plate. Effective thermal coefficients as low as 0.2 μm/K can be achieved, which limits the displacement accuracy to about ±10 μm on Mars. The half-sphere also contains a temperature sensor and two getters for maintaining vacuum (to reduce viscous forces on the suspension).

The natural frequency of the seismometer is 2.3 Hz and the seismometer can run in either of two modes. The first mode uses a high-sensitivity (160 V/m/s) velocity transducer, which can be used to achieve extreme sensitivity close to the natural frequency. The second mode uses a displacement transducer, hybridized in the core of the suspension, based on a differential capacitive measurement. Resonance flattening is achieved by feedback.

*ISAS penetrator seismometer.* The Japanese lunar mission, LUNAR-A, to be launched in 1997, aims to study the lunar interior using a seismic network that will be established with three penetrators. The seismometer installed in the penetrator must be strong against the shock loading expected at impact of the penetrator into the lunar surface and yet must be sensitive enough to detect very small seismic signals.

The principle of the ISAS penetrator seismometer is the same as that of electromagnetic seismometers widely used on the Earth. A coil wound with 20-μm Cu wire acts as a pendulum, which is supported by three spiral leaf springs. The coil is positioned in a strong magnetic field produced by a newly developed rare-earth magnet. The strength of the magnetic field and number of the turns of coil control the sensitivity of this seismometer, both of which are in turn constrained by the mass and size of the seismometer. For the seismometer in a penetrator, it is important to make the natural frequency of the coil-pendulum system compatible with its mechanical strength. It is easy to make a short-period seismometer strong enough against shock loading, but it is technically difficult to make a long-period seismometer strong enough, because the long-period seismometer requires a weak (less stiff) spring. This problem is partly addressed for the ISAS seismometer using a nonlinear property of the spring material.

The damping constant of this seismometer is adjusted by appropriately selecting the material and structure of the coil bobbin. The characteristics of the ISAS seismometer are given in Table 4.1. Note that the high-frequency limit of the frequency range given in Table 4.1 is not due to the seismometer itself but is determined by the sampling rate of the LUNAR-A penetrator.

## 4.2. HEAT FLOW

The importance of planetary heat flow measurement has long been recognized. Heat flow is the only direct indicator of the internal temperature and heat transfer mechanism of planets that can be measured at the surface. Some planetary bodies are believed to be convective, whereas others are thought to be inactive or "dead." A convective planet like Venus probably develops thermal boundary layers at the surface, which may mimic the movements of the lithospheric plates of the Earth (e.g., *McKenzie*, 1994). Heat flow observations would provide constraints on their thermomechanical properties and time evolution (e.g., *Sclater et al.*, 1980; *Stein and Stein*, 1994). In addition, constraining the global heat budgets of planets would help to understand their individual histories and the history of the solar system as a whole.

### 4.2.1. Balance Between Scientific Objectives and Logistical Limitations

Generally speaking, knowledge increases with the amount of data. However, the time and monetary constraints of planetary missions severely limit the opportunities of data collection. Thus, scientists must know in advance what scientific objectives are likely to be accomplished with a very limited number of measurements. We believe that even a single heat flow measurement on a planet would be useful in providing a rough constraint on the internal temperature, especially for thermally inactive ("dead") planets, because there should not be drastic horizontal variation in thermal structure. However, lateral variations in topographic elevation and megaregolith thickness can lead to some variation in heat flow on "dead" planetary bodies. This effect is believed to be important in interpreting heat flow data from the Apollo 15 and 17 landers, both of which were sited at mare-highlands boundaries (*Warren and Rasmussen,* 1987).

If the planet is likely to be "alive," or convective, it is highly desirable that heat flow is measured at multiple stations that are strategically distributed. In this case heat flow through the planetary lithosphere will probably show a large variation. For example, heat flow through oceanic lithosphere of the Earth varies from >2000 $mW/m^2$ on young, shallow seafloors to ~40 $mW/m^2$ on old, deep seafloors. Thus, the first-order question for another convective planet like Venus would be whether heat flow varies systematically between the highlands, which are considered by many to be upwelling points, and the low basins (*McKenzie,* 1994). For such a purpose, the surface topography of the planet also needs to be mapped before the heat flow mission.

Even though some scientific objectives require multiple stations, it does not necessarily follow that all the measurements need to be done on a single mission. Even if only one measurement is possible on a single mission, several such missions to one planet would, over time, accomplish the objectives.

### 4.2.2. Measurement Technique

Heat flow is usually obtained as the product of two separate measurements: thermal gradient in and thermal conductivity of the near-surface rock/soil. In order to obtain the thermal gradient, one needs to measure temperatures at different depths. On unmanned missions, a penetrator is well suited for such measurements. The essence of the technique is similar to that of measurements made routinely on the terrestrial seafloor, which also use a probe penetrating into the sediments (e.g., *Nagihara and Lister*, 1993). The penetrator probe would consist of a thin metal tube containing thermistors that are spaced along its length. When the probe pushes into the rock/soil, its temperature rises due to the dissipation of the mechanical energy, and the temperature then slowly decays and approaches an equilibrium. The thermal gradient can be calculated from the equilibrium temperatures measured at individual thermistor locations. The probe should also contain a heater, which can apply an intense, calibrated heat pulse to the surrounding soil or rock after the probe temperature has reached thermal equilibrium. The *in situ* thermal conductivity can be calculated from the temperature decay pattern of this heat pulse (pulse-probe method: *Lister,* 1979; *Hyndman,* 1979; *Nagihara and Lister,* 1993).

### 4.2.3. Environmental Concerns

The shallow (<2 m) surface layer, where planetary heat flow measurements are likely to be made, is highly susceptible to temperature changes at the surface. The thermal signals from diurnal and seasonal variations can easily wipe out the subtle geothermal signal from depth. Therefore, it is crucial that scientists monitor the temperature over a long period in order to eliminate the environmental signal from the data. It would be ideal if this period covered at least one complete cycle of seasons, but it may be possible to extrapolate the variation fairly accurately based on data from one-fourth of the cycle. A planet like Venus, which is covered by a thick atmosphere, has little surface temperature fluctuation, and thus has a relatively benign environment for heat flow measurements. In contrast, Mars and the Moon have fluctuations of large amplitudes and present a very difficult situation for heat flow investigations. On Mars, the thermal wave associated with orbital element variations (timescale ~$10^5$ yr) may significantly perturb the near-surface thermal gradient from its long-term (>$10^7$ yr) average value. Modeling suggests that the magnitude of this effect varies substantially with location on the surface (*Mellon and Jakosky,* 1982).

### 4.2.4. Instrumentation Requirements

Both geothermal gradient and *in situ* thermal conductivity can be obtained from the temperature recorded as a time series by individual thermistors placed at a number of depths. The resolution of the temperature measurement should be on the order of milliKelvins. This is based on the fact that the lowest typical geothermal gradients measured on the Earth and the

Moon are ~0.01 K/m (*Langseth et al.,* 1976; *Sclater et al.,* 1980) and on the assumption that the depth of measurement be limited to ~1 m. The conductivity measurement would require a sampling interval of ~10 s, but the long-term monitoring can be done with one measurement per day. As far as the electronics and communication technologies are concerned, no major difficulty is anticipated except for protection from the extremes of high and low temperature encountered on some planets.

In mechanical design, the penetrator requires the strength to withstand the enormous deceleration force at the impact. However, efforts should be made to minimize the diameter of the probe. The *in situ* thermal conductivity measurement requires a quick thermal response by the sensor tube (*Nagihara and Lister,* 1993). For example, the sensors used for marine measurements are typically of 0.4–1 cm diameter. The thin diameter is desirable also for the long-term temperature monitoring, because a thick-diameter probe may significantly alter the geothermal field due to the high contrast of thermal conductivity between the metal tube and the surrounding rock.

## 4.3. MAGNETISM

Magnetic measurements yield information both on the electromagnetic material properties (primarily resistivity) of the interior of a planet and on processes of internal field generation (such as a dynamo). The primary magnetic measurements of a planet are better suited to orbital techniques. However, surface measurements can play an important role in investigating the interior through electromagnetic sounding.

The transient variations of the magnetic field at the surface of a planet have a primary external source, the interaction between the environment of the planet and solar radiation, and a secondary source, the electric currents induced in the conductive planet. Continuous recording of the transient variations of the magnetic field at the surface can therefore provide information on its internal structure. The depth of penetration of an electromagnetic wave in a conductive medium depends on both the period of the wave and the electrical resistivity of the medium. The larger the period and the resistivity, the greater the depth of penetration. Electromagnetic sounding can determine the presence (or absence) of sharp variations in the resistivity to 400–500 km depth and thus provide information on the thermodynamic conditions within this zone.

Electromagnetic sounding techniques are based on the analysis of the electromagnetic field observed at the surface of the planet. The resistivity distribution within the Earth is usually determined by measuring the magnetotelluric tensor, which relates, in the frequency domain, the horizontal components of the electric field to those of the magnetic field simultaneously recorded at a station. When (1) the resistivity varies with depth only, and (2) the externally originating variations are, as a first approximation, homogeneous at the scale of the studied area, the magnetotelluric tensor is antisymmetric; the antidiagonal terms are equal to plus or minus the transfer function between the magnetic and electric fields respectively. This transfer function is called the impedance of the conductive medium.

Within the same approximation, the impedance may also be deduced from the ratio, in the frequency domain, between the vertical and horizontal components of the magnetic field at a given station, provided the geometry of the source (which is provided by the interaction of the interplanetary field with the planet and/or its ionized environment) is known. In this case, the relative error in the impedance determination is on the order of the relative error of the source wavelength determination. The electromagnetic sounding technique can therefore allow the determination of the resistivity distribution even in the case of one magnetic station operating at the surface of the planet. The effectiveness of the technique can be strengthened considerably by the addition of a magnetometer in orbit to assist in the source determination.

The impedance is directly related to the variations of the resistivity with depth. Information about these variations can then be deduced from the observed frequency dependence of the impedance. The resistivity is dependent on the petrological nature of the materials and their thermodynamic conditions. Laboratory results on terrestrial materials show that the electrical resistivity varies greatly with respect to the thermodynamic conditions such as the temperature and the percentage of conductive fluids within the solid matrix (e.g., partial melting, water-rich fluids). For nonhydrated rocks, the resistivity remains very high for temperatures up to 1200°C or even 1800°C in some cases. Molten rocks have low resistivities (1–0.1 Ω/m), and in the presence of partial melting, the effective resistivity falls sharply by several orders of magnitude at constant temperature. In the presence of even a small fraction of a conductive liquid phase the resistivity sharply drops.

Extremely light, sensitive magnetometers have been developed over the years for many deep-space and planetary missions. These instruments can be easily adapted for use on planetary surfaces. The primary difficulties encountered on the surface are deployment away from magnetically noisy landers (extremely long booms are impractical) and the extremes of temperature often encountered.

## 4.4. GEODETIC MEASUREMENTS

Geodetic measurements, as defined here, are precision measurements (as a function of time) of position and orientation of a point on the surface. These measurement can yield the dynamics of the planetary body as a whole or local strain in its crust, depending on the reference for the measurement.

On the Earth, GPS measurements and local strain determinations are making great contributions to our understanding of tectonics. However, these types of measurements will be extremely difficult and costly on other planets, and this group could not envision a practical scheme for performing such an investigation in the foreseeable future. Thus the only technique that we will consider here is precision tracking of a lander for planetary dynamics.

These types of measurements can be particularly sensitive to the deep interior structure, through its effect on the rotational dynamics of the planet (e.g., precession, nutation, variations in angular velocity), and are complementary to seismology, which is most effective in determining crust and upper mantle structure.

Dynamical measurements are fundamentally different from the other techniques discussed here in that they are not made by an instrument as such. Instead, they rely on precision (on the order of centimeters to a meter or so) tracking of the lander from Earth. Thus, advances in communications technology are expected to result in improvements in measurement. For example, the transition to higher-frequency transponders (S to X to Ka band) gives much higher precision for tracking. Laser communication links could provide an additional improvement.

Perhaps the greatest short-term improvement in obtaining scientifically useful information from tracking measurements could come from a change in the way such experiments are typically handled. Traditionally, these investigations are treated as an opportunistic low- or no-cost add-on augmentation to the navigation function. A much greater value could be obtained if investigators were involved early in the mission and hardware planning stages, and these investigations were made an integral part of the mission design.

## 4.5. RECOMMENDATIONS FOR DEVELOPMENT FOCUS

Many technologies needed for performing interior measurements on planetary surfaces have already been pursued for terrestrial applications, as very similar constraints are often encountered. Other technologies that would benefit interior measurements are generic, such as the development of lightweight, low-power, high-temperature, and/or low-temperature electronics, and will be pursued in the general course of space hardware development. However, we have identified a few specific areas in which technologies would directly benefit some of these instruments.

### 4.5.1. Seismology

Seismology has a somewhat unique requirement for the capability to record ground motion over an extremely wide dynamic range, over 11 orders of magnitude (see Fig. 4.1). On the Earth, this is often accomplished using multiple specialized instruments, each designed to respond to a narrower range. We do not have this luxury in extraterrestrial seismology, and thus would like to be able to respond to both the teleseismic signal just above the noise on an airless body (with accelerations of order $10^{-10}$ m/s$^2$) and the strong motion from a relatively close event (say, ~$10^{-4}$ m/s$^2$). Present space-qualified analog-to-digital converters have a maximum range of around 16 bits, and are inadequate for this task. The development of a 24-bit A/D would greatly benefit any future planetary seismometer.

Data compression will be required for any seismic experiment in the foreseeable future. This is due to the immense volumes of raw data generated by a sensitive, high-frequency three-component seismometer (of order 1 Gbit/day) and the limits imposed by practical telemetry systems. Lossless compression techniques are well understood, and can result in savings of perhaps a factor of 5. “Lossy” compression can achieve much higher compression ratios, at the expense of some degradation of the signal. This degradation has been intensely studied for voice and image compression, and techniques have been developed that are tailored to these applications, destroying data that is relatively unimportant for their analysis. Similar studies need to be done for seismic signals to develop data compression algorithms that will preserve the information required by seismologists.

### 4.5.2. Heat Flow

Effective heat flow measurements are dependent on devices for emplacing the temperature probes at depth. Penetrators have long been touted as ideal for this application (as well as for seismology), but there remains skepticism within the planetary science spacecraft community about the viability of this type of lander. This appears to be due in large part to the obscure nature of the existing literature on penetrator development and testing. Thorough validation and testing of penetrator technology should be done, although considerable confidence could be generated by the successful use of penetrators in the upcoming Russian Mars’96 and Japanese Lunar-A missions.

Similarly, low-power, lightweight drill technology could be developed and used for the emplacement of thermistors, and would benefit many other investigations that require access to the near subsurface of a planet.

### 4.5.3. General

On several planets, very high (e.g., Venus, Mercury) or low (e.g., Mercury’s pole, outer planet satellites, comets, and asteroids) temperatures will be encountered, which will place demands on electronic components. Therefore development of electronic technologies that will allow reliable operations at extreme temperatures will be necessary. This is particularly critical for instruments such as seismometers and magnetometers, which must be deployed well away from a spacecraft and its thermal control systems for extended periods of time.

Another common requirement for the types of measurements discussed here is for long duration. All these investigations would benefit from measurements that spanned at least a local year on the surface, or even longer. Thus longevity should be emphasized in the development of electronics and systems for both the instruments and the spacecraft.

Across the board, a critical factor for most surface measurements related to the interior is the number of independent measurement sites. Thus any system-wide (including all spacecraft and mission systems, as well as payload) development that helps to enable multiple landers (with sufficient resources and capabilities) within today's tight cost constraints would directly benefit these types of investigations.

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# 5: Atmospheres from Within

***—Thomas Morgan, James Abshire, Todd Clancy, Ghee Fry, Bo Gustafson, Michael Hecht, Theodor Kostiuk, Jonathan Rall, Dennis Reuter, and Robert Sheldon***

## 5.1. INTRODUCTION

While lander instruments cannot provide the global coverage that is typically associated with atmospheric science objectives, they still contribute key atmospheric data that are unobtainable from orbiter instrumentation. These measurements include *in situ* analyses of trace components (e.g., isotopic and noble gas abundances); unambiguous definitions of diurnal and meteorological variations; and, most importantly, a detailed characterization of the atmospheric region just above the planetary surface. This region, which includes the boundary layer up to approximately one scale height above the surface, is not well suited to study from orbit due to the extreme difficulty in separating the atmosphere from the surface in nadir- or even limb-viewing remote observations. Yet it is this same atmospheric region that exhibits the most intimate surface-atmosphere interactions, ranging from dust storms and volatile behaviors in the Mars atmosphere to the whole-scale evolution of surface material into atmospheric outflow from comets. Lander instruments provide unique capabilities to probe this surface-atmosphere boundary with remote sounding from below, *in situ* analyses, and *in situ* descent profiling. Lander instrumentation will address such fundamental issues as the current and past climatic balance on Mars and the primitive molecular compositions and structures of cometary volatiles.

In the following review of atmospheric investigations from planetary surfaces, we do not emphasize prioritization of science or measurement objectives. We call attention to a wide variety of measurement and instrument techniques that would be relevant to atmospheric studies from future planetary lander missions. To the extent possible, we list science, measurement, and instrumental goals for atmospheric studies from such planetary landers. The great diversity of planetary surface environments within the solar system precludes complete or highly specific coverage. We consider lander investigations for Mars and cometary missions as specific cases that represent the broad range of atmosphere-surface boundaries, and also correspond to high-priority goals for future national and international lander missions.

## 5.2. CRITICAL SCIENCE NEEDS

### 5.2.1. Mars

Given the interest in Mars as our nearest and most habitable planetary neighbor, it is surprising how many critical science goals remain unfulfilled for Mars atmospheric studies. We lack even a basic understanding of the current climatic balance for volatiles ($CO_2$ and $H_2O$) within the atmosphere, the regolith, and the polar ice caps of Mars (e.g., *Jakosky and Haberle*, 1992). Consequently, we do not understand the striking north-south asymmetries of Mars' atmospheric water vapor and polar (residual) water ice abundances that are evident today, much less the long-term behaviors of these asymmetries and their relationship to the remarkable polar layered deposits (which are possibly related to periodic variations in the Mars orbit; e.g., *Toon et al.*, 1980). The Mariner 9 and Viking missions of the 1970s have helped to formulate the key questions we now pose for Mars' climate, but they have not provided the observations necessary to answer these questions. This is largely because vertical profiling of temperatures, water vapor, dust, and clouds have yet to be obtained with even minimal seasonal/global coverage. These measurements should be gathered from future Mars orbiter missions, but perhaps not until after the year 2000. Vertical profiling of these parameters within the lower Mars atmosphere will require lander observations.

The paucity of atmospheric measurements of Mars becomes more significant when one considers the extreme interannual variability of the Mars atmosphere. Although we know little about the frequency or mechanics of Mars' global dust storms, it is evident that they do not occur every Mars year (see *Zurek and Martin*, 1993). When they do occur, the global average temperatures of the Mars atmosphere can increase by 30–40 K over altitudes of 0–70 km (e.g., *Pollack et al.*, 1977; *Clancy et al.*, 1994). The thermal and surface albedo effects of Mars dust are important for processes ranging from the general circulation of the Mars atmosphere to the temperatures and compositions of the polar seasonal and residual ice caps (see *Kieffer et al.*, 1992). Because atmospheric dust plays such a large role in the global balances of atmosphere and surface volatiles, it is unlikely that the Viking atmospheric measurements during the very dusty 1976–1978 period reflect the average balance of the Mars climate system. A reliable understanding of the current Mars climate will require long-term observations of the Mars atmosphere for many of the science and measurements objectives we list below regarding future lander instrumentation.

*Surface-atmosphere interactions.* A dramatic example of the importance of surface-atmosphere interactions in the Mars climate is the Viking observation that ~20% of the Mars atmosphere becomes seasonal surface $CO_2$ ice twice in every Mars year (i.e., during the southern and northern fall/winter seasons; *Hess et al.*, 1980). The residual water ice caps and the fine dust that covers the surface of Mars (and, in combination with water ice, forms the polar layered deposits) are also elements of surface volatiles that transition from the surface to the atmosphere and back over diurnal, seasonal, interannual, and climatic timescales. The Mariner 9 and Viking observations have identified these processes as important to the Mars climate, but they have not provided sufficiently diagnostic measurements to quantify the climatic or even seasonal balances of these processes. Key unanswered questions include: Why is the north polar residual ice cap 5–10× larger than the south residual ice cap? Does the larger north polar water ice content and the resulting greater abundance of atmospheric water vapor in the northern atmosphere represent climate balance, or is water currently transferring into the southern hemisphere? How much water and $CO_2$ are absorbed in the Mars regolith, and do they contribute to seasonal and climatic variations in the global distributions of Mars volatiles? What are the radiative properties of the atmospheric dust? Are there climatically significant interactions between atmospheric dust, water vapor, and water ice clouds in the current Mars atmosphere? How is dust incorporated in the seasonal $CO_2$ and residual water ice caps. Why does the southern seasonal cap exhibit a lower albedo than the northern seasonal ice cap, and is the year-round $CO_2$ ice covering of the southern residual ice a fundamental aspect of the current Mars climate?

*Variability of the atmosphere.* The variability of the Mars atmosphere in terms of temperature, dust content, clouds, water vapor, and even total atmospheric pressure, is extreme on all timescales. In the lower atmosphere of Mars (below 1 km altitude), diurnal temperature variations exceed 20 K, and seasonal variations can exceed 50 K (e.g., *Zurek et al.*, 1992). As noted above, the interannual variability of the global Mars atmosphere is forced by poorly understood variations in the occurrence of global dust storms. Such interannual dust storm variations may also force interannual variabilities in Mars clouds, hemispheric water transport, and polar ice behaviors (*Clancy et al.*, 1995). On the $10^4$–$10^6$-year timescales of Mars obliquity and eccentricity variations, even more dramatic changes are predicted for dust, surface ice, and atmospheric pressure variations (*Toon et al.*, 1980; *Kieffer et al.*, 1992). Finally, it is widely believed that a much thicker (pressure >100 mbar) Mars atmosphere was present very early in Mars history (within the first billion years), which led to the formation of the fluvial surface features apparent in Mars spacecraft images (e.g., *Fanale et al.*, 1992). Once again, the 1970s missions to Mars have served to define many of the key questions, for which definitive answers await future observations: What are the seasonal and interannual frequencies of global and regional dust storms on Mars? What roles do atmospheric dynamics, dust radiative properties, and clouds play in the interannual variability of global dust storms? How do the seasonal and residual ice caps vary on interannual timescales? Does the current north-south asymmetry of water vapor and ice represent climatic balance or evolution conditions? What is the origin of the polar layered deposits? Was there a much thicker Mars atmosphere during its very early history?

*Circulation/dynamics.* The COMPLEX report identified the understanding of global atmospheric circulation and climate history as key focus areas in martian atmospheric science. Tied to this is a need to understand the relative importance of several energy sources in driving martian weather and atmospheric evolution. For example, what roles do atmospheric perturbations (such as dust storms, gravity waves, Rossby waves, and tides) play in distributing the global atmospheric energy budget and in transporting energy poleward from lower latitudes? Also, does the deposition of energetic particles (solar protons, electrons, and cosmic rays) contribute significantly to the character and dynamics of the middle atmosphere?

*Aeronomy.* Studies regarding the long-term evolution of the Mars atmosphere (as discussed above) require knowledge of the atmospheric escape rates for volatile components such as atomic H and O. Because of the lack of a significant Mars magnetic field, these escape rates reflect direct solar wind interactions with the upper Mars atmosphere (e.g., *Luhmann et al.*, 1992). Current models of this process provide reasonable agreement with measurements of isotopic ratios for the Mars atmosphere, and suggest important loss rates for Mars water over geological timescales. However, these models rely on significant extrapolations of the calculated loss rates backward in time, for which time-dependent changes in the Mars upper atmosphere and the solar flux/wind are inferred. Furthermore, we do not have an entirely reliable picture of the photochemical balance of the current Mars atmosphere. Recent photochemical modeling suggests that the stability of the $CO_2$ atmosphere from photolysis into very high CO and $O_2$ levels is adequately explained by HOx chemistry (e.g., *Nair et al.*, 1994). These models no longer require extreme vertical transport rates or unallowable high water vapor concentrations, but they still do not fit the observed abundances of CO, $O_2$, and $O_3$ simultaneously. Outstanding questions include, What are the loss rates for O and H over time? How does the ionosphere of Mars vary with solar cycle and during global dust storms? Does the photochemistry of Mars vary seasonally? Is surface or aerosol heterogeneous chemistry important?

*Lightning.* Optical and radio signatures characteristic of lightning have been detected on several gaseous planets by the Pioneer and Voyager spacecraft, and on Venus by a number of missions (*Williams et al.*, 1983; *Levin et al.*, 1983; *Rinnert*, 1985; discussion in *Uman*, 1987). Although it is difficult to see how large lightning events might be produced in the martian atmosphere, smaller-scale electrostatic discharges may take place (*Eden and Vonnegut*, 1973; *Briggs et al.*, 1977). Such events produce molecules that would not otherwise be present, and therefore affect the atmospheric chemical composition (*Chameides et al.*, 1979). This also has important implications for exobiology. Lightning probably occurred on the early Earth. It may have served as a source of energy for, and operated to, produce compounds that serve as the necessary building blocks for life (*Miller and Urey*, 1959; *Chameides and Walker*, 1981). Planetary electrostatic discharges are best studied *in situ* (*Uman*, 1987), and for the terrestrial planets, this means either from the surface or from an airborne platform such as a balloon.

*Meteoroids.* The rate of meteors occurring in the martian atmosphere is estimated to be comparable to that on Earth (*Adolfsson et al.*, 1996) because the atmospheric densities of the Earth and Mars are comparable at a height of 120 km. The low flux makes direct spacecraft-borne impact detectors ineffective on meteoroids and large dust particles. The problem is overcome by using the atmosphere of Mars as a giant detector. Our current knowledge of particles of this size range is confined to the orbit of Earth. The extension to a second region will give a first cut at the spatial variation of the large dust and meteoroid population.

*Solar wind and cosmic-ray interactions.* An understanding of the structure and dynamics of the martian middle atmosphere and ionosphere provides insights into the processes that changed early Mars to its present state. The solar wind and energetic particle environments at Mars interact with its atmosphere and have substantially influenced its evolution (*Luhmann and Bauer*, 1992). Planetary missions over the last three decades have led to an improved understanding of the martian atmosphere, ionosphere, and interaction with the solar wind. Missions planned for the near future [e.g., Mars Global Surveyor, Mars Pathfinder, Mars '96, Planet-B, Mars Surveyor (98) orbiter and lander, etc.] will provide even more details. However, in spite of the numerous observations, we still do not have a complete picture of the solar wind/ionosphere interaction, or for that matter, of the martian ionosphere itself. Observations that allow a comparison of Earth with Mars provide insights into the relative importance of the planets' respective magnetospheres in controlling or modulating the solar and solar-wind-driven ionospheric behavior.

### 5.2.2. Comets

Comets are thought to be the least-modified materials in the solar system, and thus their chemical and physical structures contain important clues to the formation and early evolution of the solar system. In the last decade, our knowledge of the physics and chemistry of comets has grown enormously from Earth-based IR and microwave observations using improved instrumentation, and from spacecraft-based measurements of Comet P/Halley during its last apparition. Of particular note is the increase in the number of known parent and possibly nucleogenic chemical species in cometary comae. Before the 1986 P/Halley measurements, CO was the only parent molecule that had been definitely identified in cometary atmospheres. The presence of $H_2O$ and $CO_2$ were deduced from observations of the ionic and radical species H, OH, $H_3O^+$, $CO_2^+$. Observations of P/Halley and several other comets since 1985 have added $H_2O$, $CO_2$, $H_2CO$, $CH_3OH$, $H_2S$, and HCN to the list of identified parent species (see, for example, *Mumma et al.*, 1993 and references therein for a review of cometary composition and formation mechanisms; see also *Crovisier*, 1994, and *Bockelee-Morvan et al.*, 1995 and references therein). Several critical isotopic ratios, including H/D, $^{12}C/^{13}C$, and $^{18}O/^{16}O$, have also been measured for a few comets (*Eberhardt et al.*, 1995 and references therein). Data such as these are needed to answer the fundamental questions of cometary formation and evolution, which will have profound implications for our understanding of the origins of planetary systems. Two critical areas that can be uniquely addressed by landers are discussed below.

*Volatile and refractory evolution.* We want to know what a comet is made of, how its components are assembled and arranged, and how they disaggregate under insolation. A focus for our interest is that comets may be preserved samples of original solar nebula condensates; we hope to constrain the evolution of the presolar nebula from the materials of comets.

The structures of grains in a comet, before they are significantly altered, might give insight into several fundamental issues of condensation and agglomeration of solids in the early solar nebula. Knowledge needed includes the degree to which volatiles condensed on refractory grains before the grains aggregated, grain-grain velocities during aggregation, the frequency of break-up vs. aggregation as an outcome of intergrain collisions, and the degree of grain compaction during collisions. These data will help in understanding processes in the early solar nebula, e.g., if grains in the solar nebula went through cycles of aggregation and break-up; if gases condensed, evaporated, and recondensed on partially aggregated grains; or if turbulence in the early solar system increased the relative speeds of particles.

The structures of cometary dusts, volatile condensates, and gases should be probed above active regions on comet nuclei, particularly within a few nuclear radii of the surface before the material becomes significantly modified from its pristine state. Also, dusts and volatiles should be investigated deep within comets. Such observations have the greatest potential to bear on primitive matter.

It would also be valuable to study inactive areas on comets and to extend measurements to a range of distances from the nucleus to characterize dust-release mechanisms and gas-dust interactions. This is also an opportunity to study key physical and chemical processes that took place in the presolar nebula in an astrophysical setting. Similar processes take place in star-forming regions, and wherever gas and dust interactions are important. An understanding of these processes is necessary to trace dust and gas to the site of its origin and to model the modifications at release and any subsequent evolution. It is also needed to model the overall evolution of the nucleus.

*Parent molecules.* It is apparent from groundbased studies that comet comas are dominated by photodissociated fragments of molecules and thermally dissociated vapors of minerals, rather than the molecular species that actually compose the solid nucleus. Species in the plasma tails are derived from coma material by further processing, such as photoionization and ionic reactions. Chemical models have attempted to infer the composition of the nucleus from coma and plasma tail species and abundances. The key uncertainty lies in the identification of parent molecules originating in the nucleus. This, unfortunately, is extremely difficult to do because the surface and near-surface atmosphere are obscured by the coma.

While it may be possible to penetrate the surface of a comet and sample its constituent material, it seems likely that the drilling capabilities of any lander would not permit penetration deep enough to reach truly unprocessed material. Relatively unaltered material, however, may be accessible in the jet outflows from cometary nuclei. Near the nucleus, photodissociation and chemical reactions are minimal because solar UV flux is severely attentuated by the surrounding coma. The cometary vapor expands initially like a freely expanding gas with velocities much larger than needed for escape. From what has been understood from observations of Comet P/Halley, it seems likely that this gas flow occurs in jets originating in discrete regions on the cometary nucleus. A landed spectrometer near a jet could identify its chemical constituents and measure its velocity flows. In addition, a lander close enough to a jet could sample its outflow directly, perhaps by a mechanical arm.

Water must be the principal constituent of cometary nuclei, e.g., to explain the abundances of OH in comae. Ammonia is less abundant but required to explain the observed presence of $NH_2$ and NH. Beyond these two species, little is known with certainty about the parent molecules for cometary comae. The identification of HCN and CN in comae, for example, suggests that much of the N is present as an unsaturated, high-temperature species. The presence of CS and S might suggest $CS_2$ as a parent, but is also consistent with organic SH compounds (thiols). The low abundances of C indicated by present observations of comets may imply that much C in the nucleus forms involatile organic polymers. Positive identification of the molecular species present in cometary nuclei will provide insight into their formation and evolutionary histories, e.g., their thermal processing histories. In addition, knowledge of the molecular species will allow insight into biochemicals that can be formed in a comet to assess the possible linkages between comets and the origins of life.

## 5.3. MEASUREMENT OBJECTIVES

It will only be possible to include a sampling of the measurement objectives that naturally follow from the broad range of scientific objectives outlined above. We will, however, continue to discuss these in terms of our two endmember interests: Mars and comets.

### 5.3.1. Mars

Here we have selected a few topics in atmospheric dynamics and in particles and fields.

*Atmospheric dynamics.* (1) Gravity waves: *In situ* observations of the martian neutral atmosphere and ionosphere are limited to the measurements by the two Viking landers as they descended to the surface in 1976 (*Hanson et al.*, 1977). That data showed large variations in neutral temperature almost all the way through the atmosphere to the surface, indicating the presence of atmospheric gravity waves, tidal forcing, or both (*Stewart and Hanson*, 1982). Thermospheric models support the evidence that gravity waves propagate in the martian atmosphere and provide an important source of energy deposition in the lower thermosphere (*Bougher et al.*, 1990; *Mayr et al.*, 1992). The wave phenomena must be characterized in order to assess the relative importance to atmospheric energetics and dynamics.

(2) Tides: On Earth, the interaction of tidal influences on the ionized plasma with the geomagnetic field results in an electric current system, with the equatorial electrojet being a significant feature (e.g., *Rishbeth and Garriott*, 1969). Detailed measurements of the surface magnetic field might detect variations due to ionospheric electric currents. Although Mars does not have a strong magnetic field, it is important to determine if currents induced by the solar wind/ionosphere interactions play a significant role in modifying the tide-driven circulation in the upper atmosphere.

*Particles and fields.* (1) Sources: Mars possesses an ionosphere similar to the Earth's, and the sources and dynamics in some ways are probably similar. A key measurement objective is to characterize the local-time variability of the martian ionosphere and magnetic field. This will provide a global picture of solar wind/ionosphere interaction, which is difficult to obtain from orbiting spacecraft that generally are confined to orbit planes fixed in local time. For example, ionospheric instruments deployed on the surface of Mars would provide observations of the ionosphere that span all local times once each sol (martian day, ~25 hr). Surface-based aeronomy measurements also provide access to the bottomside ionosphere, which cannot be remotely sensed by topside sounders on orbiting spacecraft. The bottomside martian ionosphere is of considerable interest because middle-atmosphere dynamics are often manifested by changes in the ionosphere at these heights.

(2) Electron density: The bulk of our knowledge of the martian ionosphere comes from radio occultation measurements using orbiting spacecraft (*Zhang et al.*, 1990a,b and references therein) and from brief *in situ* measurements obtained as the Viking landers descended to the surface in 1976 (*Hanson et al.*, 1977). The orbit of Mars lies outside the Earth's, so the geometry of the radio wave path limits occultation observations to solar zenith angles of greater than about 45°. Also, the occultation technique is not effective for ionospheric sensing below an altitude of about 100 km. There-

fore, we have no direct measurements of the midday or midnight martian ionosphere, and no observations of the bottomside ionosphere (that region of the ionosphere below the electron density peak) where important energetic phenomena occur. It is possible that, in addition to solar EUV radiation, energetic particles may be a significant source of energy deposition. For example, there are indications that precipitating electrons may be responsible for maintaining the observed nighttime ionization (*Zhang et al.*, 1990b; *Verigin et al.*, 1991). Based upon our experience with the terrestrial ionosphere, investigations of the martian ionosphere might reveal enhanced D-region ionization due to high-energy solar protons and X-rays, and possibly precipitating keV electrons or meteors; traveling ionospheric disturbances (the ionospheric manifestation of propagating atmospheric gravity waves); drifting patches of ionization driven by martian solar-wind/ionosphere electrodynamics; and possibly new sources of ionospheric variability unique to Mars, such as atmospheric heating during global dust storms.

(3) Magnetic field: Unlike the Earth, Mars does not have a strong intrinsic magnetic field. It is important to characterize the local and global magnetic field in order to obtain a ground-truth reference that will serve as a point of departure for theories of the martian internal and external dynamos and their evolution. Magnetic variability will provide insight into possible ionospheric current systems generated by the interaction of the supersonic solar wind flow past the martian atmosphere.

(4) Radio absorption: Changes in ionization produce measurable variations in absorption of transionospheric HF signals (i.e., radio waves from galactic radio sources), and in turn provide insights into the phenomena responsible for the changes. The amount of absorption of a radio wave as it propagates through the ionosphere is a function of the radio frequency, the electron momentum-transfer collision frequency, and amount of ionization integrated along the radio-ray path. Absorption measurements indicate changes in ionization at the heights of maximum absorption, and they provide insights into the causal processes. For example, studies of the temporal variations of absorption have provided information on the sources and energy spectra of auroral electrons in the terrestrial ionosphere (*Rosenberg and Dudeney*, 1986; *Stoker*, 1987).

(5) Radio emission: A number of natural sources of radio emissions have been identified from groundbased observations on Earth (*La Belle and Weatherwax*, 1992). By analogy, some or most of the physical processes responsible for these emissions are likely to take place on other planets and should be detectable from surface observations. Cosmic radio noise passing through the ionosphere, plasma emissions driven by the solar wind/ionosphere interactions, and electrostatic discharges from wind-driven dust (in dust storms, dust devils, and volcanic activity) all contribute to the local noise environment. Other noise sources include solar radio noise bursts, jovian decameter radiation, and terrestrial auroral kilometric radiation. It is important to characterize the radio noise environment because it provides insight into the physical processes that shaped and continue to shape the martian environment.

(6) Lightning: We know that on Earth, in addition to thunderstorms, lightning-like electrostatic discharges can occur during volcanic eruptions (*Anderson et al.*, 1965; *Brook et al.*, 1974) and possibly earthquakes (*Finkelstein and Powell*, 1970). Signatures of meter-length discharges have been detected during dust storms on Earth (*Kamra*, 1972) and may also be generated by martian dust storm activity (*Eden and Vonnegut*, 1973; *Briggs et al.*, 1977). The prevalence of electrostatic discharge phenomena needs to be assessed. A broadband radio receiver is an excellent sensor for detecting the impulse noise from discharge events.

(7) Meteor trails: As meteors impinge upon and pass through the upper atmosphere and are heated by atmospheric friction, they leave behind trails of ionized plasma that may last for several seconds or longer. Radio waves will be reflected off the ionization trail. A groundbased receiver can be used to detect and count meteor events by the echoes or "pings" of the reflected signal off the ionization trail. Terrestrial meteor-burst communications systems also utilize this concept. On Mars, reflections of the lander-orbiter UHF communications signal can be used to determine the rate of capture of meteors and the height of mass deposition in the atmosphere. These are important parameters because they affect the middle atmosphere chemistry and can provide bounds for numerical models of mass accretion on early Mars.

### 5.3.2. Comets

The new generation of cometary landers for post-ROSETTA comet missions may address a number of the scientific objectives identified below.

*Dust*. The mineralogical and chemical compositions of cometary dust are indicators of conditions during their formation and of subsequent evolution. We wish to measure the abundances of the major elements (including their isotope ratios) and to determine the physical state of the material—whether it is crystalline or amorphous. Dust particle structure is indicative of the conditions at formation. Thus, we wish to determine if comet dust particles are aggregates of submicrometer silicate and organic refractory grains, perhaps originating as interstellar dust grains onto which nebular gases condensed. Measurements of the size distribution of the refractory grains are required in order to compare the size distributions of interstellar grains and the degree to which the condensation occurred before aggregation. The size distribution can be assessed by a combination of observations, including imaging at a resolution of 0.1 µm or better, particle density measurements, and light-scattering measurements.

The processes affecting the physical parameters of the flowing dust in the coma are poorly characterized. This includes changes in volatile contents, grain velocities, temperature, and electrical charge. By studying the grain evolution, we study the dust-gas interaction in the closest analog to pristine conditions. This interaction includes the fundamental physics needed to model dust-gas interactions in many astrophysical settings, including the presolar nebula. The masses and velocities of the dust particles must be measured to derive the dust flux from the comet and therefore its mass loss rate. Velocity vectors should be measured with sufficient accuracy to allow trajectories to be traced back to approximate ejection sites. This means measurement of speed up to a few meters per second and direction to within 10°. The nominal dust velocity near the nucleus has been assumed to range from 1 m/s to several 100 m/s. These critical velocities have not been measured and cannot be derived from visible or IR dust spectra. We note that there may be complex dynamical behaviors in the transition region near 10 cometary radii, where radiation pressure and gas drag on a particle are of comparable strength. Velocity measurements should be made in this region as well to characterize the phenomenon. The loci of dust measurements should have sufficient coverage to derive the morphology of dust flow and to allow the study of its diurnal change.

*Parent molecules.* These are thought to be the least-modified remnants of the early solar system, and thus their chemical and physical structures contain important clues to its evolution. As discussed above, the last decade has witnessed a great increase in the number of known parent, and therefore possibly nucleogenic, species in cometary comae. Characterization of these parent species is a high-priority goal because of their importance for comet atmosphere speciation, for understanding volatiles in the early solar nebula, and for their possible roles in prebiotic chemistry.

A comet lander would be well situated to investigate parent species. An obvious measurement would be of high-resolution IR spectra (particularly in the 1–5 µm region) of molecular species as they evolve off the surface. A passive instrument viewing tangential to the surface could potentially measure a long path of near-surface molecules. This would serve to unambiguously identify those species that arise from the nucleus. If the spectral resolution is high enough to resolve individual rotational lines ($\lambda/\Delta\lambda$ of ~10,000 should be sufficient for all species), it would be possible to characterize the ground- and excited-state vibrational and rotational manifolds and thus serve as a probe of the vibrational and rotational temperatures and non-LTE effects in this region. Molecular production rates retrieved from these spectra would be less sensitive to model assumptions (e.g., temperature, velocity, and composition profiles) and other parameters (e.g., lifetime in the solar radiation field) than those obtained from instruments viewing the nucleus from a distance. Such measurements should be sensitive enough to measure production rates on the order of 0.01% with respect to water and to obtain isotopic ratios, especially $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{17}O/^{16}O$, and D/H, for some species. If the spectrometer's view field could be scanned, it could be used to map active gas-emitting regions of the nucleus, to determine their temporal variability, and to detect possible spatial inhomogeneity in the mixing ratios of the evolved gas. These data would be especially useful if they could be combined with high-spatial-resolution visible images of the cometary surface (e.g., from an orbiter). By scanning the field of view of the spectrometer in the vertical direction, composition profiles could be obtained, the photochemistry of the coma (e.g., radiation lifetimes) could be probed, and the spectra of the ionic and radical breakdown products could be studied. If a full vertical scan were not feasible, the most useful view would be directly up from the surface.

In addition to an IR spectrometer, an ideal surface lander would be equipped with several other instruments. Mass spectrometers, neutral and/or ionic, would provide local measurements of the parent species, including those without appreciable IR absorptions/emissions, such as noble gases and homonuclear diatomics; it would also provide near-surface concentration of rare species, such as ions and radicals. These measurements could also provide information on the temporal variability of the local production rate, which could be compared to the spatially integrated information obtained from the IR. A system to measure radial velocities and kinetic temperatures of molecular species would be required to understand the dynamics of cometary atmospheres. In order to obtain this information from spectral lines requires resolutions of $5 \times 10^5$ or greater. While this may be impractical for a spectrometer covering the full spectral range, methods could be developed (e.g., miniaturized heterodyne techniques) that could obtain the requisite resolution in the vicinity of a few lines of $H_2O$ and $CO_2$, for example. Such an instrument, when viewing above the surface, could detect jets and, in combination with an instrument for observing dust velocities (e.g., a lidar), could be used to elucidate the coupling between the dust and the gas.

The lander should also carry instruments for measuring the size distribution, physical properties and composition of the dust, and rotational state and density of the nucleus. These measurement goals are in addition to those of the volatile species, and will be described elsewhere.

## 5.4. REPRESENTATIVE INSTRUMENTS

There are many instruments available that can be used to address the measurement objectives and crucial scientific objectives to be accomplished by a particular lander mission.

### 5.4.1. Cameras and Spectrometers

*All Sky Camera.* A wide-angle imaging device with multispectral capability has many applications to atmospheric studies from landers (e.g., *Clancy*, 1994). Potential measurements range from aerosol and constituent observations of the Mars atmosphere to gas and dust emission morphology on the surface of a comet. All Sky Cameras are particularly valuable for studying the temporal and spatial evolution of atmospheric phenomena. The commercial development of CCDs has permitted substantial reductions in the cost and size of such cameras. Imaging through relatively simple filters permits imaging of molecular bands (such as ozone, water, and methane) at ultraviolet to near-IR wavelengths. Aerosol properties (size distribution, particle shape, composition) can be determined with an appropriate set of measurements (such as the angular distribution of scattering, polarization, and wavelength dependencies). Active filter devices (such as acousto-optical filters) with narrower wavelength resolutions should be possible in the near future, and will greatly expand the scientific capabilities of All Sky Cameras. It is currently possible to build small All Sky Cameras for landers with weights less than 1 kg. Power requirements are similarly small (<2 W). However, data rates may be the key limiting factor for All Sky Camera experiments.

*Microwave/IR spectrometers.* Spectroscopy at thermal wavelengths provides the best opportunity for remote measurements of the widest complement of atmospheric molecular species. It also allows for remote temperature measurements from abundant, well-mixed species such as $CO_2$ and CO. A typical microwave spectrometer is designed to measure one or two molecular species with high-frequency resolution (and can resolve Doppler line widths) and with one spatial element. Infrared spectrometers cover a much broader frequency range with frequency resolution that does not resolve the Doppler widths of individual lines, but they can achieve spatial mapping with detector arrays. Microwave spectroscopy is particularly valuable for remote measurements of strong microwave lines such as for CO, $H_2O$, HCN, $HC_3N$, and $NH_3$. This is because of the simplicity of microwave transitions, the typical unimportance of aerosol scattering, and the high-frequency resolution of microwave spectroscopic techniques (heterodyne). As such, it could be possible to obtain temperatures and windspeeds from the Doppler shifts and linewidths of single millimeter lines such as for CO. On the other hand, thermal IR spectrometers can detect a much broader range of molecular lines and species and can provide the thermal properties of aerosols. Current microwave spectrometers have been proposed for planetary missions with weights of 7–20 kg, and power requirements of 5–15 W. Data rates are typically small. Improvements in microwave technologies should reduce the weight and power requirements by factors of 2 in the near term (particular from developments in spectrometers/backends).Thermal IR (7–50 µm) spectrometers have been proposed for Mars landers with weights ~3 kg. Power requirements are ~3 W.

### 5.4.2. Integrated Aerosol/Dust Analyzer

An integrated aerosol/dust analyzer would measure the angular distribution of light scattered from individual dust grains, their velocity vectors, and masses. The instrument is based on the concept of interchangeable components to tailor the instrument to a broad range of conditions. Specifications here are for the base configuration, approximately 12 × 10 × 10 cm in size, 1 kg in mass, and with an entrance aperture of 1 $cm^2$. The instrument can detect particles as small as 1–0.1 µm diameter at velocities below 1 km/s. Normal operation is in an alert mode, when the instrument is inactive except for a light screen across the entrance; power consumption is 200 mW. On detection of light scattered from a particle, the instrument enters active mode and consumes ~1 W for the <1 s required to analyze each particle. On detection, the particle passes through two mutually perpendicularly polarized light screens and then impacts a piezoelectric mass detector array. Standard polarized scattering elements of the scattering matrix are determined at 6–10 discrete scattering angles ranging from approximately 40°–160°. The total intensity and the degree of linear polarization can then be calculated. This is sufficient to estimate particle cross section and reliably distinguish fluffy aggregate particles from compact dust and absorbing compounds from dielectrics.

The time of flight between light curtains defines the dust velocity along the instrument axis. The complete velocity vector is derived from the location of the intercepted mass detector using the knowledge of the direction to the detector from the entrance aperture. The integrated aerosol/dust analyzer is thus able to also yield an estimate of the particle density from the cross section and mass measurements.

### 5.4.3. Radio Science (Radio Receiver and Ionospheric Sounder)

Although radio techniques have seen long service on Earth, their application to the investigation of the atmosphere of another planet have been limited to orbiting radio occultation measurements. Global and long-term observations of the bottomside martian ionosphere are needed to gain a quantitative understanding of the dynamic processes at play that shaped and continue to shape the martian atmosphere.

Radio techniques are ideally suited for the *in situ* study of planetary ionospheres and atmospheric emissions. For example, a radio-science experiment deployed on the surface of Mars could provide much greater temporal and spatial coverage of the martian atmosphere than any previous mission has provided.

A key question is what radio-wave-sensing techniques are appropriate for the unique conditions expected on Mars? Three candidate instruments include the broadband (VLF-HF) radio receiver, the Relative Ionospheric Opacity Meter (Riometer), and the ionospheric sounder (or ionosonde). Using modern design techniques and components, radio instrument size, mass, and power might be reduced by an order of magnitude over present commercial systems, making these radio instruments viable candidates for landed missions. Reductions in electronics might be achievable with surface-mount technology, large-scale integrated circuits, multi-die-on-substrate modules, and multilayer circuit-board design. For further reductions, some hardware functions might be replaced by software.

*Broadband radio receiver.* Atmospheric and exoatmospheric radio noise covers a broad spectrum (kilohertz to hundreds of megahertz). Radio frequency receivers and electric field probes have flown on a number of space missions. None has been operated from the surface of Mars. However, this configuration is needed to characterize the *in situ* radio frequency environment because signals generated in the lower atmosphere and at frequencies below the local plasma critical frequency cannot penetrate through the ionosphere, and therefore are not detected by orbiting sensors.

Whistlers (dispersive radio signals that travel along the Earth's magnetic field lines) are generated by lightning and can be detected on the ground by VLF receivers. Plasma processes in the terrestrial magnetosphere also generate other signals. Recently, broadband HF radio receivers have demonstrated their utility for surface-based sensing of the terrestrial ionosphere-magnetosphere and have been used to detect and study natural plasma emissions originating or passing through the bottomside ionosphere (*La Belle and Weatherwax*, 1992; *Weatherwax et al.*, 1994). We know little about the natural radio emissions in the lower atmosphere of Mars. The amplitude and spectral of the noise environment would provide new information. A candidate broadband radio receiver for studying planetary emissions might cover a frequency range from 10 kHz to 10 MHz, with a resolution of a few kilohertz (i.e., *Clegg et al.*, 1993).

A surface-based broadband receiver could also be used cooperatively with one of the planned topside sounder missions to make ionospheric measurements. The receiver would make electron density measurements by receiving the signal from the topside sounder. This configuration would limit measurements to frequencies above the peak ionospheric critical frequency (because radio waves at frequencies below the critical frequency are refracted back toward the transmitter and into space). However, it would extend the spatial coverage of topside sounder measurements.

*Relative ionospheric opacity meter (Riometer).* The Riometer has been used to study phenomena in the lower terrestrial ionosphere (in the D and E regions) and also at higher altitudes in auroral latitudes (*Little and Leinbach*, 1958). The Riometer measures small variations in electron density at ionospheric heights by determining the absorption in the ionosphere of cosmic radio noise (RF energy emitted from stars in the galaxy). This is done by measuring the radio noise power when absorption is present and comparing it to the nonattenuated level at the same sidereal time, i.e., by comparing the same radio source during absorbed and nonabsorbed times. The Riometer consists of an antenna connected to a self-calibrating receiver, and it is generally operated at a fixed frequency in the high-HF or low-VHF range. The receiver is continuously calibrated by rapidly switching the receiver input between a noise diode and the antenna. Differences between the diode and antenna noise levels produce a square wave signal at the switching frequency. This signal is detected in the receiver, integrated, and fed back to drive the noise diode so that its noise output matches the antenna's. The current through the diode is proportional to the noise power at the antenna. This diode current is sampled as the Earth's rotation sweeps the antenna across the radio sky.

For the radio frequencies normally used for riometry (20–50 MHz), the required antenna has dimensions on the order of 3–8 m. A typical commercial Riometer receiver has a mass of about 1 kg and requires about 1 W of power, excluding the antenna and data acquisition system.

The martian ionosphere might be even more sensitive to riometry than the Earth's (*Detrick et al.*, 1995). The dominant neutral molecule affecting radio wave absorption in the terrestrial atmosphere (to 200 km altitude) is $N_2$, whereas $CO_2$ plays this role in the martian atmosphere. The electron-neutral collision frequency (which determines the efficiency of absorbing radio waves) for $CO_2$ is at least an order of magnitude greater than for $N_2$ at temperatures present in the lower atmospheres of both planets. For this reason it appears radio wave absorption is greater in the martian atmosphere even though the neutral densities are less.

*Ionospheric sounder.* The ionospheric sounder has been a workhorse for probing the terrestrial ionosphere for over 50 years. Until recently, ionosondes required large antenna structures and kilowatts of transmitted power. However, modern electronics and signal-processing techniques have considerably reduced the size, mass, and power requirements (*Barry*, 1971; *Poole*, 1985). Topside sounders have been flown on spacecraft and are planned for future missions (e.g., Mars '96, Planet-B), and should now also be considered for planetary lander missions. Ionosondes operate in one of two modes. In the monostatic mode, the transmitter and receiver are collocated. A pulse is transmitted vertically and received after being refracted back to the ground by the ionosphere. The time delay between transmitted and received signals gives the apparent, or "virtual," height of the reflecting layer. In the bistatic mode of operation, the transmitter and receivers are separated from each other by some distance. The obliquely propagated signal is refracted back to the surface beyond the horizon, and the measured ionospheric information (the ionogram) is assumed to be applicable at the midpoint of the ray path.

The actual time of travel of the ionosonde signal is a function of electron density along the radio ray path, and includes retarding effects of the ionosphere and the increased path length due to refraction of the ray. By varying the frequency of the pulse, a virtual height-vs.-frequency chart, or "ionogram," is obtained. The electron density profile can be derived from the ionogram in a straightforward manner. Successive ionograms allow measurements of the time variations of the electron density profiles. The layer shapes and other properties of the ionograms give an understanding of the plasma scale heights, and the constituents in each layer. Estimates of the time constants for growth and decay of ionization provide additional information about each layer and the chemistry that dominates each region.

Fluctuations in heights of ionospheric layers are related to standing or traveling waves that are driven by the underlying neutral gas motion. By monitoring the distribution of fluctuation periodicity, it is possible to estimate the Brunt-Vaissala frequency of the atmosphere. This indicates the natural oscillation period of the atmosphere and leads to a measure of fundamental atmospheric properties. The radio-wave attenuation as a function of frequency provides a measure of radio-wave absorption in the atmosphere. The absorption rate depends upon the constituent species and the electron-neutral and electron-ion collision frequencies, and provides insights into the ionization sources and energy deposition in the absorption region.

## 5.5. INSTRUMENT CONFIGURATION ISSUES

Multiple landers and lander/rover combinations provide new opportunities for planetary studies that use contemporaneous results from several locations to understand the dynamics of atmospheres. Indeed, the European Rosetta mission includes two landers, and the proposed joint ESA/NASA INTERMARSNET mission includes four lander packages.

### 5.5.1. Networks, Descent Measurements, and Rovers

Lander science package networks are highly recommended for planetary missions. We have in the Viking landers an illustrative model for the value of a network (*Hess et al.*, 1980), particularly for global circulation studies. The capability to obtain continuous data over long periods of time from a network of sites is an absolute requirement if we are to develop meaningful global climate models for the atmosphere of Mars. Similarly, the entry phase of every lander should be utilized as much as possible to obtain both compositional profiles and profiles of the major thermodynamic variables (temperature and pressure), particularly since the instrumentation required is likely to be very small and light. Ideally, a common "micro-" probe descent package could be included on each lander in a network. These entry probe data would then provide a basis for interpreting sounding experiments from the surface. Mobility is not recommended for atmospheres studies because the horizontal sampling of atmospheric properties must be done using parallel measurements, not series measurements.

### 5.5.2. Lander-Orbiter Cooperation

Atmospheric measurements that make simultaneous use of instruments on both the orbiter and the lander will be highly specific because such experiments will depend on the instrumentation on both the lander and the orbiter and on the orbit of the orbiter with respect to location of the lander. However, there are several very important possible cooperative measurements. The best example would be a topside sounder-lander broadband receiver combination that would effectively extend the topside sounder measurements.

### 5.5.3. Deployment and Timebase

These are two vital issues for atmosphere measurements. The performance of a magnetometer or a thermal probe can be seriously compromised by improper deployment. More generally, deployment of the instrument after landing is a serious issue with a measurement of any quantity whose behavior can be modified by ground effects. Likewise, meteorological data, dust, and aerosol data all require a long timebase of data in order to demonstrate diurnal and seasonal effects. In the case of a comet, both diurnal effects and perihelion-aphelion differences are important.

## 5.6. CONCLUSIONS

Lander instruments will make key atmospheric measurements that are unobtainable with instruments on an orbiting platform. Landed instruments can provide *in situ* analyses of trace components such as isotopic and noble gas abundances, and can provide unambiguous definitions of diurnal and meteorological variations. Perhaps more importantly, a detailed characterization of the atmospheric region just above the planetary surface is possible from a lander. This region, which includes the boundary layer up to approximately one scale height above the surface, cannot be efficiently studied from orbiting instrumentation due to the extreme difficulty in separating the atmosphere from the surface in nadir- or even limb-viewing remote observations. It is this region of the atmosphere where surface-atmosphere interactions, ranging from dust storms and volatile behaviors in the Mars atmosphere to the whole-scale evolution of surface material into atmospheric outflow on comets, are most effectively investigated. Lander instruments provide the unique capabilities to probe this surface-atmosphere boundary with remote sounding from below, *in situ* analyses, and *in situ* descent measurements.

Mars and comets are the focus of most current interest in landers by the scientific community. Much is still unknown about both. In the case of Mars, we still lack a basic understanding of the current climatic balance for volatiles ($CO_2$ and $H_2O$) within the atmosphere, the regolith, and the polar ice caps. Given the extreme interannual variability of the martian atmosphere, a reliable understanding of the current martian climate will require long-term observations of the martian atmosphere.

Comets are widely held to be the least-modified remnants of the early solar system. Thus the chemical and physical structure of comets contain important clues to the formation and early evolution of the solar system. Although the last decade has witnessed an explosion of knowledge concerning the physical and chemical makeup of comets, there is still much to do. Two critical areas that can be uniquely addressed by landers are volatile and refractory evolution. If we understand the origin and evolution of the gas and dust that we observe remotely, we can determine what a comet is made of, how the components are put together, and how they come apart. Comets may be preserved samples of original solar nebula condensates.

We have given some examples of representative instruments that could be placed on a lander. In general these instruments are small and consume little power. Thus, the science return from these instruments could be quite high in terms of both their delivery costs and their costs of spacecraft resources (mass, power, and data rate). Lander science networks are highly recommended for planetary missions. Indeed, the European Rosetta mission includes two landers, and the proposed joint ESA/NASA INTERMARSNET will deploy landers at four locations. Lander and lander/rover combinations provide new opportunities for planetary studies that use simultaneous results from different sites to study the dynamics of atmospheres and comae.

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## APPENDIX 5.1. A MINIATURE LIDAR FOR ATMOSPHERIC MEASUREMENTS FROM PLANETARY SURFACES

*James Abshire and Jonathan Rall*

Miniature lidar are small, lightweight, low-power lidar that can characterize several important properties of the planetary atmospheres. They are designed with diode laser transmitters with small (typically <15 cm diameter) receiver telescopes. Although the system parameters can vary greatly with the application, a typical minilidar weighs a few kilograms, consumes a few watts, and produces a data stream of ~10 bits/s.

Lidar measurements are well suited for the measurement of planetary atmospheres. They can address the following questions (from TePSWG) about atmospheres of terrestrial planets: (1) chemistry, pressure, and temperature of the atmospheric volatiles; (2) composition, temperature, and pressure of the lower atmosphere; (3) surface wind regime; and (4) mechanisms to transport materials at the surface.

Lidar measurements can address the following questions (from SBSWG) about the atmospheres of comet and asteroids: (1) characterizing the chemical and physical natures of the atmospheres; (2) characterizing the processes that occur in them; (3) measuring development of gas and dust coma as a function of time; (4) characterizing dynamics of comet tails with solar wind and radiation; and (5) detecting gas or dust in the vicinity of asteroids as evidence of endogenic activity.

The study of optical scattering by gases and aerosols has a long and rich history (*McCartney*, 1976). Lidar techniques have been employed since the early 1960s to study many properties of the Earth's atmosphere (*Measures*, 1984; *Reagan*, 1991). Although lidar systems for Earth can be large, using diode lasers permits a miniature version for planetary applications. The diode lasers used in minilidar are small and very efficient producers of laser radiation (*Thompson*, 1980; *Zory*, 1993). A typical semiconductor laser package is similar to those used in CD players and handheld laser pointers. Diode lasers are single semiconductor chips and are the smallest, lowest-mass, most efficient, and most rugged lasers that exist today. The diode laser chip is inside this package, and its light is transmitted through the front window.

One possible configuration of a landed minilidar is shown in Fig. A5.1. For a landed mission, the lidar would likely be attached to a platform for zenith-viewing instruments. The diode laser transmitters are on the left and the backscattered signal is collected by the telescope. The small box under the telescope contains the receiver optics, detector, and electronics.

A view of a representative minilidar for aerosol measurements is shown in Fig. A5.2. The diode lasers transmit their light to zenith, and the backscattered light is collected by the telescope. After passing through a field stop and bandpass filter to reject background light, the signal is focused onto a solid-state photon-counting detector. The resulting detector pulse stream is recorded into a histogram register used to accumulate the backscatter vs. range profile. Since the diode laser has a limited peak power, the lidar receiver must use signal averaging to develop a sufficient signal-to-noise ratio (SNR). The received SNR scales directly with the scatter's backscatter coefficient, with the square root of the averaging time and inversely with the range squared.

The diode light is highly polarized and anisotropic scatterers such as ice crystals depolarize the backscattered laser signal. Using a second detector that senses the orthogonal polarization permits the backscatter profile to be accumulated for the orthogonal polarization. Measuring signal profiles for both the parallel and orthogonal polarizations allows range vs. density of the anisotropic particles to be computed.

A block diagram of a breadboard minilidar is shown in Fig. A5.3 and typical characteristics are summarized in Table

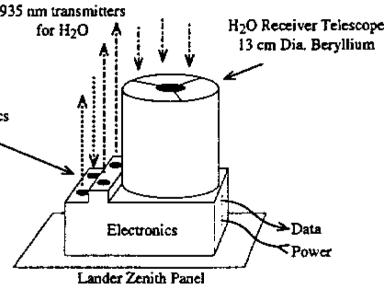

**Fig. A5.1.** Concept sketch of landed minilidar instrument.

A5.1. The transmitter is a single diffraction limited diode laser, whose intensity is digitally modulated at 1 Mbit/s. Either pseudonoise (PN) (*Dixson*, 1976; *Takeuchi et al.*, 1983, 1986) or conventional low-duty-cycle pulse-code modulation can be used. The receiver telescope focuses the backscattered signal and background light onto the photon-counting Si APD detector. The optical background light is reduced by using a small field of view with a narrow optical bandpass filter. The electrical pulses from the detector are passed through a threshold circuit and accumulated in a histogram circuit. After the signal integration is complete, the backscatter vs. range profile is computed by numerically cross correlating the accumulated histogram signal with a stored replica for the transmitted code (*Abshire and Rall*, 1993). This can either be computed within the instrument, or the histogram can be transmitted and the lidar profile computed on Earth.

### A5.1.1. Typical Measurements

The minilidar instrument is well suited for the following types of atmospheric measurements:

*Aerosol and polarization profiles.* The simplest minilidar measures the strength of the laser's backscatter signal vs. range. The scattering strength vs. range can be derived by first applying the $R^2$ correction to the profile and then by applying a lidar inversion. If the properties of the scatterer particles are known, this measurement can be converted to a number-density profile. Scattering particles such as ice crystals are anisotropic, and the scattering process can rotate the laser's polarization. By adding a cross-polarized channel to the lidar receiver, both the parallel and perpendicular lidar profiles can be measured. With these, the ice vs. dust ratio can be measured along the measurement path.

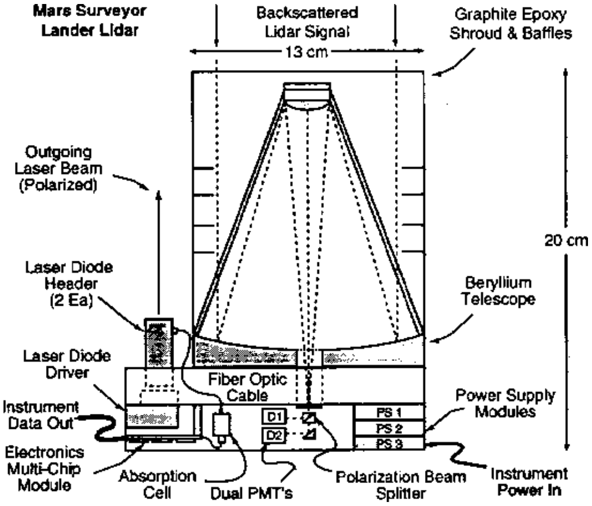

**Fig. A5.2.** Minilidar cross section.

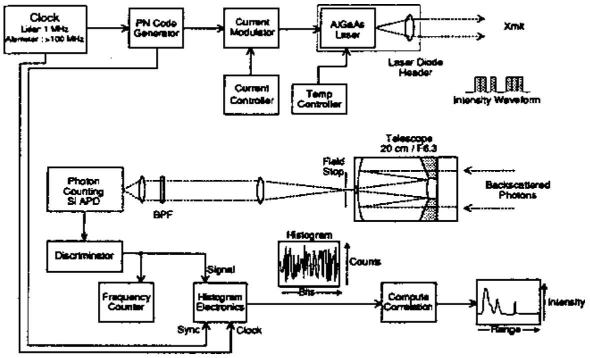

**Fig. A5.3.** Block diagram of aerosol minilidar.

*Species density profiles.* An atmospheric species density vs. range profile can be measured by using the differential absorption lidar (DIAL) technique. An atmospheric absorption line is selected that is well isolated and temperature insensitive. A laser is selected with a linewidth that is narrower than the molecular absorption line. Two lidar profiles are measured, one with the laser locked onto the peak of the absorption line and one with the laser tuned to a nearby line-free region. By taking the ratio of the two range-corrected lidar profiles, the density profile of the species can be obtained (*Rall et al.*, 1994). Since direct current modulation used to impress a ranging signal can also broaden the diode emission spectrum, an external optical modulation can be required for DIAL measurements with diode lasers.

TABLE A5.1. GSFC diode minilidar: Configuration of November 1992.

| | |
|---|---|
| Laser type | diode laser, AlGaAs, SDL 5410 |
| Laser power | 35-mW average, 70-mW peak (typical) |
| Laser modulator | current steering, negative drive |
| Collimating lens | three-element, NA = 0.5 |
| Beam expander | ×8 ratio nominal |
| Transmitter div. angle | 100 μrad |
| PN code generator | 255- and 4095-bit, 1-MHz bit rate |
| Range resolution | 150 m/bit |
| Telescope | Schmidt-Cassegrain, 20 cm diameter, f6.3 |
| Interference filter | 810-nm, 10-nm bandpass |
| Receiver field-of-view | 160 μrad |
| Detector | Geiger mode Si APD, EG&G |
| Signal processor | histogram circuit sync'ed to transmit code |
| Controller | Gateway 486/33 |

*Measurement of trace-gas concentrations.* The DIAL technique is also useful to make sensitive measurements of trace-gas concentrations. In this case the lidar can be pointed horizontally across a planetary surface, where the trace-gas concentration is expected to be approximately uniform. Both the on-line and off-line signal undergo a constant absorption for each range bin, and the online signal has a small additional absorption due to the trace gas. By fitting negative exponential functions to the range-corrected lidar profiles, the small additional extinction coefficient of the trace gas can be measured. This approach has the advantage that the absorption path can be many kilometers long, allowing a more sensitive and representative measure of gas density.

*Wind profiles.* The velocity of atmospheric scatters can be determined by measuring the Doppler shift of the backscattered lidar signal. These lidar operate by using a transmitter laser with a narrow linewidth. To preserve the linewidth, the ranging signal is typically impressed with an external modulator. The receiver collects the backscatter and measures the optical frequency shift vs. range. This is most commonly done by using a heterodyne receiver, which optically mixes an optical local oscillator signal with the backscattered light. This down-converts the signal to an electrical signal at a convenient frequency, where its frequency is determined by signal-processing electronics.

Optical heterodyne techniques can be difficult, since they place several additional constraints on a miniature lidar in the area of optical alignment, laser mode control, receiver telescope quality, and mode and polarization matching. Because of this, several research groups are investigating using simpler direct detection receivers for Doppler measurements. One approach is to use receiver optical filters whose transmission is frequency selective. Candidate filters include the edge of a molecular absorption line, an edge of a Fabry-Perot filter transmission, or an optical interferometer. The ratio of the received backscatter to the receiver detectors depends on the optical frequency and hence to the Doppler shift.

*Temperature profiles.* The temperature profiles of atmospheric gases can also be measured with minilidar. One technique uses DIAL measurements, but it uses two nearby well-isolated molecular lines that have a large difference in their temperature sensitivity. DIAL profiles are measured on each and are range corrected. Since the gas-density profile is assumed to be the same for both measurements, the ratio of the measured DIAL profiles depends on the temperature of the absorbing gas. The sensitivity of this technique depends on the difference in temperature sensitivity of the selected molecular lines.

### A5.1.2. Key Technologies

Minilidar is based on recently developed electro-optics technology. The key component is the diode laser, which was developed to serve the commercial markets in optical recording, laser printing, and fiber-optic communications. Diode lasers are now available that operate efficiently at room temperature over wavelength spans from ~600 to 1600 nm. The diode laser output can be directly coupled into the atmosphere or can be coupled into single-mode fibers. Using fiber optics saves mass by largely eliminating the need for optical benches, turning mirrors, and mounts. The laser backscatter from the atmosphere can be collected by either telescopes or lenses. Advances in Be and SiC optics now permit rugged small telescopes to be produced that are temperature insensitive with mass <200 g.

Since the peak power from diode lasers is limited, using sensitive detection techniques is essential. When operating at wavelengths <1000 nm, avalanche photodiodes operated in the Geiger mode can be used as photon-counting detectors. These are small, solid-state, and have photon-counting efficiencies of >25% when operating at wavelengths <840 nm. For laser wavelengths >1000 nm, photon-counting detectors have poor quantum efficiency and high internal noise. Optical heterodyne techniques are best suited for these wavelengths. Heterodyne receivers are used regularly for both 2.0- and 10.6-μm lidar. However, they require good control of the transmitter wavelength stability, its spectrum, and its spatial beam pattern. There are additional requirements in the receiver of polarization and mode matching the local oscillator and receiver. However, the diode laser transmitters, receivers, and fiber-optic components are small and available for fiber-optics communications near the 1300- and 1500-nm regions. The component size and maturity makes this an attractive option for future investigations.

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# 6: Mineralogy

*—M. Darby Dyar, Allan Treiman, Patricia Beauchamp, David Blake, Diana Blaney, Sun S. Kim, Goestar Klingelhöfer, Greg Mehall, Richard Morris, Zoran Ninkov, Ann Sprague, Michael Zolensky, and Carlé Pieters*

## 6.1. INTRODUCTION

Minerals are described and defined not only by the elements they contain, but by the positions of the atoms relative to each other in their structures. Strictly speaking, minerals must be naturally occurring crystalline solids, since only crystalline materials can have stoichiometric elemental compositions and only crystalline materials can be phases in the thermodynamic sense, and can be placed on a stability diagram. The power of mineralogical analysis as a descriptive or predictive technique stems from the fact that only a few thousand minerals are known to occur in nature (as compared to several hundred thousand inorganic compounds), and all have specific stability ranges in pressure, temperature, and composition (PTX) space. A specific knowledge of the mineralogy of a planet's surface or interior therefore allows one to characterize the present or past conditions under which the minerals were formed or have existed. Thus, mineralogical studies are extremely well suited for characterization of planetary histories. For the purposes of this chapter, we will choose to adopt a slightly broader definition of mineralogy by including not only crystalline materials found on planetary surfaces, but also ices and glasses that can benefit from *in situ* types of analyses.

Because minerals make up the small-scale constituents of rock, they can best be studied by using *in situ* measurements. *In situ* mineralogical observations provide significant advantages over remote observations for several reasons. Perhaps the most important is that a variety of mineral-specific, mineral-sensitive techniques can be used. This permits better constraints on mineral identification and relative abundances than can be obtained from remote sensing. *In situ* measurements are made at spatial resolutions not obtainable from orbit. Mineral identification, abundance, and spatial distribution are essential for understanding formation and weathering processes.

In keeping with the theme of this volume, this chapter addresses the instrumentation needs for planetary surface exploration through two avenues. In the first section, 13 analytical techniques for mineral analysis and identification are presented, including estimates of state-of-the-art precision and current implementations of each method (Table 6.1). A brief discussion of the scientific background for each technique is presented, along with a reference list for further information of the topics tabulated here. It is hoped that this section will provide a background reference for future mission planning and instrument development.

In the second section of this chapter, mineralogical problems that can be studied with these methods are addressed. The types of mineralogical questions that can be answered on different planetary surfaces vary widely according to the type of body being studied. Due to the need to customize instrumentation for various conditions, this section is subdivided according to three different body types: primitive bodies, differentiated bodies without atmospheres, and differentiated bodies with significant atmospheres (Table 6.2, Table 6.3, and Table 6.4). Furthermore, the mineralogical questions are organized according to the types of planetary processes they address. Mineralogical studies can be used to constrain a number of planetary processes that are highlighted here: condensation, differentiation, volcanism, impact cratering, physical weathering, chemical weathering, and metamorphism. Tables in this section summarize which types of mineralogical instrumentation are needed to address which types of processes on each type of extraterrestrial body. Again, these tables are constructed to provide easy references to the instrumentation needed to address body-specific planetary processes from a mineralogical perspective.

## 6.2. METHODS

### 6.2.1. Visual Imagery at Microscales

Visual examination is among the most rapid and powerful tools for mineral identification, but is easily overlooked amid the plethora of "high-tech" spectroscopies available for robotic probes to planetary surfaces. Visual examination is the first step in mineral identification. It is taught to beginning geology students, used by professional mineralogists and petrologists in nearly all phases of investigation, and is almost always applied before more detailed or quantitative techniques (like electron microscopy, X-ray diffraction, etc.). Visual mineralogy has an honorable history in planetary exploration; it was the principal mineralogic tool on the Apollo missions and led directly to important discoveries, like "Genesis Rock" anorthosite found by the Apollo 15 astronauts. Unfortunately, robotic imaging instruments on past probes to planetary surfaces (Surveyor, Viking, Venera, VEGA) were not useful for mineralogy because their spatial resolution was too poor.

Visual examination as a mineral identification tool relies on the optical reflection properties of mineral surfaces. In effect, these properties are observed, and the observations compared with a huge database of similar observations on all known minerals (terrestrial, meteoritic, and lunar). The com-

TABLE 6.1. Analytical techniques for mineralogy.

| # | Technique | Uses | Precision | Status* | References |
|---|---|---|---|---|---|
| 1 | Visual Imagery | Mineral and texture identification | To 100-µm scale | 2 | *Compton*, 1962; *Fry*, 1984; *Jakeš*, 1992; *Jakeš and Wänke*, 1993; *Thorpe and Brown*, 1985; *Tucker*, 1982 |
| 2 | X-Ray Diffraction (XRD) | Mineral identification and abundance, size >0.1 mm | Identification unequivocal; abundances ~5% | 3 | *Bish and Post*, 1992; *Brindley*, 1980; *Clune*, 1974a,b; *Goldsmith et al.*, 1961; *Hill and Howard*, 1987; *Howard and Preston*, 1989; *Jones and Bish*, 1991; *Kastalsky and Westcott*, 1968; *Klug and Alexander*, 1974; *O'Connor and Raven*, 1988; *Post and Bish*, 1989 |
| 3 | Mössbauer | Fe oxidation state and mineralogy of bulk samples | 1% of total Fe; 1–50% of bulk | 1 | *Klingelhöfer et al.*, 1995; *Agresti et al.*, 1992; *Burns*, 1993 |
| | | Evalution of magnetic properties | | | |
| | | Fe oxidation state on microscales | | 5 | *Agresti et al.*,1992; *Fegley and Wänke*, 1992; *Knudsen et al.*, 1991; *Kankeleit et al.*, 1994a,b; *Klingelhöfer et al.*, 1992 |
| 4 | Visible-Near-IR Spectroscopy | Abundances, cation OH stretches, $CO_2$ overtones, OH, $H_2O$, and $CO_2$ ions, $SO_2$ frosts, N ices; phase identification and abundances | To ±5% abundance | 1 | |
| 5 | Mid-Thermal-IR Spectroscopy | Silicate groups, composition; ionic salts; clays and hydroxyl-bearing phases; phase identification; ions and suspected glasses; thermal conductivity | Presence/absence | 1 | *Arnold and Wagner*, 1988; *Hapke*, 1993; *Logan et al.*, 1972; *Nash*, 1991; *Nash and Salisbury*, 1991; *Pieters and Englert*, 1993; *Sprague et al.*,1994; *Vilas et al.*, 1984; *Wittebom and Begman*, 1984 |
| 6 | Electron Magnetic Resonance (EPR, FMR) | Paramagnetic transition, metal ion abundances (FeO, $Fe^{3+}$, $Mn^{2+}$, $Ti^{3+}$, $V^{4+}$, etc.); also paramagnetic rare earth elements, radicals, defects | ppb in the lab | 5 | *Abragam and Bleaney*, 1970; *Hall*, 1980; *Kittel*, 1948; *McBride*, 1990; *Pinnavaia*, 1982; *Rado and Suhl*, 1963; *Tsay*, 1971; *Vonsovskii*, 1966 |
| | | | ppm in flight | 3 | *Kim and Bradley*, 1994 |
| 7 | Nuclear Magnetic Resonance | $H_2O$, H, OH | 0.1 wt% | 3 | *Abragam*, 1961; *Martin and Martin*, 1980; *Pople et al.*, 1959; *Wilson*, 1987 |
| 8 | X-Ray Fluorescence (XRF) | <millimeter beam size analysis of major elements | <1 mm | 1 | *Bertin*, 1978; see Chapter 2 |
| 9 | Scanning Electron Microscope/Energy Dispersive X-Ray Analysis (SEM/EDX) | <micrometer beam size analysis of major elements; mineral form and texture | Images, 50 nm; analyses, 1 µm, ± 0.5 wt% | 4 | |
| 10 | Raman Spectroscopy | Mineral identification, abundances | <5% abundance on 50-µm area | 4 | *McMillan and Hofmeister*, 1988; *Wang et al.*, 1994; *Wdowiak et al.*, 1995 |
| 11 | Optical Fluorescence Spectroscopy | Mineral presence, particularly ionic salts | <5% abundance on 50-µm area | 3 | *Barnes*, 1958; *Geake and Walker*, 1975; *Marfunin*, 1975; *Waychunas*, 1988 |
| 12 | Thermal Analysis (Differential Thermal Analysis, Differential Scanning Calorimetry) | Identification and abundances of minerals containing volatile species (OH, $CO_3$, $SO_4$) and other with phase transitions | | 2 | See also Chapter 3 |
| 13 | Magnetization (adherence to magnets of varying strengths) | Abundance and identity of ferromagnetic minerals in powdered samples | <1% of amount present | 1–2 | *Madsen et al.*, *Knudsen and Madsen; Madsen et al.* |

*Status: 1 = at least one instrument flight-qualified; 5 = laboratory/concept only.

parison can be broadened to include all inorganic and organic substances and glasses. Visual examination is usually performed with some magnification because most mineral grains in rocks are too small for naked-eye examination. In the laboratory, binocular microscopes are the visual instruments of choice. In the field where space, weight, and convenience are at a premium, a hand lens of 5×–15× is the preferred tool for visual mineralogy.

The properties usually observed in visual examination are color, cleavage, fracture, luster, and habit. The property color is obvious; the human eye acts as an imaging three-color spectrometer, and can be trained to recognize subtle color differences that are strong indications of mineral identity. Fracture characterizes the morphology of broken mineral surfaces: smooth, irregular, conchoidal, etc. Many mineral species break along well-defined crystallographic directions;

TABLE 6.2. Mineralogic measurement goals: Primitive bodies.

| Process | Information Desired | Measurement Goal | Instruments* |
|---|---|---|---|
| Condensation | (From pristine subsurface samples:)<br>1. Phase composition and zonation of silicates, ices, salts, etc.<br>2. Modal abundance<br>3. Structure, crystallinity<br>4. Oxidation state<br>5. Hydration<br>6. Mineral textures and fabrics (intergrowths, overgrowths, crystal form, grain size) | A. >90% *mineral phases* identified (including hydrous phases and ices, clathrates, glasses) [1, 2, 3, 5]<br>B. Fe, Mg zonation in minerals [1]<br>C. *Mineral composition*: C, N, O, Na, K, Fe, Si, Mg, Ca, Al, Ti, S, Ni of minerals to 10% of CI relative compositional abundance [1]<br>D. *Modal abundances* to 5% [2]<br>E. $Fe^{2+}/Fe^{3+}/Fe^0$ to 5.2% [4]<br>F. *Grain size, shape, and texture* down to 10-µm scale [6] | A: 1–13<br>B: 1, 8, 9<br>C: 3, 4, 8, 9<br>D: 1, 2, 6, 7<br>E: 2, 3, 6, 7<br>F: 1 |
| Differentiation | 1. Texture of metal, silicates, and oxides (igneous?)<br>2. Composition of metal, silicates, and oxides<br>3. Mg# of mafics (equilibrium assemblage?) | A. Spatial *scale of* $Fe^0$ from meters to centimeters [1]<br>B. Mineral phases identified [2]<br>C. *Mineral composition*: trace-element abundance to 10% of CI; Na, K, Fe, Si, Mg, Ca, Al, Ti, S, Ni of minerals to 10% of CI relative compositional abundance [2,3]<br>D. Grain size, shape, and texture down to 10-µm scale [1] | A: 1, 6, 7 ,13<br>B: 1–13<br>C. 3, 4, 8, 9<br>D: 1 |
| Volcanism | (Vents and jets:)<br>1. Mineral assemblage and crystal form (vapor-phase condensation) | A. Mineral phases identified [1]<br>B. *Mineral composition*: trace-element abundance to 10% of CI: Na, K, Fe, Si, Mg, Ca, Al, Ti, S, Ni of minerals to 10% of CI relative compositional abundance [1]<br>C. Grain size, shape, and texture down to 10-µm scale [1] | A: 1–13<br>B: 3, 4, 8, 9<br>C: 1 |
| Impact Cratering | 1. Modal mineralogy (including glass)<br>2. Texture and grain shape (veins, breccias)<br>3. Shock and thermal effects | A. *Mineral phases* identified; identify *high-pressure phases* (e.g., coesite) [1]<br>B. Grain size, shape, and texture down to 10-µm scale [2,3]<br>C. Spatial relation of glass, breccias, and mineral phases from meter to millimeter scale | A: 1–13<br>B: 1, 2<br>C: 1 |
| Physical Weathering | 1. Grain-size distribution, melt, and lithic abundance<br>2. Solar wind effects<br>3. Soil "maturity"<br>4. Depth variations<br>5. Spatial variations of exposure history on meter to millimeter scale | A. *Grain size, shape, and texture* down to 10-µm scale [1, 3, 4, 5]<br>B. $I_s/FeO$ to 10% [3, 4, 5] (+ total Fe)<br>C. *Spatial relation* of glass, breccias, and mineral phases from meter to millimeter scale [1, 3, 4, 5]<br>D. Solar wind effects [2, 5]<br>E. Detection of alteration rinds to 10 µm [2, 5] | A: 1<br>B: 3, 6<br>C: 1<br>D: 1, 12<br>E: 1, 3, 6 |
| Chemical Weathering | 1. Compositional homogeneity across grains, rocks<br>2. P/T conditions<br>3. Rate estimates<br>4. Replacement and overgrowth textures | A. Mineral phases identified [1, 2, 3, 4]<br>B. *Spatial relation* of glass and mineral phases from meter to millimeter scale [2, 4] | A: 1–13<br>B: 1 |
| Metamorphism | 1. Mineral fabrics<br>2. Degree of zoning<br>3. Mineral characteristics | A. Mineral phases identified [2, 3]<br>B. *Modal abundances* [3]<br>C. *Grain size, shape, and texture* down to 10-µm scale [3]<br>D. *Spatial relation* of mineral phases from meter to millimeter scale [1,3]<br>E. *Mineral composition* [3]<br>F. Fe, Mg *zonation* in minerals [2, 3] | A: 1–13<br>B: 1–7<br>C: 1, 2<br>D: 1<br>E: 2–6, 8, 9<br>F: 8, 9 |

* See Table 6.1 for a list of instruments.

this property is cleavage. The number of cleavage planes, the ease with which the mineral breaks, and other structures revealed by cleavage can be indicative or conclusive mineral identifiers (e.g., the characteristic lamellar twinning in plagioclase feldspar is best observed by the orientations of cleavage surfaces on individual twin lamellae). Luster describes the reflective properties of the surface, e.g., dull, glassy, resinous, adamantine (diamond), etc. Habit refers to the shape of a mineral grain; in many geological settings, minerals grow in characteristic shapes or crystal forms, which can be useful in their identification. These properties alone, along with some sense of the regional geological setting, are usually enough to allow mineral identification to at least group level. Equally important, the habits and relationships among mineral grains, their parageneses, can be characteristic of their conditions of formation and can constrain mineral identification. For instance, a white mineral associated with olivine could likely be plagioclase but would not likely be wollastonite.

A visual mineralogy system for a robotic probe to a planetary surface involves five elements: a source of illumination; a light input element (e.g., lens or aperture); a mobility system that allows the input element to be positioned close to the target sample; a light transfer path from the input system to the imaging sensor; and an imaging sensor element, which converts the optical image to electrical signals for storage/transmission. Each of these elements can be implemented in many ways.

TABLE 6.3. Mineralogic goals for differentiated bodies without atmospheres.

| Process | Information Desired | Data | Instruments* |
|---|---|---|---|
| Condensation | 1. Volatile content<br>2. Fe oxidation state<br>3. Other oxidation states<br>4. Elemental S content<br>5. Fe blebs | 1.% for all measurements at *spatial scale* micrometers to meters | 1–13 |
| Differentiation | 1. Mineralogic composition; evidence for fractional crystallization | Spatial *scale*: meters to centimeters | |
| | 2. Chemical composition of rock-forming minerals pyroxene, olivine, feldspars, others (unexpected?) | Trace-element *abundance* to 2% of CI; Na, K, Fe, Si, Mg, Ca, Al, Ti, S, Ni | 1–13 |
| Volcanism | 1. "Exotic" minerals and mineral assemblages (obsidian, cristobalite, tridymite, calcopyrite, wurtzite, pyrrhotite) for pressure/temperature of formation chronology of volcanism exothermic events (oldhamite, sphalerite, daubreealite)<br>2. Basalts: late-stage heating to surface? Sequences that give clues to interior cooling rate<br>3. Grain coatings, fumarole activity, S in atmospheres, glass | 1% abundances<br>*Spatial scales*: micrometer to centimeter | 1–13 |
| Impact Cratering | Scan crater walls for composition in variable stratigraphy | *Mineral phases* identified; *grain size, shape*, and texture to 10-µm scale | 1–13 |
| | | Spatial relation of glass, breccias, and mineral phases from meter to millimeter scale | 1 |
| | Identify *high-pressure phase* (e.g., coesite) | | |
| Physical Weathering | 1. Size distribution of grains | *Grain size, shape, and texture* >10-µm scale | 1, 9 |
| | 2. Percent glass | *Spatial relation* of glass, breccias, and mineral phases from meter to | |
| | millimeter scale | | 1, 9 |
| | 3. Alteration rinds | *Alteration rinds* to 10 µm | 9, 10 |
| Chemical Weathering | 1. Degree of cosmic-ray bombardment | *Spatial scale*: micrometer | 1, 9 |
| | 2. Water of hydration | Spatial scale: micrometer and larger | 2, 4, 5, 7, 10, 12 |
| | 3. Disequilibrium mineral assemblages | *Precision*: 0.2% | |
| | *Spatial scale*: millimeters to several meters | | 1, 4, 5, 9 |

* See Table 6.1 for a list of instruments.

A functional implementation is the Mikrotel instrument, which has demonstrated the feasibility and usefulness of such an imaging system (*Jakeš*, 1992; *Jakeš and Wänke*, 1993; see also Chapter 9). The Mikrotel incorporates the whole system except the mobility element in a single hardware unit; mobility is provided by a robot arm or moving vehicle (e.g., Nanokhod; see *Rieder et al.*, 1995) that positions the hardware unit over the surface of interest. The target scene is viewed through a magnifier lens group as the light input element; the choice of magnification depends on detail to be imaged (i.e., grain size of the soil or rock), and is adjustable to trade off the depth of focus and resolution. Light travels from the magnifier lens group to a commercial three-color CCD television camera through ambient atmosphere. The Mikrotel system produces good, European TV-quality (PAL) images of rock and sand surfaces and allows identification of millimeter-sized mineral grains. The Mikrotel system offers great flexibility, allowing different magnifications, imaging sensor elements, and data recording devices. In addition, the Mikrotel could be used as an imaging spectrometer if it had sensors active into near-IR wavelengths and tunable monochromatic light sources.

It is not known if the Mikrotel system is the most advantageous for robotic planetary instruments, because there have been no trade studies on possible element implementations. However, the success of the Mikrotel system appears to validate the general concept of a robotic "hand lens" as a remote system for mineral identification.

A visual mineralogy system cannot answer all questions relating to the mineralogy of planetary surfaces, but will provide rapid identification of common minerals, rapid constraints on less common minerals, and rapid guidance about which samples would yield the most return from analyses by more quantitative methods. Visual mineralogy also will supply critical constraints to assist in interpreting the results of more quantitative analytical methods (e.g., X-ray diffraction, IR reflection spectroscopy). A visual hand lens system is important or critical to field geology and regolith studies (see Chapters 8 and 9), and so appears to be among the highest priorities for development of planetary surface instruments.

### 6.2.2. X-Ray Diffraction Analysis

The most definitive and widely used technique of mineral identification and structural analysis is X-ray diffraction, or XRD (*Klug and Alexander*, 1974; *Bertin*, 1978; *Brindley*, 1980). When X-rays impinge on a sample, they interact with all the electrons present; most of the X-rays are scattered elastically (without change in energy). In a solid with a

TABLE 6.4. Mineralogic goals for differentiated bodies with atmospheres.

| Process | Information Desired | Data | Instruments* |
|---|---|---|---|
| Condensation | See Table 6.3 | | |
| Differentiation | See Table 6.3 | | |
| Volcanism | Rock types (mineral abundances) | Grain size and shape (in rocks)<br>Mineralogy of the phases in the rock/iron-bearing phases<br>Volatiles in magma and their relation to atmosphere composition | 1–5, 8, 10 |
| Impact Cratering | See Table 6.3 | | |
| Physical Weathering | See Table 6.3 | | |
| Chemical Weathering | 1. History of water | Hydrous phases (mineralogy, abundance, timing, distribution, and source); phase identification, 5% detection, degree of crystallinity, spatial relationships to other minerals, Fe-bearing minerals at present | 1, 2, 4, 5, 7, 10, 12 |
| | 2. Presence/depth ground ice | Permafrost at depth (meters)? | See regolith |
| | 3. History of the atmosphere | Ionic salt minerals (carbonates, sulfates, nitrates, halides, others); identification, abundances, distributions | 1–13 |
| | 4. Polar processes | Clathrates, ices | 1, 2, 4, 5, 9, 10, 12 |
| | 5. Hydrothermal systems | All mineral phases (volatile-bearing, impact glass, igneous minerals, hydrates, sulfates, carbonates, nitrates, Fe oxides, sulfides); identification, degree of crystallinity, abundances, distribution | 1–13 |
| Metamorphism | See Table 6.3 | | |

* See Table 6.1 for a list of instruments.

repeating pattern of atoms (i.e., a crystal), X-rays scattered from a layer in the pattern interfere with those scattered from other layers in the pattern. When the X-rays interfere constructively, they form a *diffracted* beam of X-rays that emanates from the sample and can be detected. The directions of the diffracted beams are given by Bragg's law: $n\lambda = 2d \sin(\theta)$, where $n$ is an integer, $\lambda$ is the wavelength of the impinging X-rays, $d$ is the distance between successive diffracting layers, and $\theta$ is half of the angle between the incident and diffracted beam directions.

If the target is a single crystal, the directions and intensities of all possible diffracted beams form the three-dimensional Fourier transform of the electron distribution (charge density function) in a unit cell of the crystal. In theory, the results of a full single-crystal diffraction experiment will yield the positions and identities of all atoms in the unit cell, the positions of bonding electrons, and the characteristics of the bonds (e.g., ionic vs. covalent). In practice, single-crystal XRD is difficult in laboratories on Earth because of the need to chose an appropriate single crystal, mount it precisely, and orient it precisely (which does not use the same X-ray detection device as taking the actual beam position and intensity measurements). The single-crystal XRD device then must be able to rotate the crystal around one axis (at least) and be able to move the X-ray detector around the crystal on two independent axes. Clearly, this analytical method is impractical as a robotically operated instrument on a planetary surface.

More commonly used (and much simpler to implement) is powder XRD, in which a powdered mineral sample is exposed to a collimated X-ray beam. The powdered sample will contain individual crystals in all possible orientations, so that X-ray intensities need only be collected around a single axis centered on the sample. In laboratories on Earth, this is usually implemented with the X-ray detector on an arm that swings around the sample in a single plane (the sample needs to be rotated around the same axis), and yields a graph or table of diffracted intensity vs. angle $\theta$, or vs. $d$ by Bragg's law (above). The resultant list of $d$ values and intensities can be compared to equivalent listings from standards or known minerals (published in computerized databases such as the ICDD powder diffraction file) to identify an unknown mineral. Where the sample is a mixture of minerals, many methods can be applied to identify the different minerals (*Chung*, 1974a,b; *Bish and Chipera*, 1988; *O'Connor and Raven*, 1988; *Howard and Preston*, 1989; *Jones and Bish*, 1991). A mineral abundance of a few percent is probably the minimum detection limit for conventional powder XRD on Earth. It is sometimes possible to obtain complete mineral structures (all atom positions) from powder XRD data (*Bish and Howard*, 1986, 1988; *Snyder and Bish*, 1989; *Bish and Post*, 1993).

Powder X-ray diffraction is limited as to sample type and geometry:

1. Many crystals must be exposed to the X-ray beam simultaneously. The X-ray beam (whether from a radioactive or electrical source) is typically less than about 1 mm in diameter, so the target crystals must be small. If the target material is fine grained (e.g., wind-blown dust, soil), it may be analyzed without preparation. If the target material is coarse-grained (>50 $\mu$m), its grain size must be reduced, e.g., by a drill or grinder. Alternatively, a small single crystal can be precessed through a large number of random orientations relative to the beam.

2. Results of X-ray diffraction results may not be representative of a rock or rock unit. XRD analysis of a hand sample, even if finely polycrystalline, will characterize only its outermost hundred micrometers (approximately). Unless

the sample is broken or abraded to expose fresh surfaces, the XRD analytical volume may thus include weathering rind and powdered soil. Preferred orientation of crystals within a rock may render a rock sample unsuitable for quantitative or even qualitative analysis.

### 6.2.3. Mössbauer Spectroscopy

Mössbauer spectroscopy makes use of the resonance absorption of recoil-free emitted γ-rays (the Mössbauer effect) by certain nuclei in a solid to investigate the splitting of nuclear levels that is produced by interaction with its surrounding electronic environment. Resonance absorption and emission take place only under certain favorable conditions, for instance, when the absorbing (or emitting) atom is bound in a crystal lattice. In general, the nuclear energy levels of the source and absorber will be different because of different oxidation states and/or chemical environments. To achieve resonance conditions, the energy of the emitted γ-quanta has to be modulated. This is done by using the Doppler effect by mounting the source on a velocity transducer and moving it with respect to the absorber. A Mössbauer spectrum thus is the measurement of the rate of resonance absorption as a function of the relative velocity between source and absorber.

The shape of a Mössbauer spectrum is determined by the hyperfine interaction of the Fe nucleus with its electronic environment. Three hyperfine parameters can be determined by Mössbauer spectroscopy: (1) isomer shift (IS), (2) quadrupole splitting (QS), and (3) magnetic hyperfine field (Bhf). These parameters are different for different minerals. Therefore each Fe-bearing phase has its own characteristic Mössbauer spectrum. The Mössbauer spectrum of a mixture of different Fe-bearing phases is simply the superposition of the spectra of the individual Fe-bearing compounds, with the relative intensities (or relative areas) of the individual mineral spectra directly proportional to the relative amount of mineral present in the mixture. The Mössbauer parameters for individual phases are also dependent on temperature. Therefore measurements made during day and night would supply additional information.

Mössbauer spectroscopy can be performed in either transmission or backscatter geometry. In transmission geometry, the sample is placed in between the source and radiation detector and an adsorption Mössbauer spectrum is obtained. A relatively thin and homogeneous sample is needed to avoid thickness effects. Rocks could not be analyzed in this transmission-mode geometry on planetary surfaces. However, in backscatter geometry, the source and radiation detector are on the same side of the sample, so an emission Mössbauer spectrum is obtained. Backscatter geometry has no restrictions on sample shape and thickness. No sample preparation is required because the active end of the instrument is simply placed in mechanical contact with the soil or rock sample that is to be analyzed.

*Major instrument parameters.* Miniaturized Mössbauer instruments have been developed for use on the surfaces of the Moon or Mars (*Agresti et al.*, 1992; *Klingelhoefer et al.*, 1995). The major instrument parameters are very similar.

1. Six-detector-channel version—mass: >500 g; dimensions: ~600 cm$^3$; power: ~4 W; data: ~100 kb/sample analysis. Instruments of this class were included in two Discovery-class proposals for the Moon and as part of the Russian Mars '96/98 mission, installed on the Russian Mars rover "Marsokhod."

2. Two-detector-channel version (MIMOS-II)—This version was developed for use in space missions with very limited power resources, such as the Small Stations of the Russian Mars '96 mission. Mass: <300 g; dimensions: ~150 cm$^3$; power: ~0.5 W; data: ~60 kb/sample analysis. This instrument is shown in Fig. 6.1a and Fig. 6.1b.

For all instruments described above, a radioactive source of about 200–300 mCi of $^{57}$Co (at launch) in a Rh matrix would be needed for a mission to Mars because the half-life of the source is 271 days. This lifetime has to be considered in each mission planning.

### 6.2.4. Visible to Near-IR Spectroscopies

Diagnostic mineral absorption bands span the near-IR, typically between 0.35 and 3.5 μm. There are two principal

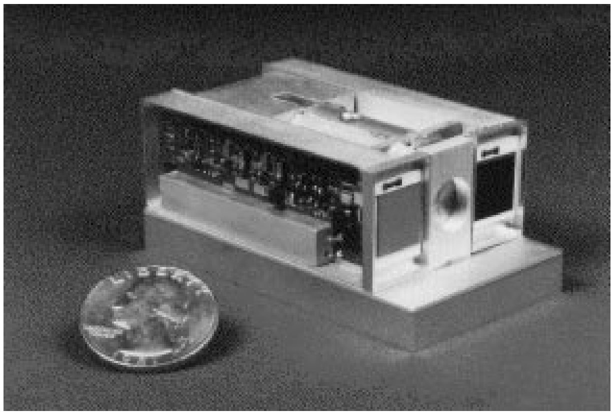

**Fig. 6.1a.**

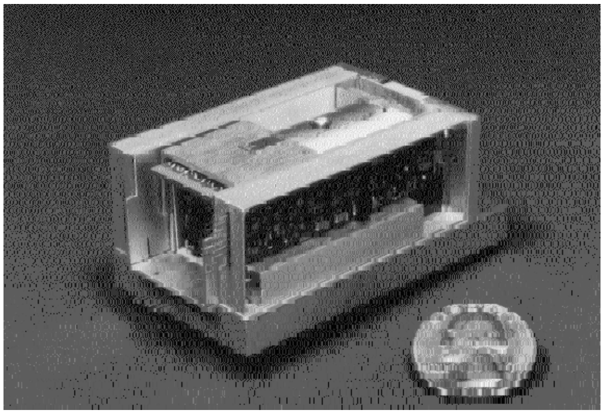

**Fig. 6.1b.**

causes of diagnostic features in this part of the spectrum. The first are electronic transitions of d-orbital electrons of transition element ions in a well-defined crystal field such as within an octahedral or tetrahedral site of a mineral. The energy (wavelength), strength, and width of these absorptions are a function of the ion (e.g., $Fe^{+2}$, $Fe^{+3}$, $Cr^{+3}$, etc.) and the size, shape, and symmetry of the site. These properties characterize specific minerals, allowing them to be identified by the nature of the observed absorption bands. Such bands are often referred to as crystal field electronic transition absorptions and occur from 0.4 to 2.5 µm. The second type of absorption bands arises from fundamental molecular vibrational and rotational modes and their overtones and combinations (typically OH, $H_2O$, and $CO_3$). These molecular absorption bands occur from about 1.4 µm to longer wavelengths.

Visible and near-IR spectrometers have a long heritage in their use for remote determination of mineralogy. The basic concept is simple: The spectral properties of light reflected from a surface are measured through a large number of contiguous spectral channels (typically a few hundred). This radiation has interacted with the surface, has been transmitted through several grains, and has obtained an imprint of absorption bands and other spectral features that are diagnostic of the minerals present. The technology developments over the last few decades have concentrated on making spectrometers more accurate, more flexible, and more capable. These trades are very important in selecting a specific design for a given application. Parallel progress has occurred in the analytical area in which tools for information extraction have been developed. These have concentrated on mineral identification, mineral abundance determination, and mineral composition determination.

Some of the most recent new technology advancements have been the development of high-precision spectrometers (imaging spectrometers) that produce “image cubes” of data: three dimensions of 10–14-bit data numbers, each with several hundred elements. Two of the dimensions contain spatial elements and the third contains spectral elements or channels. The important scientific application is the ability to evaluate diagnostic spectral properties of individual surface elements in a spatial (geologic) context. There are several spectrometer designs that will obtain image cubes, each with its own strengths and weaknesses, depending on the application. Almost all use two-dimensional arrays as the prime detector, with the third dimension derived through time-sequential measurements. If the target of interest is not moving, then the two dimensions of spatial information can be recorded simultaneously and the spectral dimension obtained sequentially with a dispersive element or filters. Alternatively, one dimension of spatial information can be recorded simultaneously with one dimension of spectral information obtained with a dispersive element or an interferogram. The second dimension of spatial information is then built sequentially as the system scans across a field of view. A more simple design is a spectrometer, which uses a dispersive element and a single or composite linear array to measure an individual spectrum; this design does require a more complex scanner to scan across two spatial dimensions.

### 6.2.5. Mid-/Thermal-IR

Visible and near-IR reflectance spectra are valuable in discriminating some elements and molecular groups in geologic materials, e.g., Fe, $CO_3$, and $H_2O$ and OH-bearing clays and other weathering products (*McCord et al.*, 1982a,b; *Singer*, 1982; *Goetz et al.*, 1982). Many geologically important elements (like Si, Al, O, and Ca) do not absorb directly in the visible or near-IR, although they can influence the shape and location of other absorption bands (*Hunt and Salisbury,* 1970). However, many of the major rock-forming elements and their complexes have fundamental vibration frequencies corresponding to mid- and thermal-IR wavelengths, 5–50 µm. Nearly all silicates, carbonates, sulfates, phosphates, oxides, and hydroxides show mid-IR and thermal-IR spectral signatures (e.g., *Lyon*, 1962; *Hunt and Salisbury*, 1974, 1975, 1976; *Farmer*, 1974).

The strong spectral activity in the mid-IR results from structural, chemical, and physical properties of silicate rocks and minerals (e.g., *Lyon,* 1962, 1964; *Hovis and Callahan,* 1966; *Goetz,* 1967; *Lazarev,* 1972; *Farmer,* 1974; *Hunt and Salisbury,* 1974, 1975, 1976; *Karr,* 1975; *Vincent et al.,* 1975; *Salisbury and Walter,* 1989; *Walter and Salisbury,* 1989; *Hapke,* 1993; *Pieters and Englert,* 1993). *Nash et al.* (1994) give a review of mid-IR spectroscopy of the Moon. Mid-IR spectral features are characteristic of photon interactions with the material in the “transition region” where absorption bands show up as troughs in reflectance and peaks in emission. Bands in the 4–7-µm region are mostly overtones and combination tones of the stretching and bending of Si-O and Al-O fundamentals with some lattice modes present. Also, carbonates have strong absorptions from $CO_3$ internal vibrations in the 6–8-µm region; these bands are easily distinguished from silicate absorptions (*Adler and Kerr,* 1963; *Hunt and Salisbury*, 1975).

The 7–11-µm region is largely dominated by surface scattering except at the Christiansen frequency or feature (CF). The CF is a reflectance minimum (and corresponding emittance maximum), typically between 7 and 9 µm, representing the strongest molecular vibration absorption band in silicate rocks and minerals. The CF wavelength is a function of the polymerization of the silicate lattice, and so is diagnostic of rock type and the chemical compositions of minerals (*Vincent and Thomson,* 1972; *Hunt and Salisbury,* 1974; *Hunt,* 1980). Glassy and powdery samples yield more subdued spectral features than crystalline or slab samples, at least in the laboratory, but the CF wavelength is independent of grain size or texture. Emission spectra obtained by telescope or method are approximately the “complement” of reflectance spectra as given by Kirchhoff’s Law: fractional absorptivity = 1 – the fractional reflectivity. Note also that, in strict thermodynamic equilibrium, fractional emissivity = fractional absorptivity.

Infrared spectral features at wavelengths longer than 11 µm are "transparency features"; quartz and feldspar have strong and unique features in this region. Several examples are given in the laboratory compendia of Salisbury and others (see reference list). The features in the 12–40-µm range include Si, O, and Al stretching and bending modes. Hydroxide-bearing minerals (clays) also have characteristic mid-IR spectra (*van der Marel and Beutelspacher,* 1976), with spectral features from the fundamental bending modes of OH attached to various metal ions, such as an H-O-Al bending mode near 11 µm in kaolinite (*Hunt,* 1980). Phosphates and sulfates also have diagnostic absorption bands associated with their anion complexes ($PO_4^{3-}$ and $SO_4^{4-}$), as do oxides, nitrites, and nitrates. Sulfides and halogenide salts are also readily distinguished (*Hunt and Salisbury,* 1975).

For natural surfaces, thermal emission spectra are modified by scattering of the outgoing energy within the surface. Thus, physical properties such as particle size and packing can affect emission spectra (*Logan et al.,* 1973; *Salisbury and Estes,* 1985; *Salisbury and Walter,* 1989). These effects only become significant as the particle size becomes small (<~100 µm) and are most important as the size approaches the wavelength being observed (*Lyon,* 1964; *Hunt and Vincent,* 1968; *Hunt and Logan,* 1972; *Salisbury and Walter,* 1989). To deal with the effects of scattering, the thermal emission data can be modeled using radiative transfer techniques that incorporate Mie scattering theory (*Conel,* 1969; *Moersch and Christensen,* 1991), and Chandrasekhar scattering theory (*Hapke,* 1981).

For airless body studies like Mercury, asteroids, and the Moon, the diagnostic utility of the mid-IR spectral regions benefits from the vacuum environment surrounding the surface materials, which enhances spectral contrast over that obtained in laboratory spectra most commonly obtained at ambient 1-bar pressure. For Mars, the atmospheric emission spectrum will mix with that from the surface materials. Mars Observer carried the thermal emission spectrometer (TES) on board for planned surface and atmospheric studies.

One thermal emission spectrometer design is flight-qualified, flew on Mars Observer, and is slated for the Mars Global Surveyor mission (*Christensen et al.,* 1992). That instrument, the TES, weighs 14.4 kg and consumes 14.5 W on average. Individual mineral species were clearly distinct in their thermal emission spectra, such that a grain of olivine could confidently be distinguished from pyroxene. Mineral mixtures could also be discriminated. Sulfates were detectable at a few weight percent (*Christensen et al.,* 1992), but it is not clear how well silicate mixtures could be discriminated.

### 6.2.6a. Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy studies atoms, ions, or molecules with unpaired electron(s) in an applied magnetic field (e.g., 1–6 kG) by irradiation of microwaves (~9 GHz for X-band EPR) to induce transitions between electronic spin states. The electronic states and their energy levels are modified through various interactions, such as interaction with nuclear spin(s) (within the same atom or molecule or neighboring ones), molecular environment, or amorphous or crystalline matrix. Magnitudes of such interactions can be deduced through EPR spectra and used to obtain information about molecular structures of radicals, oxidation states of ions, electronic structures, symmetry of ionic sites, and the surroundings. Samples of all phases, gas, liquid, or solid, can be studied by EPR. In conventional EPR experiments, the microwave frequency is fixed at a tuned value, and resonance condition is searched by scanning the applied magnetic field through an electromagnet.

EPR has been extensively applied for the study of geologic materials of all phases, including crystalline, powder, and amorphous samples. The analysis can be carried out with little disruption of surface structures or chemical equilibria, and requires little sample preparation, with milligram- to gram-sized samples.

Specific applications of EPR for planetary exploration include: the nature of oxidant (radicals) in martian soil; oxidation state of paramagnetic ions in soil (mineralogy); characterization of volatiles (carbonates, sulfates, nitrates); color centers in icy samples (impurity level chemicals in ice, inorganics, organics, carbonates); and detection of possible organics from subsoil.

### 6.2.6b. Ferromagnetic Resonance (FMR)

Compared with the paramagnetic samples in which individual electron spins are isolated or weakly interacting, the spins in ferromagnetic samples, e.g., metals of Fe, Co, and Ni and some rare-earth elements, are strongly coupled and possess a spontaneous magnetic moment even in the absence of an applied magnetic field. Spectroscopic principles and instruments are the same as EPR, except that in the interpretation of spectra, the ferromagnetic nature of the samples must be considered. Detection and characterization of ferromagnetic particles are the most important applications of FMR for planetary exploration.

### 6.2.7. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) studies atoms or molecules with nuclear spin(s); in most other aspects, its principles of operation are similar to those of EPR. NMR exploits the fact that many isotopes in molecules possess unique nuclear gyromagnetic ratios. Through interactions with electrons and neighboring nuclei, NMR spectra of molecules show unique line shapes or chemical shifts, and such information is utilized for characterization purposes. Through NMR spectroscopy, one can obtain information about the constituent nuclei and chemical structure of molecules. From the time of inception, the proton has been the most frequently studied nucleus and thus proton magnetic resonance has become almost synonymous with NMR. Using proton-NMR, one can accurately determine the quantity and physical and chemical nature of water, i.e., $H_2O$, OH, in geologic samples. Proton NMR is operated with samples (0.1–1 g) in an applied magnetic field by irradiation of radiofrequency (e.g., ~13 MHz at ~3 kG) to induce transitions between proton spin states.

NMR can be obtained by scanning a magnetic field at a fixed radiofrequency or by scanning radiofrequency at a fixed magnetic field. Like EPR, the method is nondestructive, and requires little sample preparation. A miniature magnetic resonance spectrometer (<500 g, <5 W) with combined capabilities of EPR and NMR is being developed at JPL (*Kim and Bradley,* 1994). A permanent magnet assembly (Nd-B-Fe) is used for the spectrometer.

Specific applications of NMR for planetary exploration include the presence of water in the soil, minerals, and rocks; free water in rock pores; adsorbed water on surface; and chemically bound water.

### 6.2.8. X-Ray Fluorescence Analysis (XRF)

XRF is principally a bulk chemical analysis method, and is described in Chapter 2. However, bulk chemistry of single mineral grains can provide important clues to their identity; when coupled with other structural data, identification is almost assured. One proposed instrument that uses XRF primarily as a mineralogic tool is under development. It is designed to analyze powder samples in a transmitted, forward reflection geometry either as received (e.g., wind-blown dust) or as the result of grinding or drilling operations (David Blake, personal communication). This instrument would yield bulk composition and X-ray diffraction data simultaneously. This instrument is proposed for inclusion on the Champollion lander and the Mars '98 missions. Its principal engineering parameters are energy range: 150–8050 eV; diffraction range (2-θ) 5–50; X-ray source: copper anode X-ray tube (or radioactive source, where appropriate); detector: 1024 × 1024, 18 µm pixels CCD; size: 11 × 11 × 8 cm; mass: 800 g; power (operating): 3 W; energy per sample: 6 W-h.

### 6.2.9. SEM/EDX

A scanning electron microscope with chemical analytical capability using energy dispersive analysis (SEM/EDX) could be useful in mineralogy as a source of morphological and compositional data on individual mineral grains. SEM/EDX is briefly discussed in Chapter 2.

### 6.2.10. Raman Spectroscopy

Laser Raman spectroscopy is an optical scattering technique that can provide molecular and crystal-structural information about solid materials (*McMillan and Hawthorne,* 1988; T. Wdowiak, personal communication). Raman spectroscopy is an established laboratory method for identification and characterization of organic/hydrocarbon and inorganic/mineral substances (e.g., *Wang et al.,* 1994). When light interacts with a material, a small portion of the incident photons (one photon per $10^8$–$10^{12}$) is scattered inelastically, with energy loss/gain to/from the material; this is the Raman effect. The energy losses or gains associated with Raman scattering are characteristic of molecular and lattice vibrational modes (fundamental, combination, and overtone) of the target material, and can be used to identify and characterize the target material.

The spectral frequency shifts of Raman scattering are related to molecular structures in essentially the same way as the absorption/emission transitions in infrared absorption, reflectance, and emission spectroscopy; however, different transitions are observed by the two techniques, as the quantum selection rules are different for absorption and Raman scattering. Additionally, many of the common difficulties in interpreting infrared spectra such as particle size effects, transparency peaks, volume scattering, and thermal gradients are not problems in Raman. Instead of the broad absorption bands of visible and infrared spectra, Raman spectra record discrete, sharp emission peaks. Laser-light-induced fluorescence of some species can be an interference, but techniques are available for minimizing its effect. These include algorithms for extraction of the narrower Raman features, long-wavelength lasers that induce less fluorescence, and time gating of the detector that excludes fluorescence because of its longer duration.

Raman spectra are taken by illuminating the sample with a monochromatic light source and obtaining spectra at wavelengths longer (and shorter) than that of the source. In the laboratory, Raman spectra of solids are usually obtained on prepared powders, although spectra can also be obtained on individual mineral grains through an optical microscope ("micro-Raman" spectroscopy). The analytical depth is effectively the depth of light penetration into the solid.

The Raman spectrometer consists of five components: laser light source, absorption filter (notch) at the light source wavelength, monochrometer, optical coupling, and detection (CCD) system. The light source must be monochromatic, and laser diodes are suitable. Single-mode laser diodes with efficiencies of 23–40%, power draws of 3–500 mW, and wavelengths of 630 nm or longer are suitable sources for Raman spectroscopy. Light can be conducted to the sample by a fiber-optic cable. The filter and monochrometer prevent all light with wavelengths near that of the incident light from hitting the detector. Holographic notch filters at laser wavelengths of sufficient absorption efficiency are available for this purpose commercially. Light scattered from the target material must be conducted to the detector. The monochrometer and detector can be at the site of analysis, or the light can be conducted by fiber-optic cable from a remote sample to the monochromator/detector system. Cables of sufficient clarity and length (up to 1 km) are available commercially (*Schoen,* 1994); temperatures as low as 77 K can be tolerated. Finally, the monochrometer must be able to disperse light by wavelength and the detector must record a spectrum of sufficient signal/noise. Available CCD spectrometer systems of small size and weight are apparently adequate for this task.

While Raman spectroscopy is a powerful laboratory technique, its value in robotic sensing of planetary surfaces (*Wdowiak et al.,* 1995) remains to be validated through actual testing. The low efficiency of Raman excitation implies low signal/noise in the detector, and requires either long analysis times, high-power light sources, or both. Stimulated Raman spectroscopy (*McMillan and Hofmeister,* 1988) permits much higher excitation efficiencies, but at the cost of large power flux and sample heating. Once a Raman spectrum is obtained, it is not clear how well spectra of mineral mixtures can be deconvolved to yield species or abundances of the constituent minerals, and what the minimum detectable mineral abundance is. The answer may lie in the use of microscopic Raman spectroscopy on single mineral grains, a standard laboratory technique. However, Raman spectra can readily distinguish crystalline and glassy materials, a difficult task for most methods. These questions are obvious points for future research in this promising technique.

### 6.2.11. Optical Luminescence Spectroscopy

Optical luminescence is emission of nonthermal optical photons (near-UV through IR) as a response to energy input (*Barnes,* 1958; *Geake and Walker,* 1975; *Marfunin,* 1975; *Waychunas,* 1988). On absorption of energy, an atom (or ion) will enter an excited state; the most probable decay mechanism of many such excited states involving valence-band electrons is emission of an optical photon.

Fluorescence is prompt emission in response to high-energy photons, and can be useful in determinative mineralogy, especially of ionic salts (e.g., carbonates, sulfates). Fluorescence can arise from essential elements (or ions), trace-element substituents (activators), or defects. Common activators in salts of alkali and alkaline earth elements include $Mn^{2+}$(VI), other transition metals, the rare earths, and the actinides (*Waychunas,* 1988). Trace substituents of other species can enhance fluorescence (e.g., $Pb^{2+}$), while other species (e.g., $Fe^{3+}$) quench it effectively. Fluorescence can also arise from defects in crystal structures, including those caused by radiation and shock.

Minerals may also luminesce on heating, thermoluminescence (TL), as structural defects like radiation damage anneal out. Thermoluminescence can be readily related to radiation exposure, and a suitable heating chamber [like a differential scanning calorimeter (DSC)] may be available on the lander.

Optical luminescence may be particularly useful for surface investigations on Mars, as atmosphere-surface interactions may have produced ionic salts of the alkali and alkaline earth elements (*Gooding,* 1978, 1992; *Sidorov and Zolotov,* 1986; *Fegley and Treiman,* 1992; *Treiman,* 1992; *Treiman et al.,* 1993). One possible Mars surface mineral, scapolite, has distinctive optical luminescence, and should be readily detectable (*Clark et al.,* 1990; *Treiman,* 1992).

Instrumentation to permit fluorescence spectroscopy is simple: a VIS-NIR spectrometer and a short-wavelength light source. The former is likely to be manifested for reflection spectroscopy, and the latter might be manifested for other purposes (e.g., a laser range finder, atmosphere sounder, or chemical analytical tool). However, fluorescence spectroscopy has severe limitations, and cannot be considered a mature analytical method. In most cases, fluorescence spectroscopy cannot provide mineral proportions or compositions, as luminescence response of a mineral depends on many aspects of its trace-element composition and structural state. Also, there has been little systematic investigation of luminescence at infrared wavelengths or of faint luminescences (that interfere with Raman spectroscopy). This is a field with considerable potential, as many common minerals that do not luminesce at visible wavelengths may do so in the infrared.

### 6.2.12. Thermal Analyses

Many minerals transform or react during heating, and the thermal effects of those transformations can be characteristic of particular minerals, and nearly unequivocal for mineral identification. These thermal effects are the basis for the standard thermal methods, which include differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In both methods, an unknown sample is introduced into a heating chamber in close proximity to a reference sample, and both sample and reference are heated. In DTA, heat is added to sample and reference at a constant rate (usually linear with time) and the temperature difference between the sample and reference is recorded. In DSC, sample and unknown are heated separately so that both stay at the same temperature; the recorded quantity is the difference in heat added as a function of reference temperature. DSC can be more quantitative that DTA with respect to the abundances of phases (the heats absorbed or evolved); this quantification, however, requires accurate masses of the analyzed samples. DSC also is currently limited to thermal effects below 700°C (*Wendlandt,* 1986). DTA is semiquantitative with respect to mineral abundances, but is easier to implement than DSC and is limited only to temperatures below 1200°C (*Wendlandt,* 1986).

Thermal analysis (DSC or DTA) by itself can detect the heat effects associated with crystalline phase changes, magnetic order/disorder transition, chemical reactions such as devolatilizaton, and melting. However, thermal analysis techniques are especially powerful when coupled with a method of analyzing the gas (if any) emitted during a thermal event. There are many available methods for analyzing the gases evolved during heating. Mass spectrometric methods are discussed in Chapter 3. Gas chromatography (GC), also discussed briefly in Chapter 3, involves passing the evolved gas in an inert carrier through a long column of porous, chemically adsorbing material. As they pass through the column, the evolved gas species become separated according to how well they bind to the column material. Properly calibrated, GC can be nearly definitive for presence and abundance of some species. For samples that contain only a few known volatile species, or for applications where concentrations of only a few species are needed, gas-specific chemical sensors are favored. Most compound-specific sensors are designed so the compound of interest sets up an electrochemical potential (voltage) across the sensor; the potential is a calibrated function of the compound abundance. Many compound-specific electrodes respond (to varying degrees) to nontarget compounds, so sensors for a number of specific compounds may be required to yield unambiguous analyses. For water, other types of sensors can measure relative humidity or dew point. Sensors for $H_2O$ and $CO_2$ were available in 1994 (*Boynton et al.*, 1994; *Gooding*, 1994), and development of other compound-specific sensors is in progress.

This combination of methods, thermal and evolved gas, can provide significant mineralogical information about unknown samples, including mixtures and complex soil samples (*Wendlandt,* 1986). Thermal/evolved-gas methods are particularly powerful for volatile-rich materials, such as terrestrial soils. Their analytical values presumably extend to martian soils, regoliths of primitive asteroids, and regoliths of comets. Thermal analysis is a bulk technique for the sample collected; it is not sensitive to surface coatings and weathering rinds (*Schwartz et al.,* 1995), except as the coatings and rinds become a significant portion of the sample mass. With thermal analysis and evolved gas analysis, it is relatively straightforward to distinguish among clays, silicates, feldspars, zeolites, glasses, and evaporites as well as to determine if organics are present, even for some phases to the 0.02 wt% level (*Boynton et al.,* 1994). Thermal and evolved gas methods are also discussed in Chapters 3 and 7 as they relate to trapped/implanted gases and C-based chemistry/exobiology.

No thermal analysis instruments are currently flight qualified, but a number are at brassboard stage, and are competing for inclusion in the Mars Surveyor Lander. Current concepts couple thermal analyses with evolved gas analysis: *Mancinelli et al.* (1994) proposed a DTA with a evolved gas analysis by chromatography; *Boynton et al.* (1994) and *Gooding et al.* (1994) have proposed DSCs with evolved gas analysis by compound-specific sensors. Gooding et al.'s instrument (TAPS) has a mass near 1 kg, including a sampling device, and consumes ~5 W-hr per analysis of a 20–50-mg sample. Minerals with thermal effects alone (e.g., quartz) are detectable at near 1% of the sample. Minerals that evolve gas may be detectable at much lower levels (e.g., carbonate detectable at the 0.02% level).

### 6.2.13. Magnetization

A remarkable result from the Viking missions was the discovery that the martian soil is highly magnetic, in the sense that the soil is attracted by a small permanent magnet. The soil was found to adhere almost equally to a strong and a weak Sm-Co magnet attached to the Viking lander backhoe at both landing sites. The strong magnet had a surface field and a surface field gradient of 0.25 T and 100 T/m respectively (2500 G, 10,000 G/cm). The corresponding numbers for the weak magnet were 0.07 T and 30 T/m (700 G, 3000 G/cm). Based on the returned pictures of the amount of soil clinging to the magnets, it was estimated that the particles in the martian dust contain between 1% and 7% of a strongly magnetic phase, most probably a ferrimagnetic ferric oxide intimately dispersed throughout the soil.

Appropriate limits for the spontaneous magnetization (ss) were advanced:

$$1\ \mathrm{Am^2(kg\ soil)^{-1}} < \mathrm{ss} < 7\ \mathrm{Am^2(kg\ soil)^{-1}}$$

The essential difference between Permanent Magnet Arrays for coming landers and the Viking Magnetic Properties Experiment is that arrays on future landers should include magnets of lower strengths than the weakest Viking magnets. The reason for this is that both the strong and weak magnets on the Viking Landers were saturated with dust throughout the mission. The proposed Magnet Array contains five magnets of different strengths, with a total mass of about 70 g. The outer diameter of the magnets is 18 mm each. The center and ring magnets are magnetized parallel to their axes, but in opposite directions. When mounted the magnets are completely immersed in a thin Mg plate. The magnets are of equal strengths, but mounted at different depths below the surface of the Mg plate. Discrete (single-phase) particles of the strongly magnetic minerals ($\gamma$-$Fe_2O_3$, $Fe_3O_4$) will stick to all five magnets, while composite (multiphase) particles will stick only to the strongest magnets. The two strongest magnets have the same strengths as the backhoe magnets on the Viking landers. The plate with the magnets will be placed on the surface of the lander. The Magnet Array will be periodically viewed by the onboard camera and the returned pictures are the data on which conclusions will be based. If the Magnet Array is placed on the surface of the lander, it will be possible to perform X-ray fluorescence and Mössbauer analysis of the dust on the magnets.

## 6.3. PRIMITIVE BODIES

The many different types of undifferentiated bodies in the solar system share a collection of surficial and interior processes that can be profitably studied by determining the mineralogy of reactant and resultant phases. The types of processes and the unique instrumentation required to address them are presented in Table 6.2. Specific issues for each type of body are further (briefly) summarized here. First, the reader should recognize that the basic types of undifferentiated bodies are somewhat arbitrarily divided into (1) asteroids and (2) comets and Kuiper Belt objects. While the latter are assumed to be the more primitive, in reality there is a complete gradation between these objects and their effective discrimination hinges on the presence or absence of an ephemeral atmosphere. The analysis concerns with regard to mineralogy are similar for all primitive bodies.

The key questions for primitive bodies focus on the recognition and identification of interstellar, nebular, and protoplanetary minerals, and the phases resulting from oxidation, sulfidation, heating (and further crystallization of amorphous materials), carburization, and aqueous alteration state of the primary materials. Some primitive phases are known to be amorphous, and subsequent heating and annealing will produce materials with a varying degree of crystallinity. For this reason, techniques that can probe atomic structure (X-ray diffraction, Mössbauer, optical spectroscopy, differential scanning calorimetry) will be critical tools. The oxidation state of minerals and bulk samples is also critical information, and this can be analyzed by Mössbauer, electron magnetic resonance, and visible-NIR spectroscopic techniques. Major-element compositions can be probed using SEM/EDX and XRF instruments. Mineral textures are important records of formation processes, and these can be studied using SEM or visual imaging techniques.

## 6.4. DIFFERENTIATED BODIES WITH NO (OR NEGLIGIBLE) ATMOSPHERES

The many different types of differentiated bodies in the solar system that lack significant atmospheres share a collection of surficial and interior processes that can be studied using mineralogy. The types of processes and the unique instrumentation required to address them are presented in Table 6.3. Specific issues for each type of body are further (briefly) summarized here.

On Mercury, key mineralogical questions focus on the oxidation state of the surface mineralogy and the composition of the polar deposits. In the former case, mineralogy (which is dependent on knowledge of oxidation state) of surface sulfides may give significant insight into the oxidation state of the planet at the time of formation and core formation. Related to this is the Mg/(Fe + Mg) ratio, a parameter that places important constraints on petrology but cannot be evaluated because the oxidation state is not known. In the latter case, knowledge of the composition of the polar deposits on Mercury can yield important insight into volatiles and differentiation on the planet. Finally, knowledge of the Na content of feldspar on Mercury's surface could provide constraints on surface evolution.

On the Moon, we note that the Apollo program, groundbased observations, and Clementine have been effective in studying the composition of the lunar surface. Thus, these authors believe that more emphasis should be placed on other airless bodies in this document. However, key issues that have not been explored to date include knowledge of the composition of polar deposits, and sampling of xenoliths or deep craters to attempt to sample the lunar mantle.

For differentiated asteroids, mineralogy could provide knowledge of the surficial evolution by determining the presence or absence of hydrated minerals, the elemental abundances at the surfaces, and any mantle signatures that might be present. Finally, for Galilean and saturnian satellites, the surface mineralogy and bulk composition are again important. For these bodies, such information could provide insight in the fractional amount of water on the surfaces, other imbedded gases, dimers, molecules, and the rates of sputtering, outgassing, and accretionary processes present.

## 6.5. DIFFERENTIATED PLANETS WITH ATMOSPHERES

The surface mineralogy of differentiated planets with atmospheres (i.e., Venus and Mars) differs dramatically from that found on primitive bodies and differentiated planets that lack an atmosphere, and therefore deserves more extensive discussion herein. The types of processes and the unique instrumentation required to address them are presented in Table 6.4.

Rock-atmosphere-hydrosphere interaction on Mars and rock-atmosphere interactions on Venus have undoubtedly led to a wide variety of minerals that reflect specific processes that have occurred. These interactions are broadly called "chemical weathering" because the initial mineralogy of the source rock has been changed. Because mineral phases are stable only for specific ranges of pressure, temperature, and composition, the mineralogy of the alteration products and their spatial and petrologic associations provide insight into the environments in which they formed. In this context, it is important to note that minerals, once formed, can persist metastably for extended periods of time.

In the case of Mars, for example, hydrated minerals formed early in its history could persist to the present time under the cold dry conditions that prevail now. Surface mineralogy can also provide information critical to the exobiological exploration of Mars.

There are two principal reasons for this. First, life as we know it requires liquid water, and a knowledge of surface mineralogy provides insight into the activity of water. Second, the biogenic elements H, C, N, O, and S are also the principal volatile elements comprising the present and past atmospheres of Mars. In this section, we attempt to present a sampling of the critical questions that can be answered if surface mineralogy is known.

### 6.5.1. Chemical Weathering

Throughout the last 4 b.y. the atmospheres of Mars and Venus has been interacting with the surface to alter initially igneous material. Minerals are a permanent reservoir of $CO_2$ and S for both Venus and Mars and for $H_2O$ on Mars. Elemental abundances, such as those measured by the Viking XRF experiment, can constrain the present state and allow inference of the starting composition of the source material but not reveal the processes that have occurred. The mineralogy of the alteration products is a sensitive indicator of formation conditions such as oxidation state, pH, abundance and phase of water, atmospheric chemistry, temperature, and surface pressure. This knowledge is critical in understanding the Mars and Venus volatile cycles during the present epoch and throughout the planets' history.

Types of secondary minerals that are especially important are sulfates, carbonates, Fe oxides, and, on Mars, where water has been involved in weathering the environment, hydrates. In addition to determining the mineralogy of the weathering product, the mineralogy of unaltered material needs to be determined. We need to know the mafic mineralogy of the source rock (e.g., olivine and pyroxene composition and abundance) in order to separate weathering products derived locally under current conditions from material formed under other conditions. Contextual information such as the composition of any weathering rinds on rocks and how it differs from soil mineralogy and the mineralogy of any duricrusts is needed to derive an integrated picture of what processes have occurred and when.

For instance, consider weathering under current martian conditions. Two weathering paths may be occurring. The first is gas-solid reactions at 240 K, while the second assumes that occasional films of liquid water are present at 273 K (applicable in the equatorial regions). Using mineral reaction diagrams, the thermodynamically stable alteration products for each reaction path can be determined (*Gooding,* 1978; *Gooding and Keil,* 1978; *Gooding et al.,* 1992). For gas-solid reactions at 240 K the dominant weathering products are clays (including the smectite Ca-beidellite) and the carbonates magnesite ($MgCO_3$), dolomite [$CaMg(CO_3)_2$], or calcite ($CaCO_3$).

With liquid-solid reactions at 273 K in addition to the minerals mentioned for solid-vapor interactions, Mg-phyllosilicates (talc, saponite, and montmorillonite) and (Na,K) beidellites would be present. The composition and abundance of currently formed alteration products provides a mechanism to estimate the rate at which $H_2O$ and $CO_2$ are being removed from the martian atmosphere-cap regolith cycle today.

Another martian example is that the mineralogy of weathered materials formed during an early clement period on Mars where liquid water was abundant would be rich in carbonates. Dissolved $CO_2$ in water would react quickly to form massive carbonate deposits (e.g., *Fanale and Cannon,* 1979; *Pollack et al.,* 1987). The abundance and mobility of water during this period would determine the mineralogy of the clays based on the solubility of different ions.

Sulfur is fairly abundant on the martian surface; soils analyzed by both Viking Lander XRF instruments contained 5–9 wt% $SO_3$. The elemental analyses of the red fine-grained material that dominated the surface at both sites were nearly identical for most elements, except S, whose concentration was variable in the different soil samples collected at the two sites (*Clark et al.,* 1982). The oxidation state of the surface and the concentration of S in clods was interpreted as a sulfate duricrust formed by the upward migration of water containing the sulfate anion (*Toulmin et al.,* 1977; *Burns,* 1988) or alternatively deposited from volcanic aerosols (*Settle,* 1979). Knowledge of the mineralogy and distribution of martian sulfates is critical in determining how the duricrust formed.

Understanding the nature of chemical weathering on Mars cannot be done without knowing the mineralogy of Fe. This is the case because it is abundant on the martian surface (~12% Fe according to *Clark et al.,* 1982), forms stable compounds in both divalent and trivalent oxidation states, and changes oxidation state in response to external conditions. Arguments developed by *Morris et al.* (1989) and *Morris and Lauer* (1990) suggest that well-crystalline hematite ($\alpha$-$Fe_2O_3$) is present as an optically important constituent on Mars. This may imply that the surface of Mars is anhydrous and/or that formation process were at high enough temperatures to form hematite relative to ferric oxyhydroxide phases. It is also important to establish the size distribution of Fe oxide particles. Small particles (nanophase ferric oxides) are formed during low-temperature processes like palagonitization, and well-crystalline ferric oxides are formed by higher-temperature hydrothermal processes.

On Mars, the alteration of material in impact ejecta blankets or volcanic geothermal regions would also have a distinctive geochemical signature due to the circulation of hydrothermal fluids interacting with impact glasses and breccias. Calculations based on minimizing the Gibbs free energy of the chemical system by *Zolensky et al.* (1988) show that gibbsite ($Al(OH)_3$), kaolinite (an Al-rich clay), and nontronite (an Fe-rich smectite clay) would be present. The abundance of each clay would depend on the amount of rock that has reacted and the initial composition of the rock. If only a small percentage of the rock reacts, carbonates would not form.

### 6.5.2. Importance of Mineralogy for the Exobiological Exploration of Mars

According to a recent study document (*Carr et al.,* 1995, "An Exobiological Strategy for Mars Exploration"), three scenarios exist that are of high exobiological interest: (1) Prebiotic organic chemistry occurred but life never developed; (2) life developed in some form during an earlier clement period but is now extinct; and (3) life exists, perhaps in "clement" niches in or below the surface.

Unless one assumes that life forms were delivered to Mars from elsewhere, (1) above is required for (2) and (3), and evidence of (2) is likely to exist in the rock record if (3) is true. The Viking life detection experiments revealed the presence of a strong oxidant in the Mars soil that could have destroyed any evidence of organic materials. It appears that, until much more is known about the geology, mineralogy, and surface chemistry of Mars, exobiological investigations should be undertaken that have the broadest possible scope.

### 6.5.3. Early History of Martian Volatiles

Mars is a dry eolian planet with a tenuous atmosphere of ~7 mbar pressure, composed mostly of $CO_2$. However, ancient surface morphological features such as stream channels and other fluvial and lacustrine features provide compelling evidence that liquid water once existed on the surface of Mars in large quantity. This abundance of liquid water implies that early Mars was once wetter and warmer, and had a dense atmosphere, perhaps of a greenhouse gas such as $CO_2$ (*Clifford et al.,* 1988). The ultimate fate of atmospheric $CO_2$ is of exobiological interest because this compound figures prominently in prebiotic organic chemistry, and because a full inventory of the $CO_2$ sinks is required to provide a balanced volatile budget for the planet. A major reservoir for the $CO_2$ could be in the form of carbonates deposited as chemical sediments or as hydrothermal precipitates.

Alternatively (or additionally), $CO_2$ could be stored in the form of clathrate hydrates beneath the surface or in the polar caps (*Miller,* 1973), or as solid $CO_2$ at the poles. Each of these phases can be unequivocally distinguished and characterized by mineralogical techniques. In the case of carbonates, the crystal symmetry (rhombohedral or orthorhombic) and the extent of cation solid solution (Ca, Mg, Fe, Mn, etc.), cation order/disorder, and cation stoichiometry can all be determined through mineralogical analysis.

Each of these distinguishing characteristics provides information about the specific origin of the mineral phase and its environment of formation. The total quantity of water that apparently existed on the surface of Mars early in its history cannot be accounted for by the polar caps alone. It is likely that hydrated phases exist either as a consequence of their direct deposition from aqueous solution or as products of the reaction of anhydrous igneous minerals with water. The quantity, type, and degree of crystallinity of clays, micas, and other hydrated phases can be determined by mineralogical analysis and their known stability relationships can constrain the conditions under which they were formed.

### 6.5.4. Presence and Lateral Extent of Hydrothermal Systems

Abundant morphological evidence exists for early and extensive volcanic activity on the surface of Mars, and for the presence of liquid water. The juxtaposition of these features is permissive if not compelling evidence that hydrothermal systems once (or have always) existed on Mars. Isotopic data from the SNC meteorites also suggests that there was an exchange of H and O between the crust and the atmosphere. The depletion of volatiles such as S and C is puzzling, and these elements may now be contained within minerals precipitated in hydrothermal systems. A knowledge of the presence and distribution of S and C containing mineral phases is important first because they are biogenic elements, and second because compounds containing them could have been utilized by autotrophic organisms as energy sources. Ancient hydrothermal systems could have been eroded or exhumed, exposing minerals and mineral assemblages at the surface that were formed at depths inaccessible in presently active systems. The mineralogical characterization of such a system could provide an evaluation of the role hydrothermal processing has played in modifying the early martian atmosphere and in altering deep-seated volcanic rocks. Hydrothermally altered rocks, dissected and exposed at the surface by erosion, could contain fossil evidence of the nature of the early Mars atmosphere and of the fate of its volatiles.

### 6.5.5. Evidence of Prebiotic Organic Chemistry

On the Earth, all evidence of prebiotic organic chemistry has been erased. In the earliest terrestrial rocks for which conditions of metamorphism would permit it, evidence of life is present. Therefore, even if life never originated on Mars, it would be exceedingly valuable to find some evidence in the geologic record of martian prebiotic organic chemistry. This would be possible on Mars more than on the Earth, since extensive regions of ancient terrain exist on Mars that have not been subject to metamorphism. The current notions of prebiotic organic chemistry are that many important reactions may have occurred in hydrothermal systems where energy could have been provided by mineral hydration reactions. Hydrothermal systems also provide a means for gas exchange with the atmosphere and transport of reactants to the sites of reactions. Ancient hydrothermal systems exhumed by erosion could provide surface material that contains distinctive mineral assemblages. It is often the case that hydrated minerals and their anhydrous counterparts are compositionally very similar. Thus, elemental analyses would not easily distinguish one from the other. Mineralogical analysis, comprising both compositional and structural information, can provide a definitive answer.

### 6.5.6. Evidence of Extinct Life

Evidence of life on the Earth occurs in the earliest rocks that could have preserved signs of its presence ~3.5 b.y. ago. However, much of the geologic record from the earliest sedimentary sequences has either been heated to the extent that metamorphism would have removed evidence of life, or has simply been destroyed by subduction. Due to the apparent lack of tectonic activity on Mars, a great deal of the sediment deposited on the ancient martian surface still exists and was probably not heated to the extent of equivalent sediments on the early Earth. Therefore, it is likely that if life originated early in Mars history, some record of its existence would be manifest in the earliest geologic record.

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## APPENDIX 6.1. A TUNABLE DIODE LASER (TDL) SPECTROMETER AS A PLANETARY SURFACE INSTRUMENT

*Albert Yen and Randy May*

Tunable diode lasers (TDLs) are high-resolution (0.0005 $cm^{-1}$), near- to mid-IR sources that have been used for over 15 years in balloon and aircraft instruments to make absorption measurements of trace atmospheric constituents (*Webster et al.,* 1994). Traditional lead-salt TDLs operate between 3 and 30 µm but require cryogenic cooling (liquid He and N temperatures) and are, therefore, not practical for planetary surface experiments. Recent advances in semiconductor laser technology, however, allow operation at room temperature for wavelengths between 1.1 and 2.06 µm (Forouhar, 1986, personal communication). These new InGaAsP lasers are well suited for *in situ* evolved gas analyses of planetary surface samples and offer greater sensitivity (measurable absorptance of 0.001%) than existing mass spectrometry techniques for many species. Within the next year, GaSb-based TDLs operating between 2 and 5 m will become available and will provide additional flexibility in theselection of molecular transitions.

A planetary surface instrument for evolved gas analysis based on a TDL would consist of a laser, a detector for the operating wavelength (e.g., InGaAs), a thermoelectric cooler for temperature stabilization of the laser, control and data processing electronics, a sample collection mechanism, a heat source for volatilizing constituents in the sample, and an optical path between the laser and detector through the evolved gases. The wavelength scan range of a TDL is a few reciprocal centimeters and is typically achieved by applying a current ramp across the diode. Since temperature variations also affect the output wavelength of the laser, a thermoelectric cooler is necessary to maintain the TDL within approximately 0.1 K of a preselected set point. If the output of the TDL is modulated at a high frequency (typically kHz), then absorption sensitivities of 0.001% can be achieved by harmonic detection techniques using integration times of less than one second (*May and Webster,* 1993). Recent development work at JPL indicates that the TDL and its associated electronics can fit into a volume of less than 10 $cm^3$ and consume less than 1 W. The mass and volume of the overall instrument will be dominated by the design of the soil collector, optical chamber, heat source, etc. The power requirements will increase if electrical heating is used.

As a specific example, consider an evolved water analysis experiment for a Mars lander. A TDL operating at 7294 $cm^{-1}$ would only need a 2.5-cm path from the laser to the detector to detect 15 ppmv of water vapor. If desired, a multipass (e.g., Herriott) cell could be used to increase the path length and lower the detection limit within a similar volume. Taking measurements every few seconds as the soil sample is heated would provide an evolved water signature. Additional TDLs scanning over different wavelengths could be used to quantify other evolved molecular species of interest (e.g., the isotopes of $CO_2$).

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# 7: Carbon-based Compounds and Exobiology

***—John Kerridge, David DesMarais, R. K. Khanna, Rocco Mancinelli, Gene McDonald, Fillipo Radicati di Brozollo, and Tom Wdowiak***

## 7.1. SCIENTIFIC OBJECTIVES

The ultimate issue in this area concerns life: Is there evidence anywhere in the solar system besides Earth for life, either extant or extinct? *COMPLEX* (1994) concluded that "Further study of Mars, with its record of abundant liquid water early in its history, is of major importance in regard to the origin of life. Whether or not evidence is found for extinct, or even extant, organisms, the exobiological exploration of Mars will lead to a more constrained definition of the planetary conditions that constitute a 'window of opportunity' for the emergence of life." Furthermore, COMPLEX noted that "Organic materials are thought to be significant components of comets . . . . Such substances and the mechanisms that form them likely contributed to the pool of organic chemistry that led, on Earth, to life." These considerations led COMPLEX to pose the following questions to be addressed by space missions during the 1995–2010 time frame:

Did Mars ever accumulate a reservoir of prebiotic organic compounds, and does any trace of such material remain on Mars today? Is there any evidence that organic matter underwent prebiotic chemical evolution on Mars?

Did life emerge on Mars and, if so, did it leave any record of extinct life forms? Is there any evidence for life on Mars today?

[What is] the population of carbonaceous materials in cometary nuclei?

## 7.2. MEASUREMENTS/OBSERVATIONS NEEDED AT MARS

The scientific objectives listed above translate into a series of measurements and/or observations to be performed by landed spacecraft. (Note that these measurements/observations should follow a reconnaissance phase of exploration employing a series of orbital spacecraft.) The following measurements/observations, in no particular order of priority, are considered necessary for the exobiological exploration of Mars:

1. Detailed assessment (mineralogical, chemical, and textural) of rock diversity at a landing site. This is a necessary early step in the search for either extinct or extant life. It is also of importance in the study of prebiotic chemical evolution.
2. Chemical characterization of the materials at a local site. Of interest are the elemental abundances in rocks and in surficial deposits of fine materials, focusing on the rock-forming elements and C.
3. Abundance of H at any accessible sites. In most cases, this will be present in chemically combined form as a hydrated lithology, though it may be possible to find a location where subsurface ice is accessible by drilling beneath a landing site.
4. Identification of specific minerals that would be diagnostic of aqueous processes. Such minerals would include carbonates, cherts, evaporites, and phosphates.
5. Textural examination of lithologies thought to be formed by aqueous activity. Such textures could be characteristic of the mode of secondary alteration and potentially indicative of fossiliferous lithologies.
6. Search for minerals that might have been produced as a result of biological processes, such as phosphates, manganese oxides, and certain carbonates.
7. Mapping the distribution, in three dimensions, of the oxidant(s) identified on the martian surface by the Viking mission.
8. Definition of the local chemical environment. Available chemically reactive species in the upper surface would be assayed, as well as the nature of the environment when moistened or wetted, including pH, Eh (oxidizing potential), ionic strength, presence of micronutrients, and other aspects of the soils and soluble minerals.
9. Determination of stable-isotope ratios for the biogenic elements (C, H, O, N, and S) in surficial mineral deposits, e.g., evaporites. This would provide an additional constraint on volatile history and reservoirs.
10. Quantitative analysis of organic (= noncarbonate) C.
11. Elemental and isotopic composition (C, H, O, N, and S) of bulk organic material.
12. Search for specific organic compounds that would yield information about synthetic mechanisms, in the case of prebiotic evolution, and about possible biomarkers, in the case of extinct or extant life. Key compound classes for which evidence should be sought include lipids, amino acids, and carbohydrates.
13. Coring, sampling, and detection of entrained gases ($CH_4$, $H_2$, $H_2S$, etc.) and cosmic-ray-induced reaction products (e.g., HCOH) at the polar ice cap.

*An Exobiological Strategy for Mars Exploration* (NASA SP-530) concluded that "The most immediate [surface] instrumentation needs are the following: design and construction of instrumentation for *in situ* mineralogical identification, description of the microenvironment (including oxidant distribution), and detection and characterization of organic matter; development of a capability for acquiring samples from a depth of several meters in the regolith and from the interiors of rocks; and early deployment of the above." Later stages of the exobiological exploration of Mars would likely involve more highly focused biological experiments, such as a search for morphological fossils and/or tests for active metabolism, such as were flown on the Viking landers. Positive results from such experiments would undoubtedly lead to biologically focused sample return missions.

## 7.3. MEASUREMENTS/OBSERVATIONS NEEDED AT A COMET NUCLEUS

Unlike the case for Mars, there is little doubt that organic compounds are ubiquitous within cometary nuclei, and that they are of interest in their own right, rather than as a result of their possible involvement in biological processes. There is a large dataset in existence on the molecular composition of cometary comae (*Newburn et al.*, 1991). Groundbased spectroscopic observations have detected numerous molecular species, and these data have been augmented by both spectroscopy and mass spectrometry from the Giotto and Vega missions to Comet Halley. Water makes up about 80% of the volatile content of Comet Halley, and possibly up to 50% of the mass of the nucleus. Other molecules of prebiotic interest detected in cometary comae include CN and HCN, CO, $CO_2$, $CH_3OH$, HCOH, and $NH_3$. Many of the molecules observed in cometary comae are probably ionized fragments of larger parent molecules that are condensed on the surface of the nucleus. The identities of these parent molecules are not known, since the presence of the coma makes it virtually impossible to observe the comet surface directly, even from nearby spacecraft.

The dust in the coma of Halley has been examined by mass spectrometers on board both Giotto and Vega. Of primary interest to exobiology is the detection of "CHON" particles, dust particles containing C, H, O, and N. Intermediate-mass organic macromolecules have also been detected in the coma, with mass spectra indicating repeating 14–16 amu units in a linear polymeric structure. These data have been interpreted as a signature of either hydrocarbons, with a -$(CH_2)$n- structure, or polyoxymethylene (POM), a polymer of formaldehyde, with a -$(CH_2O)$n- structure. The $^{13}C/^{12}C$ ratio of $C_2$ and CN in the coma of Halley is approximately solar (with a rather large uncertainty), but a significant proportion of CHON grains analyzed by the Giotto and Vega spacecraft revealed substantial enrichment in $^{12}C$, suggesting an interstellar source for some cometary organics.

The following measurements/observations are considered necessary during the exploration of a cometary nucleus:

1. Abundances and stable-isotopic compositions of biogenic elements (C, H, O, N. and S). In addition to bulk measurements, evidence of spatial inhomogeneity should be sought.

2. Identification and quantitative determination of individual species within major classes of organic compounds. Such information will aid in discriminating between possible synthetic and/or alteration mechanisms.

3. Isotopic analysis (for C, H, O, N, and S) of specific organic compounds. This information will assist in identification of source regions for different organic compounds.

4. Isotopic analysis of all volatile phases. Such information would help clarify the source region(s) of the major components of the cometary nucleus and could reveal evidence of subsequent processing of cometary volatiles, possibly including organics.

## 7.4. MEASUREMENTS/OBSERVATIONS ON OTHER SOLAR SYSTEM OBJECTS

Although Mars and cometary nuclei constitute the most promising surface sites within the solar system to pursue exobiological questions, the C-based chemistry of several other objects should not be overlooked. (The organic chemistry of Titan has attracted much interest, but it seems likely that the Cassini mission will address many of the outstanding issues in that area, and, furthermore, the feasibility of conducting surface science *sensu strictu* on Titan is problematic at this time.)

### 7.4.1. Moon

Analysis of Apollo samples showed that lunar rocks are essentially devoid of C but that the regolith contains significant quantities (up to about 100 µg C/g) that are believed to be largely, and possibly wholly, of solar wind origin. This regolith C reveals a wide range in $\delta^{13}C$ value, from a few per mil below the terrestrial standard to about 20‰ above. These values fail to correlate with any other known parameters, so this issue certainly deserves further study. It seems likely that sample return will be needed for such studies, but the possibility of developing sufficiently sophisticated robotic experiments should not be ignored.

The very low O fugacity characteristic of lunar rocks suggests that indigenous water has not existed within the Moon during its history. Prospects for aqueous chemical evolution on the Moon therefore seem to be ruled out.

### 7.4.2. Asteroids

The majority of astronomically observed asteroids reveal spectral evidence for abundant surface C. In fact, for sampling purposes, it may be that there is an effective continuum from rocky asteroids containing some C to cometary nuclei extremely rich in carbonaceous material. Throughout such a range, the scientific objectives and desired measurements and observations remain essentially the same. We have almost certainly already performed many organic analyses on samples of some of the moderately C-rich asteroids, in the form of carbonaceous chondrites and, possibly, interplanetary dust particles. Whether a landed spacecraft mission to an asteroid could yield exobiologically relevant data beyond what could be derived from a comet nucleus or from analysis of carbonaceous chondrites is problematical.

### 7.4.3. Europa

It has been remarked on several occasions that fissures on the surface of Europa may be the only place in the solar system outside the Earth where liquid water might be in contact with both carbonaceous material and sunlight. It follows that such places could be sites of organic synthesis that, while not likely to lead to emergence of life, could nonetheless be of interest to exobiology.

## 7.5. AVAILABLE INSTRUMENTATION

Table 7.1 lists the instrumentation currently available for addressing exobiological objectives on planetary surfaces. Note that not all the techniques listed generate key exobiological data; several are needed for obtaining important environmental information and/or site or sample characterization during earlier stages of exobiological exploration. We shall discuss, in alphabetical order, the techniques listed in Table 7.1, focusing mainly on key exobiological experiments within the context of Mars exploration, but including where relevant their employment in other planetary settings.

### 7.5.1. Alpha-Proton-X-Ray

Perhaps more than any other material, the fine martian dust embodies the end products of impacts, weathering, volcanism, and aqueous activity. How extensive were the contributions of aqueous weathering, and therefore how pervasive on Mars were those aqueous environments that might have hosted the origin of life on Mars? With its broad coverage of the elements, α-proton-X-ray (APX) should give us a better estimate of the chemical composition of martian fines relative to the composition of basalts or the highland materials. If liquid water were a key erosional agent, then chemical separations of the elements should occur when igneous rocks disaggregate to form shales and chemical precipitates, as on Earth. For example, aluminum is strongly fractionated relative to calcium and other alkaline-earth elements by aqueous alteration of igneous silicates. APX analysis is discussed in detail in Chapter 2.

TABLE 7.1. Instrumentation currently available for addressing exobiological objectives on planetary surfaces.

| To obtain: | An Understanding of Planetary Environment | Identification of Key Sample | Key Chemical or Morphological Measurement |
|---|---|---|---|
| Alpha-proton-X-ray | X | X | |
| "Aqueous chemistry" | X | | |
| Gamma-ray spectroscopy | X | | |
| Gas chromatography | X | X | X |
| Imaging | X | X | X |
| Infrared spectroscopy | X | X | X |
| Mass spectrometry (isotopes) | X | X | X |
| Mass spectrometry (organics) | X | X | X |
| Mössbauer | X | X | X |
| Neutron activity | X | | |
| Neutron spectroscopy | X | | |
| Raman spectroscopy | X | X | |
| Scanning electron microscopy | | X | X |
| Secondary ion mass spectrometry | | X | X |
| Thermal analysis | X | X | X |
| X-ray diffraction/fluorescence | X | X | X |

### 7.5.2. Aqueous Chemistry on Mars

Because a principal focus of exobiology is to understand the extent to which liquid water has modified the martian crust, it seems relevant to assess the composition of a water solution that has been in contact with the martian soil (*Clark*, 1994). In addition to learning more about soil composition, such an experiment might help to establish the extent to which this composition can be attributed at least in part to a history of chemical weathering. Perhaps evidence for pervasive chemical weathering indicates that indeed Mars' early environment was well suited for chemical evolution.

Upon addition of water, determinations should be made for the pH, Eh, enthalpy of solution, and evidence for soluble minerals (especially salts) and trace elements. Soil properties such as absorptivity and particle-size distribution should also be determined. Such measurements could be achieved in a flight instrument because an array of chemical microsensors are now available. In addition to Eh sensors, ion-specific electrodes can be deployed to measure pH, soluble anions (e.g., chloride, sulfate, carbonate), and cations (Ca, Fe, Mg, K, Na, etc.). It would be useful to treat the soil with pure water and with an acidified solution in order to extract less-soluble minerals (e.g., certain carbonates and sulfates) that still might have been deposited in aqueous environments.

The presence and nature of clays in the martian soil are also quite relevant for assaying the history of water activity on the planet. Methods for measuring particle-size distribution and adsorption characteristics of soil particles would be informative. Such an instrument would have to address several technical challenges associated with maintaining liquid water in the martian surface environment, with its low pressures and temperatures. Additional challenges are associated with the selection of the most robust microsensors and methods for measuring soil grain size.

### 7.5.3. Gamma-Ray Spectroscopy

The technique of γ-ray spectroscopy relies on the detection and quantitation of natural γ radiation emitted by planetary material. The elements whose abundance can thereby be measured are either those with long-lived radionuclides (e.g., K, Th, U) or those that generate γ rays when exposed to cosmic-ray-produced neutrons (e.g., O, Na, Mg, Si, Cl, Ca, Mn, Fe, and Ni). When used in conjunction with neutron spectroscopy, as is commonly done, this technique also yields the abundance of H, i.e., in most cosmic settings, the abundance of water. It is this feature that makes it of such importance to exobiological exploration. Gamma-ray spectroscopy is described in more detail in Chapter 2.

### 7.5.4. Gas Chromatography

Gas chromatography (GC) is a powerful and reliable technique for the analysis of gaseous mixtures. Because of its reliability it has been one of the most useful analytical methods used in planetary exploration missions to Venus by the Pioneer Venus spacecraft and Mars by Viking (*Oyama et al.,* 1980; *Oyama and Berdahl*, 1977). Moreover, the utility of GC has been proven for determining gaseous components evolved during pyrolysis, both terrestrially and during landed missions to Mars (Viking). Volatiles of primary interest to exobiology are those that contain the biogenic elements and include organics, water, $CO_2$, $NO_x$, $NH_3$, $H_2S$, and $SO_x$.

In the vast majority of gas-chromatographic determinations, a sample is introduced at the head of a chromatographic column. This column is usually packed or coated with a stationary phase. As the sample is carried through the column by a gas stream (the carrier gas), it is physically separated into discrete bands by the process of differential migration, based on the differences in the abilities of the gases within the sample to adhere to the stationary phase of the column as it passes through it. At the end of the column the separated bands emerge, each containing a component of the mixture, and are measured by a general-purpose detector. Identification is determined by the retention time of a compound on a given column, which is commonly unique, though it can vary with some analytical conditions (*Pollock et al.*, 1982; 1984).

General broad-range detectors include the common thermal-conductivity detectors (TCD) and the metastable ionization detectors (MID). TCDs have been used as detectors in GCs that have conducted analyses during the Viking and Pioneer Venus missions. In a TCD, as a sample of gas passes into the detector it changes the thermal conductance within the detector. The change in conductance is transformed into a voltage, the size of the voltage being proportional to the quantity of the gas flowing through the detector. In the MID, the carrier gas (usually one of the noble gases such as He, Ne, or Ar) is ionized. As a gas sample passes through the detector, the ionization potential of the detector changes. The change in ionization potential is transformed into a voltage that is proportional to the quantity of gas flowing through the detector (*Woeller et al.*, 1984). The advantage of the MID over the TCD is that it is usually 2–3 orders of magnitude more sensitive to most gases.

Coupling DTA (see section 7.5.16) with GC enables one to detect the physical changes associated with the volatilization of certain substances, providing substantial additional information that synergistically couples with the DTA data. Specifically, the data from the GC will unequivocally identify any evolved gases such as $CO_2$, $H_2O$, organics, etc., and will allow one to correlate DTA events with the specific gases evolved during that event. The combination of thermal and evolved gas analysis distinguishes between phase changes and chemical reactions that evolve water, $CO_2$, or other volatiles (e.g., complex mixed organics). By relating the gases evolved from minerals, as identified by GC, and the DTA temperature at which gas evolution occurred, it is possible to distinguish among closely related soil components such as clays, zeolites, and silicates as well as evaporites (*Banin et al.*, 1993).

An example of the necessity of determining if a gas is evolved during a thermal reaction of soil is that shown when quartz is heated. Quartz is identifiable by its sharp endothermic $\alpha$ to $\beta$ transition occurring at 580°C. This transition occurs within the same temperature range as the broad endothermic water-producing dehydroxylation reaction of clays. Because the dehydroxylation reaction in clays is broad and produces water vapor that can be detected by a gas chromatograph, whereas the quartz transition reaction is sharp and produces no gas, they are easily distinguished in the sample using DTA/GC, but difficult to distinguish in the same sample using either DTA or DSC alone. The advantage of a GC over specific compound detectors (such as those for $CO_2$, $H_2O$, etc.) is that if an unanticipated gas is produced, an instrument equipped with specific compound detectors will not be able to identify it, but a GC, with its broad analytical range, can, provided the appropriate standards have been run. The evolution of several gases simultaneously from a single reaction (an unlikely event) is easily dealt with by the inherent capability of the GC.

### 7.5.5. Imaging

Clearly a lander camera would be crucial for locating rocks whose formation involved liquid water. On Earth, such chemically precipitated sediments constitute no more than a few percent of the very ancient (early Archean age) rock sequences that have been examined. Thus, boulder fields must be surveyed extensively for the “right” rocks. Once prospective rocks have been located, a closer inspection of their textures would reveal more details about their environments of deposition. For example, sedimentary layers, grain-size distributions, and even preliminary identification of minerals would all be facilitated by a hand-lens type of imager. In principle, fossils might be located using a remotely deployed microscope; however, this strategy probably offers only a low chance of success. On Earth, fossiliferous rocks usually require extensive preparation (thin-sectioning, etc.). Furthermore, locating microfossils usually requires considerable searching of ancient rocks. The detection and confirmation of a fossil occurrence will probably require a sample return or human mission to Mars. Cameras, including the hand-lens type, are discussed in Chapter 9.

### 7.5.6. Infrared Spectroscopy

Perhaps the most promising site for extant life on Mars today is in a subsurface aquifer where water has been maintained in its liquid state by geothermal heat. A definitive demonstration that volcanism or hydrothermal activity persists today would help to strengthen the evidence for this possibility. Perhaps atmospheric trace gases would be the most accessible line of evidence for such subsurface activity. Gases such as $CH_4$, $SO_2$, etc. are prospective candidates that might be detectible by infrared observations of the atmosphere. Regarding the search for evidence of extinct life or prebiotic chemical evolution, imaging of surface materials in the near- and midinfrared could help to survey rocks in the vicinity of the lander or rover to facilitate sampling of carbonates and other lithologies of exobiological interest.

Infrared spectroscopy has also proven to be a useful tool in remote sensing of planetary atmospheres and surfaces. In particular, remote sensing of several planetary bodies using near-IR spectroscopy (NIR) has provided information on the chemical constituents on their surfaces, e.g., condensed $SO_2$ on the jovian moon Io, $CH_4$, $CO_2$/CO, $N_2$ ices on Triton and Pluto, and $O_2$ on Ganymede. Similar studies are likely to be of value in analyzing the constituents of a cometary nucleus.

The near-IR (0.8–5 µm) region displays characteristic features associated with the combination and overtones of bond stretches, bends, etc., as well as the fundamental C-H stretches of hydrocarbons. There is considerable difference in the frequencies of the bands associated with aromatic and aliphatic groups. A typical spectral resolution of 2–5 $cm^{-1}$ is adequate to distinguish between different components. In the 2–2.5-µm region, the spectra provide information on $H_2O$; water of hydration and $H_2O$ bonded internally to inorganic salts can be easily distinguished. Most inorganic ions, like $CO_3^{=}$, $NO_3^{-}$, and $PO_4^{3-}$, have strong fundamental modes in the thermal-IR region and their overtones fall in the near-IR range. Use of fiber optics can permit probing beneath a weathered veneer.

Thermal-IR spectra also provide a sensitive technique for the identification of surface constituents. Such an instrument may be employed in emission mode, if there is an inherent temperature gradient near the surface, or in reflectance mode using solar radiation as a source. An instrument operating in the range 2–25 µm, with a signal-to-noise ratio of 400, is being developed for use on the martian surface (*Christensen et al.*, 1992).

A prototype miniaturized NIR laboratory-scale instrument has been developed commercially (SpectralChem 100, AnalytiChem Corp.). This weighs less than 5 kg but has a power requirement of 60 W. For use on a lander/rover, this power consumption needs to be reduced. One of the advantages of NIR spectroscopy is that in weakly absorbing regions the radiation penetrates deeper into the surface, enabling components below the surface to be investigated.

### 7.5.7. Mass Spectrometry (Isotopes)

Stable-isotopic measurements of the "biogenic" elements, C, H, O, N, and S, can in many instances be utilized to gain insights into those processes that have affected the reservoirs of these elements in a planetary environment. For example, the atmospheric H budget on Mars can be examined using stable-isotopic abundances (e.g., *Donahue*, 1995). Isotopic measurements are significant to exobiology for several reasons. First, such measurements might help us to reconstruct the atmospheric composition, hence the environmental conditions, during the first 0.5–1.0 G.y. of martian history (e.g., *Owen*, 1992). It was during this putatively more-clement period that liquid water apparently persisted on the surface and the opportunity was best for martian life to begin. Second, isotopic analyses of surface materials might help to characterize any materials that contain biogenic elements and to determine whether these samples formed in equilibrium with the current atmosphere. For example, a carbonate rock with $^{13}C/^{12}C$ value significantly lower than that expected at equilibrium with the atmosphere might have formed during an earlier epoch, when the atmospheric isotopic composition had been perhaps less fractionated by processes involving loss of C to space. This earlier epoch might have had a climate more suitable for chemical evolution or life, therefore the carbonate might also contain material of significance for exobiology. Third, if any organic matter is detected, either on Mars or on the surface of a comet, stable-isotopic measurements might help to infer the processes responsible for its origin. For, example, this approach might identify components on a comet that originated from outside our solar system by detecting anomalous $^{13}C/^{12}C$ values. In another example from early Earth, $^{13}C/^{12}C$ values of organic C are lower by typically some 2–4% than the corresponding values in carbonates. This particular depletion is characteristic of biological organic synthesis. Such a measurement might detect whether a characteristic pattern exists on Mars that could implicate a particular mechanism (biologic?) for organic synthesis.

Stable-isotopic measurements are best performed using magnetic-sector or quadrupole mass spectrometers. Miniaturized mass spectrometers have been built routinely for spaceflight applications (e.g., *Niemann et al.*, 1992). Atmospheric measurements of $CO_2$ on Mars could be performed using a stand-alone mass spectrometer. An instrument with mass resolution ($M/\delta M$) of at least 200 and a precision for the isotopic measurement of perhaps 1% is necessary to provide meaningful constraints for models estimating either rates of loss to space or to estimate exchange rates with crustal reservoirs. Of particular interest are recent developments that promise to effect significant weight reductions in isotope mass spectrometry by means of two different approaches: the construction of a "mass-spectrometer on a chip" (*Young et al.*, 1994) and the use of tunable diode-laser spectroscopy (*Sauke and Becker*, 1994).

Measurements of C, H, O, N, and S species in crustal materials would require that a device liberate gases from these materials and deliver them to the mass spectrometer. Heating the sample of martian rock or soil, or cometary regolith might be one such approach. Isotopic measurements of organic C should have an associated precision of 1% or better in order to interpret mechanisms of organic synthesis or to detect exotic sources of C (such as those originating from outside the solar system). For organic analyses, the sample also must be combusted (or the sample heated and the evolved gases combusted) to obtain the isotopic measurement. In some cases, where the soil is heated, gases that coevolve might also have overlapping mass spectra, which could interfere with the isotopic analyses. Some provision must therefore be made to reduce this interference. Chemical trapping or gas chromatography to separate the gases would be effective. For example, an appropriate system for analyzing the stable-isotopic composition of a sample might include analytical components that (1) liberate the elements as gases (e.g., a heater), (2) separate the gases (gas chromatograph), (3) combust any reduced or oxidized species to $CO_2$ and $N_2$ (oven with catalyst), and (d) perform the isotopic measurement (mass spectrometer).

### 7.5.8. Mass Spectrometry (Organics)

Mass spectrometry (MS) is a powerful instrumental technique for organic analysis on a planetary surface because it is the only major organic analytical technique that can detect, identify, and quantify most classes of organic compounds. Small, neutral, volatile organics such as HCN and HCOH could be detected in solar system ices by direct MS. In a low-temperature, volatile-rich environment such as a comet nucleus or martian polar cap, a sample of ice potentially containing organic molecules could be simply warmed under vacuum until volatilized and injected directly into the mass-spectrometer ionization source. The use of soft-ionization techniques, which generate molecular ions without fragmenting the molecule, would allow a first-order inventory of volatile organic compounds to be quickly carried out. Soft ionization, however, might add significantly to the weight, cost, and complexity of the instrument. A hard-ionization technique such as electron ionization, which fragments the analyte molecule but requires less complex instrumentation, could be coupled with groundbased computer-aided mass-spectral analysis to identify volatile organics. Amino acids, purines, pyrimidines, and other nonvolatile prebiotic compounds could not be detected by this method. For more-highly-altered samples, such as martian regolith or cometary-nucleus lag deposits, mass spectrometry can be coupled with thermal-analysis techniques to achieve either simple quantitation of total organic C or, with limited thermal exposure, identification of some structural elements of the original analyte.

Identification of nonvolatile organic species can best be achieved when MS is coupled downstream from a molecular separation system, allowing a mass spectrum of each species in the sample to be obtained independently. The only molecular separation technique flown on a spacecraft so far is gas chromatography. In most cases a quadrupole mass spectrometer is used as a chromatographic detector, although other MS types can also be used. The utility of gas chromatography coupled with mass spectrometry (GC/MS) for planetary-surface organic analysis was convincingly demonstrated by Viking (*Biemann*, 1979). The GC/MS on board each of the two landers was the only instrument capable of general organic molecule detection and identification, with detection limits in the parts-per-billion range. This capability served as an important control for the biology experiments, without which the initial positive results might have been misinterpreted. Chromatographic techniques are also capable of separating optical isomers of chiral compounds such as amino acids. This capability can help answer questions about the origins of biomolecular chirality, and serve as a monitor of forward biological contamination of solar system environments.

The use of any chromatographic separation system, however, introduces additional problems and limitations. One of the drawbacks of GC/MS for spacecraft use is that many prebiotically important compounds, such as amino acids, purines, and pyrimidines, must be chemically derivatized to make them volatile enough for GC separation. A chamber and fluid-handling system for the derivatization chemistry must therefore be provided, adding to the size and complexity of the instrument package. Also, since most derivatization reagents are functional-group specific, one class of organic compounds must be targeted for analysis while others are excluded.

Liquid chromatography (LC) is a molecular separation technique that does not require volatile analytes, since the separation is carried out in the liquid phase. LC usually also requires sample derivatization, however, for the chromatographic separation to be achieved. The volumes of solvents required for LC/MS, and the amount of waste generated, are problematic for spacecraft use. Capillary electrophoresis (CE) separates molecules by electrophoretic mobility in a liquid buffer system, and can be performed without derivatization, but the analyte must contain an ionizable functional group. CE/MS can employ chiral mobility modifiers in the separation phase that allow optical-isomer resolution without derivatization, while chiral resolution in GC/MS and LC/MS requires derivatization. Both CE/MS and LC/MS must make use of liquid (generally aqueous) solvents and reagents, so the instrument must be maintained within the spacecraft at temperatures >0°C and pressures around 1 bar.

The choice of the class of organic compounds to be targeted for analysis is not an easy one. Among the most prebiotically interesting molecules are those that make up modern terrestrial biopolymers. These include amino acids, purines, pyrimidines, sugars, and fatty acids. All these except sugars have been detected in carbonaceous chondrites, and therefore may be present in cometary nuclei and perhaps in some martian environments. It may not be clear, however, whether a given molecule detected on a planetary surface was formed *in situ* by endogenous organic chemistry or was delivered to the surface by meteorite impact. Organic molecular analysis should be coupled with C, H, O, and N isotope analysis to determine the sources and formation mechanisms of planetary organic compounds.

Mass spectrometers of shoebox size are available and have flown on Viking and Galileo. Recent work in microfabrication of MS systems on single chips holds the promise of even smaller, lighter systems (*Young et al.*, 1994). A single mass spectrometer could be used both as a stand-alone mass analyzer and as a detector for one or more instruments using thermal analysis or molecular separation techniques. LC/MS instruments are now available commercially for laboratory use, and CE systems, including derivatization, if necessary, and injection mechanisms have been fabricated on single glass chips by photolithographic techniques (*Jacobson et al.*, 1994). Continuing advances in miniaturization of these techniques should allow serious consideration of their inclusion in future planetary-surface missions. Target sensitivities for future generations of mass spectrometers should be in the parts-per-billion range, comparable to that of the Viking GC/MS. High mass resolution may be more crucial than high sensitivity for organic-compound identification, and should be no lower than 1 amu, to minimize ambiguities in compound identification.

### 7.5.9. Mössbauer Spectroscopy

Because a Mössbauer spectrometer will probably be included on lander spacecraft, it is of interest to explore its suitability in an exobiology context. Along with scientific dividends regarding mineralogy and geochemical processes, Mössbauer spectroscopy may also provide clues in the search for fossil evidence of ancient life billions of years ago on Mars.

The Mössbauer spectrum, arising from a nuclear resonance process, depends on the nature of the sample investigated, providing mineral identification and data on oxidation state, particle size, magnetic order, etc. Current planning is to use Fe ($^{57}$Fe) Mössbauer spectroscopy because of the high natural abundance of Fe. The 270-day half-life of the $\gamma$ source, with the ability to start from Earth at high strength, is compatible with a typical mission to Mars, an asteroid, or many comets.

A backscatter Mössbauer spectrometer for lander spacecraft including rovers, under development since 1988, is now sufficiently mature that it is sensible to speak of its near-term deployment. Size and shape are roughly those of a soft-drink can, with mass under 0.5 kg and power consumption less than 2 W. When placed about 1 mm from a surface deposit, for example, by a robotic arm, the instrument can obtain a usable spectrum in 1 to 5 hr.

In exobiological exploration on Mars or asteroids it is of interest to determine the amount of liquid-water alteration of Fe-rich deposits, affecting, for example, the presence of goethite ($\alpha$-FeOOH) or hematite ($\alpha$-$Fe_2O_3$), distinguishable by Mössbauer spectroscopy. The technique has demonstrated aqueous alteration in the Orgueil carbonaceous chondrite through the characteristic variation with temperature of the Mössbauer spectrum of the superparamagnetic aqueous-alteration product (*Wdowiak and Agresti*, 1984).

Perhaps the most exciting potential for Mössbauer spectroscopy is to use it to prospect for minerals in which a bacterial fossil record may reside. At the bottom of Earth's oceans, geothermal vents ("smokers") harbor bacterial communities that derive energy from hot, S-rich vent effluents, something that could have existed on Mars, providing liquid water was then present. Bacteria in outlying regions of such vents are coated with Fe-rich "rust," easily analyzed with a Mössbauer spectrometer. Because bacteria are about a micrometer in size, the Fe-oxide rust must consist of particles about 100× smaller (~10 nm), "nanophase" particles. When thermal activity ceases, bacteria die, and the rust crystallizes to form a "fossil" with the Mössbauer signature of superparamagnetism, which is a property of nanophase, magnetically ordered material (*Agresti et al.*, 1994).

Sediments associated with Fe-rich hydrothermal springs on land (Yellowstone National Park), which are plausible analogs of what may have existed on Mars and where systematic sample collection is feasible, have demonstrated similar Mössbauer signatures, including deposits of nanophase Fe oxide. The biological influence on deposits collected at YNP, including the ferric/ferrous ratio, reflecting a variation of environmental redox potential possibly due to microbiological diversity with depth (becoming more aphotic and anoxygenic) and/or distance from the vent source (decreasing temperature), is being assessed (*Agresti et al.*, 1995).

All this suggests that, if bacterialike organisms existed on Mars in a hydrothermal environment, it is likely that these organisms could have also become coated with an Fe-oxide "rust." Conceivably the bacteria may somehow modify the Fe that precipitates on its surface, creating the fine particle structure. Furthermore, photosynthesizing bacteria produce $O_2$ as a by-product of their metabolism and may drive the precipitation of Fe in these systems. Yet it is still unclear whether nanophase Fe is a sure sign of life or simply an indicator of the type of Fe minerals produced in environments such as thermal springs. The nanophase signature may reflect the rapid rates of crystallization that occur within certain environments. But with Mössbauer it may be possible to distinguish hydrothermal Fe minerals, which would be an important step in exploration for life on Mars. Pinpointing hydrothermal Fe deposits on Mars would assist in the selection of sites for future missions to explore for ancient martian microbes. This strongly argues for using a Mössbauer spectrometer on a Mars lander/rover to look for such deposits. In the laboratory, sample temperature is adjusted by a refrigerator; on Mars, the diurnal (day-night) temperature variation (~240–180 K) accommodates this requirement very nicely.

### 7.5.10. Neutron Activation

In addition to being a well-known analytical technique in the laboratory, neutron activation can be employed remotely on a planetary surface. The output from a pulsed-neutron generator produces $\gamma$ rays by inelastic scattering, capture, and delayed induced radioactivity in the material within about a meter of the generator/detector assemblage. Most of the rock-forming elements can be analyzed by this means, plus two elements of particular interest to exobiology: C and H. Pulsed-neutron activation analysis is described in greater detail in Chapter 2.

### 7.5.11. Neutron Spectroscopy

A further gauge of the importance of aqueous weathering might be revealed by measurements of the H content (as either water or hydroxyl group) in martian fines. At mid to low equatorial latitudes, where no near-surface ground ice is anticipated, much of the H sensed would be bound in salts and clays. Water was detected in the dust by the Viking lander but unfortunately with poor accuracy. A neutron spectrometer should measure this H with much higher accuracy, and thus indicate the degree to which the source rock material has sustained hydration. Neutron spectroscopy is discussed in greater detail in Chapter 2.

### 7.5.12. Raman Spectroscopy

Laser Raman spectroscopy is used for the analysis of organic (hydrocarbon) as well as inorganic (mineral) substances, making it desirable as an exobiology instrument on a lander spacecraft. Integration of current technologies into a laser Raman system can meet science-yield and spacecraft-compatibility requirements including those for rovers. In the latter context, we envision the use of fiber optics to sense samples at distances as great as 1 km from the spacecraft in which the core of the instrument resides. In addition, Raman can detect, via surface enhancement techniques, species at low concentrations in samples processed (e.g., by gas chromatography) in a small onboard automated "laboratory."

Raman spectroscopy is an optical light-scattering technique for determining the molecular composition of materials or their crystal lattice structure. When light interacts with a material, almost all the light is scattered elastically (Rayleigh scattering) with no change in energy (or frequency). A tiny fraction, $10^{-8}$ to $10^{-12}$, of the incident radiation is scattered inelastically, with loss (or gain) of energy to molecular and lattice vibrational modes. A laser illuminates the sample, the resulting wavelength shift of the scattered radiation being detected using two components: a dispersive element and a photon detector. The spectral shifts are related to molecular structure in essentially the same way as the absorption transitions observed in infrared absorption spectroscopy. Selection rules governing transition intensities are different in the two cases because they are related to different molecular properties. Raman may be used to characterize certain classes of bonds as well as identify crystalline polymorphy of different organic and inorganic materials. The Raman spectrometer system consists of four basic components:

*Monochromator.* Special holographic laser notch filters have radically changed the design and efficiency of Raman instruments. A high-throughput (for all wavelengths other than the wavelength of the laser excitation) holographic notch filter can reduce the stray light ("photon fog") of elastically scattered radiation such that it does not swamp the signal at the detector. Available reduced-size monochromators suitable for a LRS system when used with a holographic notch prefilter have adequate stray-light rejection and resolution, and are even small enough to fit onto a PC card (Control Development Corp.).

*Light sources.* An important achievement is the development of single-mode laser diodes that are compact and lightweight, are 3–40% efficient, and have suitable luminescence for Raman spectroscopy (3–500 mW). These diodes can operate from 630 nm to longer wavelength (~780–810 nm) and induce less fluorescence background than shorter-wavelength sources do.

*Fiber coupling.* The third advance essential for a portable Raman instrument is in fiber optics, providing flexibility in sample excitation and data acquisition as well as permitting remote Raman spectroscopy with fiber probes as long as 1 km (*Schoen*, 1995). It is clear that fiber-coupled Raman systems are of great interest in designing a prototype Raman instrument for a planetary lander spacecraft. Deployment can be by (1) a passive appendage of the lander body that impales into the surface; (2) an active appendage of the lander or a rover in the form of a robotic arm; (3) transporting or trailing out from the lander vehicle by a microrover; (4) trailing behind an arrowlike projectile ejected from a combined projector/quiver.

*Detection system.* CCDs feature quantum efficiencies of up to 90% at wavelengths near 700–800 nm (9 of 10 incident photons are recorded). With sufficient cooling, which can be passive in most planetary environments (Mars, comets, etc.), they can be considered to be practically noiseless. Their two-dimensional nature (>10,242 pixels) enables multiple spectra to be acquired simultaneously. Using a gated intensified CCD with a pulsed diode laser will reduce the effect of interfering non-Raman long-lived luminescence of certain samples. There is now a considerable body of experience in dealing with cosmic-ray artifacts in CCD images (e.g., Hubble Space Telescope).

### 7.5.13. Scanning Electron Microscopy

"Environmental" SEM (ESEM, an electron microscope that tolerates relatively high pressures in the vicinity of the sample) would be useful for examining rock textures and mineral structures. In principle, it could also be used to detect microfossils, e.g., on Mars; however, the prospects for successful robotic detection of such microfossils seem remote at this time. Scanning electron microscopy is described in more detail in Chapter 6.

### 7.5.14. Secondary-Ion Mass Spectrometry (SIMS)

*SIMS sensu stricto.* Secondary-ion mass spectrometry (SIMS) is a useful technique in organic mass analysis as a means of volatilizing and ionizing species that are solid and would not be easily analyzable by conventional organic MS techniques. To prevent destruction of the molecular structure that one wishes to analyze, SIMS must operate within the so-called "static SIMS limit," i.e., the sample must receive a primary ion dose not exceeding $10^{12}$ ions/cm$^2$ (*Katz*, 1992).

Detection and analysis of secondary ions can be made using magnetic, quadrupole, or time-of-flight (TOF) mass spectrometers. When the analysis requires rapid acquisition of mass spectra over an extended mass range (above 500 Daltons), or when high mass resolution is desired, the TOF detection scheme becomes the preferred, if not the only, choice.

One of the most common modes of organic characterization involves the determination of a material's surface chemistry. This is accomplished through the interpretation of the fragmentation pattern in the static SIMS mass spectrum. This "fingerprint" yields a great deal of information about a sample's superficial chemical nature, including the relative degree of unsaturation, the presence or absence of aromatic groups, etc. Due to the low primary dose and absence of sputtering, static SIMS is mainly a surface analytical technique, with a penetration depth of about 10 Å.

*Laser-based SIMS.* If one wishes to analyze deeper than the sample surface, while not compromising its molecular structure, one can use a laser ablation/desorption system to effect the volatilization/ionization. Since lasers can be easily pulsed, they are naturally suited as ionization sources for TOF-type instruments. The mass-spectrometric analysis of high-molecular-weight compounds requires that the molecules, normally present in the condensed phase, be converted into intact, isolated ionized molecules in the gas phase. Two configurations are commonly used, one that uses a single laser to produce both the volatilization and the ionization of the substances of interest, the other of which decouples the volatilization (laser 1) and the ionization (laser 2). The latter configuration is often referred to as postionization (PI). Specific laser wavelengths can be used to ensure selectivity in ionization, thus creating the capability to search for specific classes of organic compounds (*Hahn et al.*, 1987; *Zare et al.*, 1988). This can be a valuable approach in a survey mode, to reduce and rationalize the complexity of molecular information in a natural system.

Another approach that can be useful in the analysis of large molecular structures is called Matrix Assisted Laser Desorption Ionization (MALDI). The "matrix" is a solid (typically a low-molecular-weight organic acid with an aromatic group) within which the analyte is dispersed. This absorbs the laser energy and redistributes it to the analyte while undergoing volatilization. As the volatilization takes place, a proton-rich environment is created that promotes ionization of the analyte via proton attachment. The value of this scheme is that the matrix shields the analyte from excessive laser energy absorption, which would lead to its destruction (*Hillenkamp et al.*, 1991).

MALDI has been applied with success in the analysis of biopolymers such as proteins, carbohydrates, DNA, etc., as well as manmade organic polymers. Masses up to 150–200 kDa are routinely detected. Most of the applications of MALDI entail the use of specific matrices tailored to the analytes that are being sought. However, water ice can also act as a matrix, as demonstrated by the success in volatilizing and ionizing frozen DNA and protein-water solutions (*Nelson et al.*, 1989).

The value of a MALDI-type analytical instrument in a cometary lander is its potential ability to detect high-molecular-weight organic species dispersed in ice at the surface or in the interior of a cometary nucleus. Its strengths include the simplicity of a TOF mass spectrometer, the low weight of a laser unit, and the flexibility in wavelength, energy, pulse width, etc., made possible by recent technology.

### 7.5.15. Particle Desorption Mass Spectrometry (PDMS)

This is another mass-spectrometric technique that could be useful in the analysis of organic materials. Its principle is to use the fragments from spontaneous fission of $^{252}$Cf (half-life ~5 yr) to penetrate, desorb, and ionize organic molecules/fragments (*Macfarlane and Torgerson*, 1976). The ions thus formed are then analyzed using a TOF detection scheme. The start signal for the TOF measurement is provided by the complementary fission fragment. Two features make this type of ionization attractive for exobiological applications in space: One is the simplicity of the ionization source itself, which does not require a power supply because it is based on spontaneous fission; the second is the range of a Cf fission fragment in low-Z material, which is on the order of 15 µm, hence the sampling depth for this type of technique is considerably deeper than in the case of static SIMS discussed above. Commercial PDMS instruments exist and are currently used in biochemical analysis. A $^{252}$Cf-based instrument for planetary science would require a thin Cf source to be located at the ionization end of a mass spectrometer, a system for placing the sample in the source, and the appropriate electronics. A calculation of the required source activity depends on several parameters, including number of secondary ions desired, distance between Cf source and sample, and sample lateral size. For realistic sample- and spectrometer-size parameters, the source activity is calculated to be in the range of 10–20 µCurie, which is quite safe to prepare and to handle.The PDMS technique can be realistically used for detection of ions up to perhaps 2000 Da. This mass range could be considered complementary to MALDI.

### 7.5.16. Thermal Analysis

Thermal analytical techniques, especially when coupled with evolved-gas analysis, are powerful methods for characterizing a variety of substances. In particular, differential thermal analysis (DTA) and the related technique, differential scanning calorimetry (DSC), can provide significant mineralogical information about unknown soil samples with relatively simple measurements (*Wendlandt*, 1986). In contrast to X-ray fluorescence, which gives only elemental-composition information about a sample, thermal analytical techniques can be quite specific regarding the mineralogical composition of soil samples. X-ray diffraction can also provide specific mineralogical information about soil samples, but volatiles and noncrystalline material are transparent to that technique. Infrared spectroscopic techniques are also capable of providing mineralogical data of samples. However, they cannot penetrate beneath the immediate weathered surface of a sample, leaving the unweathered bulk of the sample unanalyzed (*Schwartz et al.*, 1995).

DTA is a powerful analytical technique that can be used to identify the mineralogy of a sample. Of particular importance to exobiology is its ability to distinguish among clays, silicates, feldspars, zeolites, glasses, and evaporites, as well as to determine if organics are present. This is accomplished through the endothermic and exothermic processes associated with chemical reactions, phase changes, and other solid-state transition reactions occurring within the 0°–1200°C temperature range used. In DTA, the temperature of an unknown sample is measured differentially with respect to the temperature of an inert reference material, while the two samples are heated at the same rate simultaneously. As the temperature of the oven rises, any endothermic or exothermic reactions cause a change in the sample temperature relative to the reference. The size of the resulting exotherm or endotherm is indicative of the relative amount of material reacting (*Schwartz et al.*, 1995).

DSC, like DTA, monitors the temperatures of a sample and inert reference. Unlike DTA, DSC maintains the reference temperature isothermal with respect to the sample temperature during the heating process. The amount of heat required to maintain these isothermal conditions is then recorded as a function of time (or temperature). DSC is thus more quantitative than DTA because it measures directly the differential heat evolved or consumed (i.e., enthalpy) (*Wendlandt*, 1986). DTA is, however, less complex to implement than DSC (e.g., the mass of the sample must be determined in DSC, and the thermal contact between the sample and the cell wall must be tight and uniform). In contrast, data from DTA are not degraded when the mass of the sample is not known, nor does it require such tight control over the sample and cell-wall thermal contact (*Wendlandt*, 1986). An additional advantage to using DTA for geochemistry is that it can obtain accurate mineralogical information above 700°C. For example, clays exhibit a high-temperature transition between 950° and 1100°C that is critical to their identification. DSC cannot yield the enthalpy at these high temperatures and therefore cannot be used to distinguish accurately among the clays (*Wendlandt*, 1986).

### 7.5.17. X-Ray Diffraction/X-Ray Fluorescence

Many of the comments made earlier on the APX method apply also to X-ray diffraction/fluorescence (XRD/XRF). In this case, however, the ability to define mineralogy offers a more detailed and precise insight into the nature and role of aqueous processes involved in the formation of soils and sedimentary rocks. To the extent that X-ray analyses of rocks are possible, they would facilitate the identification of the lithologies (carbonates, cherts, clay-rich sediments) that are most promising for preserving a chemical record of preexisting aqueous environments, including a possible record of any now-extinct biology or prebiotic chemical evolution that took place in those environments. XRD/XRF is discussed in more detail in Chapter 6.

## 7.6. A NOTE ON INSTRUMENT ARRAYS, HYBRIDIZATION, AND NEW CONCEPTS

No single instrument, wavelength range, separation procedure, etc., is ever adequate on its own for carrying out analytical tasks in complex environments. That is why instrument hybridization occurs (discussed below), and why the analyst also brings a variety or array of instruments to bear on the sample. The lab chemist will use infrared (IR), laser Raman (LRS), ultraviolet/visible (UV/VIS), and nuclear magnetic resonance (NMR) spectroscopies, high-pressure chromatography (HPLC) and gas chromatography/mass spectroscopy (GC/MS), X-ray diffraction (XRD), and photoelectron spectroscopy (PES), etc., before coming to a conclusion about the nature of a substance. Being able to make a variety of measurements with an array of instruments is mandatory for good science in general. The architecture of the array must be considered carefully, and thus the spacecraft should not just carry a collection of individual instruments each playing its own tune, but must be an orchestra.

The keystone instrument of the array will be the general-purpose imaging system expected for all landers and, of course, roving vehicles. Other instruments also expected to exist as a matter of course are thermometers and barometers. Can these general-purpose instruments be configured with accessories (i.e., magnification, radiation thermometry instead of contact measurements) so they will have a greater dynamic range? Being able to make a spectroscopic measurement on a sample at different measured temperatures during a diurnal cycle(s) would transform a simple observation into a true experiment, characterized by varied parameters, with promise of a richer yield.

Certain instruments can also serve more than one role in that besides being a stand-alone, interrogating samples directly, they can also serve as a sensor in a more complex analytical system. The gas chromatograph/mass spectrometer (GC/MS) is the classic example of the hybrid instrument and the concept is expected to become even more widely used.

An example of what is to be expected is extension of the utility of the GC/MS with volatiles by adding, in parallel to GC, capillary electrophoresis (CE) (*Harrison et al.*, 1993), for species such as amino acids, and laser desorption (LD) of molecules such as polycyclic aromatic hydrocarbons (*Kovalenko et al.*, 1992). High-power pulses from compact diode lasers now make this possible on a spacecraft. The laser Raman spectrometer is another such an example. It can sense both an unprocessed sample, possibly at some distance via an optical fiber (*Shoen*, 1995), and a sample emerging out of a processor such as a gas chromatograph, via another optical fiber and surface-enhancement substrate (*Roth and Kiefer*, 1994).

Among the new and emerging technologies of interest for exobiological exploration are what have been referred to as the "New Microscopes." Utility for examining mineral samples suspected of harboring microfossils is obvious, but is by no means the only exobiological role for such instruments. Included are the scanning tunneling microscope (STM) and the atomic force microscope (AFM), with the AFM being of particular interest because the sample does not have to be conductive. Such an instrument is also of conventional utility for examination of crystalline texture. The dynamic range is very great, going from low magnification (100×) to atomic level. The actual instrument is compact and has negligible power requirements. The fact that it is a "table-top" instrument in the lab suggests that it probably can be used on a lander vehicle, including rovers at rest, with little problem. Also, because of its size and the fact that it does not require a vacuum, there is a clear advantage over electron-beam microscopes. However, because the piezoelectric transducer elements and allied circuitry operate at several hundred volts, attention must be paid to a potential electrical discharge problem in low-pressure environments, as on Mars.

There are also new optical microscope technologies, including scanning techniques, that result in improved performance relative to conventional microscopes (*Betzig and Trautman*, 1992). Another emerging microscope technology is the Raman microscope made possible by tunable filters (*Treado and Morris*, 1994; *Pallister et al.*, 1994). This allows imaging of a sample in terms of concentration of a molecular substructure such as hydroxyl or sulfate.

## 7.7. A NOTE ON MOBILITY AND SAMPLE ACQUISITION

Implicit in the foregoing has been ready access to the appropriate samples on the surface of Mars or another solar system body. However, achieving such access will certainly pose a number of technical challenges, such as (1) the need to transport the sampling apparatus from the landed spacecraft to the location of the sample of interest; (2) the desirability of acquiring a sample free of contamination by neighboring material (e.g., in the case of Mars, free of any surficial weathering products); and (3) the general need to manipulate the sample within the spacecraft (e.g., to move it from one point to another and to fashion it into a shape and/or form amenable to analysis). Because these are engineering issues outside the areas of expertise of this writing group, and because in most cases these are issues that are not unique to exobiology but are confronted by landed-science in general, we do not address them in detail. However, we wish to emphasize the importance of work in these areas. In particular, from the perspective of exobiology, we believe that further development work is essential on the following issues:

*Mobility on the martian surface.* Despite recent advances in rover technology, further improvements in range and capability are still needed. Actual range requirement cannot yet be specified as it depends upon factors such as spatial resolution of orbital data, size of landing ellipse, and imponderables such as the geographic distribution of "interesting" terrain and safe landing sites.

*Sampling beneath the oxidant layer on Mars.* The most likely location where an organic record might have survived on the martian surface is within a fine-grained sedimentary rock. Consequently, a requirement for the exobiological exploration of Mars is the capability of extracting an interior sample of such a rock, using a process such as coring or chipping.

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# 8: Regoliths in 3-D

***—John Grant, Andrew Cheng, Allen Delamere, Steven Gorevan, Randy Korotev, David McKay, Harrison Schmitt, and John Zarnecki***

## 8.1. INTRODUCTION

Regoliths are the fragmental, unconsolidated material forming the outer layer of solar system bodies. Because regoliths are an important component of most if not all solar system bodies, they continue to be the target of studies geared toward placing important constraints on a number of fundamental, critical science questions pertaining to body origin and evolution (e.g., *COMPLEX*, 1994). Many measurements that can be made from orbit or from Earth-based observation, such as spectral reflectance and chemical composition, provide information only about the uppermost portions of regolith and not the underlying substrate(s). Thus, an understanding of the formation processes, physical properties, composition, and evolution of planetary regoliths is essential.

We have tried to reproduce the informal character of the discussions held during the workshop and avoid duplication of discussion in alternate chapters in this report (e.g., many of the instruments listed here are cited more completely in Chapter 6). A number of statements are made that are based on the results of prior studies and workshops, but remain incompletely or largely unreferenced. Most references pertinent to these statements can be found in recent National Research Council reports (e.g., *NRC*, 1988, 1990, 1993, 1994, 1995); NASA reports (e.g., *McCord*, 1988; *SSES*, 1994; *OSS*, 1995); summaries of various science working groups (e.g., *MarSWG*, 1991; *LExSWG*, 1992); and LPI (e.g., *Elphic and McKay*, 1992; *Appleby*, 1993), JSC (e.g., *JSC*, 1988), and JPL (e.g., *McCleese et al.*, 1994) technical reports.

## 8.2. REGOLITH

A planetary regolith is any layer of fragmental, unconsolidated material that may or may not be texturally or compositionally altered relative to underlying substrate and occurs on the outer surface of a solar system body (e.g., *Short*, 1975; *Gary et al.*, 1977). This includes fragmental material from all sources (e.g., volcanic, sedimentary, meteorite infall) and derived by any process (e.g., impact and all other endogenic or exogenic processes). As such, the regolith includes fragmented material whose composition is unaltered from the *in situ* material beneath it; altered by endogenic, exogenic, or *in situ* processes; altered by radiation (e.g., solar or extrasolar); and/or altered by any combination of these or other processes.

Use of this general definition ensures consideration of the near-surface materials on all solar system bodies. For example, on airless, rocky bodies like the Moon, asteroids, and Mercury, the regolith consists largely of rock debris produced by meteoroid bombardment. On Mars and Venus, as on Earth, the interaction of fluids and the atmosphere with the rocky substrate help produce and modify the regolith. For bodies such as comets and the icy satellites, the regolith includes the outermost region of the bodies where interactions with space occur.

## 8.3. RESTATEMENT OF CRITICAL SCIENCE QUESTIONS

A number of critical science questions regarding solar system bodies in general (e.g., *COMPLEX*, 1994) are easily restated and placed within the context of regolith studies. For example, questions regarding the bulk composition of a body can be phrased as “How does the bulk composition of regolith and its component fragments reflect the bulk composition of the body?” Similarly, questions related to the differentiation of a body and its early thermal state can become “What regolith measurements made in different locations and in different material provide constraints on differentiation of the body?” Questions related to present and past geologic activity and associated thermal and tectonic evolution can be phrased as “What do regolith properties tell us about the geologic evolution of a body and of the ongoing geologic activity on and in the body?”

As the history of the Earth is recorded in the sedimentary record, planetary regoliths contain a history of early and ongoing activity. Because of this potential as “tape recorders” of past events, study of planetary regoliths can help to address questions of the impact history (at all scales) of the solar system and the role of impacts in modifying the surfaces of bodies. On a related topic, regoliths may record and preserve information, helping to resolve questions such as what information the regolith can provide regarding the global stratigraphy and the age of planetary surfaces. Regolith studies can also be used to deconvolve the irradiation history of surfaces due to solar and extrasolar activity and can help resolve questions relating to the history of magnetism of a body.

Questions related to the history of surface-atmosphere interactions and the inventory and location of volatiles on a body can also be restated in terms relevant to regolith studies. For example, what can the regolith tell us regarding the history of surface-atmosphere interactions on a body? Does the regolith provide a significant reservoir for atmosphere and/or internally derived volatiles? Does the regolith record changes in atmosphere and/or internal and/or solar exogenic derived volatiles? If so, how is this information recorded? How does the regolith influence and/or record local/global meteorological events? The potential record of biogenic activity in regoliths requires evaluation of questions such as "What can the regolith record of the distribution and history of biogenic compounds and life on a planetary body?"

## 8.4. EXAMPLES OF MEASUREMENTS REQUIRED TO ANSWER CRITICAL SCIENCE QUESTIONS

Operationally, studies of regolith samples can be divided into two categories, those involving bulk properties of regolith and those involving individual components of the regolith. For example, some of the critical science questions discussed above could be addressed by determining the chemical composition and mineralogy of bulk samples of regolith fines. However, these and some other questions can also be explored by studying individual particles from the regolith. For example, nearly all the lithologies that were found as rocks (and some that were not) at the Apollo 17 lunar site have been recognized among a random assortment of a few hundred granule-sized (2–4 mm) particles from several scoopfuls of soil (*Jolliff et al.*, 1994). Thus, any of a number of problems that might be addressed by the study of rocks scattered about the surface could also be done by studying numerous small rock fragments in the regolith from a single location. This has proven to be a great advantage for missions with limited mobility (e.g., Luna 16, 20, 24).

The collective character of measurements required to resolve the various science questions will vary widely from body to body as a result of differences in physical properties and state of understanding of those properties. For example, Table 8.1 demonstrates the general kinds of measurements that might be needed to constrain the bulk composition of regolith on solar system bodies given our present state of knowledge regarding their nature. On the Moon, considerable information on regolith bulk composition exists as the result of orbital, surface, and sample return analyses. Hence, the next stage of productive study toward this goal might include a broad spectral survey of the entire surface. By contrast, the properties of mercurian regolith remain poorly constrained and might begin with analyses of as many regolith fragments as possible to evaluate the average composition. On Mars, the next generation of regolith studies might focus on collection of ground truth for existing orbital data and conclusions drawn from the SNC meteorites. Properties of regoliths on cometary bodies are much less well understood, thereby requiring flexibility in evaluation of bulk properties and ensuring the possibility of deep penetration and sampling for pristine materials.

Despite important differences in regoliths and the present state of knowledge about these differences (Table 8.1), a number of general statements can be made about the types of measurements needed to address the critical science questions. It will be important to be able to measure the average crustal composition from orbit to identify variations. If a body is undifferentiated, the orbital measurements should directly constrain bulk composition.

The differentiation history of a body can be constrained through surface or *in situ* measurements of the major- and minor-element composition. Additional constraints on differentiation may be provided by mineral information. Detailed isotopic analysis and age dating will probably require sample return.

TABLE 8.1. Measurements required to resolve critical questions for solar system bodies in varying stages of exploration: Bulk composition as an example.

| Body | Present Level of Understanding | Measurements Required |
|---|---|---|
| Moon | Bulk composition fairly well constrained by orbital, surface, and sample analyses. | High-resolution broadband spectral survey of whole Moon from orbit and/or surface (e.g., $\gamma$-ray). |
| Mercury | Bulk properties of regolith largely unknown. | Analyze as many fragments as possible to determine average composition. Need major-element ratios relative to an incompatible. Surface patina may be a problem. |
| Mars | Some information on composition from Viking, Phobos, SNCs. | Need ground truth for orbital data and SNCs. Need composition data from more sites distributed globally. Need to constrain chemistry of dust and analyze volatiles in regolith. |
| Venus | Some information from Venera, but bulk properties of regolith remain largely unknown. | Analyze as many fragments as possible to determine average composition. Need major-element ratios relative to an incompatible. Need to be concerned with weathering effects. |
| Outer satellites | Bulk properties of regolith largely unknown. | Analyze as many fragments as possible to determine average composition. Possibly vaporize ice to get gases to constrain composition. |
| Asteroids | Bulk properties of regolith largely unknown. | Need to get fundamental elemental information ($\gamma$-ray?). Trace elements not as critical as majors—want to know if chondritic composition. Might be done best from orbit. |
| Comets | Bulk properties of regolith largely unknown. | Need fundamental composition data. Should be concerned about sampling sample pristine vs. altered materials. Pristine materials may require deep penetration. |

To evaluate the volatile inventory and history of a body, an understanding of the textural properties of regolith (e.g., crystalline texture, clasts, bulk rock, vesicles, etc.) also becomes necessary. The distribution of these volatiles and textures vertically and horizontally within the regolith and within the more general stratigraphic framework of the body is also important. Finally, it would be useful to constrain the heat capacity, conductivity, and thermal inertia of the regolith as an indicator of geologic activity and evolution.

The changing role of impact processes and the overall history of impacts on a body can be inferred from the texture, composition, distribution, and stratigraphy of the regolith. Additional information on the history of impact processes on a body as well as throughout broader portions of the solar system can be gleaned from regolith studies of cosmic-ray-exposure ages, distribution of fission tracks, and chemical and isotopic signatures of micrometeorites.

In order to understand the history of surface-atmosphere interactions on a planetary body it will be necessary to collect data at both local and regional scales. Measurements should target reservoirs of trapped gases and volatiles (e.g., water, $CO_2$) and must be coupled with chemical, isotopic, and mineralogic information from the regolith (e.g., presence of carbonates) as well as the distribution (grain size, lateral, and vertical) and stratigraphy of atmospherically altered materials.

Exploration of the history of biogenic activity on a planetary body would include a search for microfossils. Such a search should be accompanied by evaluation of regolith stratigraphy (to constrain geologic setting and the history of any life) and an understanding of where water, carbonate, silica, and clays may occur. Useful instruments for these investigations would include a gas chromatograph and mass spectrometer (needed to measure organic molecules). Studies should also emphasize mapping the occurrence of potential ecosystems in the regolith (both with depth and laterally) and might measure the optical chirality. Information on physical properties of regoliths is also required (e.g., yield strength, etc.), especially with respect to sampling effectiveness (see below).

The preceding discussion serves to provide a general sense of the range of measurements that might be made in the regolith on different bodies. It is also clear from this discussion, however, that the variation in the state of knowledge of regolith properties requires differing arrays of instruments tailored to each body (e.g., Table 8.1). In an attempt to account for such a degree of variability in regolith properties and level of understanding, Table 8.2 presents some specific examples of the science objectives, measurements, goals, and possible instrument arrays for future regolith studies on three solar system bodies of widely varying characteristics. This includes bodies for which the regolith properties are largely unknown (comets), to somewhat constrained (Mars), to fairly well understood on a regional scale (the Moon). In Table 8.2,

TABLE 8.2. Specific examples of science objectives, measurements, goals, and instrument arrays for regolith on different solar system bodies.

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*Comets*

- Basic Science via Regolith (Questions)
    - Composition
    - Dust and relation of gas to regolith
    - Composition as a function of depth
- Pristine vs. Altered Material
    - Bigger chunks
    - Extrasolar grains
- Regolith Science (Questions)
    - Bearing strength
    - Physical/mechanical properties
    - Porosity as a function of depth
    - Bulk density as a function of depth
    - Temperature and thermal conductivity profile
    - Radar and optical properties
- Regolith as a Tape Recorder (Questions)
    - How many Sun encounters (“tree rings”)
    - Micrometeorite reworking vs. solar processing
    - Layered structure
    - Interaction with supernova products
- Instruments and Sampling Strategies
    - Regolith probe sensitivity to low-density materials
    - Incorporating penetrator
    - Thermal probes
    - XRF
    - Mass Spectrometer
    - Imager

*Mars*

- Basic Science via Regolith (Questions)
    - How much water
    - Biogenic activity
    - Bulk composition/differentiation (as constrained by orbital data)
    - Endogenic activity
    - Role of impacts
    - Volatile distribution between regolith and atmosphere
- Regolith Science (Questions)
    - Sedimentary stratification (carbonates, peds., process strat.)
    - Dust composition
    - Dust vs. other particles in regolith (e.g., volcanic)
    - Duricrust origins and distributions
    - Atmosphere-surface interactions
    - How much water/$CO_2$/etc. in regolith vs. alternate sinks
- Regolith as Tape Recorder (Questions)
    - History of water inventory
    - Effects of orbital variations (e.g., layered terrains)
    - Atmospheric evolution
    - Impact history
    - Dust variations (composition, dust storm activity)
    - History of endogenic processes
- Sampling Strategy
    - 3-D sampling of targeted areas—to meters depth
    - Sampling above and below dust (if possible)
    - Find water and life
    - Short-range remote data
    - Mobility an issue
- Instruments
    - Image of sampling site (from orbit, panorama)
    - Image of atmosphere and dust (loading)
    - Coring, trenching, penetrators, drills
    - Ground-penetrating radar
    - Evolved Gas Analyzer (for water and others)
    - DSC (scanning calorimeter), Mössbauer, Mass Spectrometer
    - Laser Raman
    - Microscopic viewer for fossils, other analyses
    - IR sensor—locating lithologies favorable for bios?
    - XRF/XRD, APX, Laser Mass Spectrometer, Gamma-Ray Spectrometer

TABLE 8.2. (continued).

*Moon*

- Basic Science via Regolith (Questions)
  - Impact history of the Moon
  - History of basin-forming events
  - Basaltic volcanism
  - Pyroclastic volcanism
  - Ground truth for orbital data
  - Use regolith to provide context for analyses of rocks
- Regolith Science (Questions)
  - Stratigraphy and evolution of regoliths on atmosphereless bodies
  - Space weathering
  - Small-scale impact events and agglutinates
  - Mechanical and thermal properties of the regolith
  - Grain size variations
  - Nature and evolution of megaregolith
- Regolith as Tape Recorder (Questions)
  - Variations of solar radiation over time
  - Changes in micrometeorite flux and composition with time
  - Identify marker beds for impacts on Moon/Earth
  - Identify marker beds from endigenous events
  - Effects of supernovae
- Sampling Strategy
  - Number of samples of bulk soil vs. rock chips
  - 3-D mapping and sampling
  - Drilling
  - Trenching
  - Near-surface remote data (GPR)
  - *In situ* analyses vs. transportation of samples
- Instruments
  - Innovative drilling and trenching technology
  - Ground-penetrating radar
  - Trench and/or borehole mapper
  - 2-D array for mapping vertical/horizontal variations in major-element chemistry, phases, grain size, maturity
  - Hyperspectral imaging
  - XRF/APX
  - Mössbauer

science objectives, necessary measurements, and goals can relate to questions of overall body evolution, specific issues of regolith evolution, or the ability of regolith to serve as a tape recorder. Nevertheless, corresponding sampling strategy and instruments required to resolve these questions will vary significantly with the individual body characteristics and state of knowledge.

## 8.5. STRATEGIES AND METHODS TO SAMPLE REGOLITHS

Given the range of measurement requirements, possible instrument arrays, and uncertainty regarding the physical properties of many regoliths (e.g., comets), the ability to ensure successful sampling becomes critical and requires inclusion of highly flexible, multimission access strategies and methods. Sample acquisition is needed for some analytical instruments and in the future this technology will be needed for sample return missions from planetary surfaces. If for no other reason, we need good knowledge of regoliths because sample return is listed as a high-priority mission class in the future.

At present, scientific interest and practical technology are converging to drive the development of a new generation of planetary body surface and subsurface sample acquisition systems. Some of the developments of these "present" systems (in addition to the necessary low mass, low power, and full autonomy attributes) are described as follows. First, small samples (probably <1 cc per drill cycle) can be acquired at different depths (usually between the surface and 1 m below the surface). The samples can be sealed at depth to prevent vertical mixing, assure the sample is retained, and contain volatile regolith constituents. Second, sample acquisition systems can be built that are co-engineered with the electromechanical elements necessary to accomplish the reliable transfer (or interfacing) of the acquired sample to instruments located on landers or rovers (or to sample-return holding locations). Third, sample acquisition systems can be made "flexible" to address both task-oriented uncertainties and a cost-constrained planetary exploration environment.

Sample acquisition systems with autonomously selectable multiple modes of penetration approaches can be built to allow for the high probability that samples can be acquired from below the surface of bodies that do not yet have a well-defined surface and near-surface composition. Sample acquisition and sample-to-instrument transfer engineering can also be developed that will be applicable to multiple bodies. A sample acquisition and transfer system can, for instance, penetrate and acquire samples from below the surface of a comet and, with modest reconfiguration, the same basic sample acquisition and sample-to-instrument design can accomplish a similar function within martian regolith. Still other sample acquisition systems can be built with modular instrument integration connections. Through a standard or near-standard interface, sample acquisition systems can serve numerous instruments per mission, accommodate changing manifests, and ease planning concerns for follow-up or related missions. Finally, orbiter sensing allows for the selection of sample acquisition sites of great interest and allows for site selections possessing a high probability of matching sample acquisition to technological capability. Advance knowledge of the surface or near-surface conditions may allow prelanding control modification to best meet sample acquisition objectives.

Drilling (or augering) is gaining acceptance as a means of regolith penetration. While limitations due to mass and power may prevent practical autonomous planetary drilling into very hard rock, many planetary surface regoliths are accessible by novel multiple-mode drilling, augering, and/or percussive drilling. Low-speed drilling (less than 40 rpm) can be effective and is desired to minimize sample disturbance. However, acceptance of drilling or augering as a means of penetration does require acceptance of local mixing of the sample before it is acquired.

Samples can be acquired with sample acquisition cavities opened and exposed to regolith on command, while continued drilling fills the cavities with solid phase material. The cavities are then sealed and the sample is transported to the surface by lead screws or even tethers. Samples may possibly be transported up auger flights and coring, if necessary, and may be workable if performed incrementally with small cores lifted to the surface for analysis.

In addition to drilling/augering-based sample acquisition, consideration is also being given to pyrotechnic and other stored-energy means of penetration. Pyrotechnic sampling offers many advantages: low cost, low mass, simplicity, and excellent penetration potential for hard rock and difficult-to-penetrate regoliths. The limitations of pyrotechnic and similar stored-energy systems are the lack of control over sample acquisition depth and the fact that the amount(s) of sample acquired may be quite small and/or may be limited to a single cycle. Even if the limitations of pyrotechnic or spring-launched-based samplers are eclipsed by capable drilling systems, the pyrotechnic systems, with their potential for extremely low mass and cost-effectiveness, may find a continuing role as a backup means of sample acquisition. Miniature pile driving is another planetary body penetration technique under consideration. With sample acquisition cavities that can be opened and closed on command, pile driving systems may offer coring benefits (no local mixing), may be even simpler than pyrotechnic devices, and may be reusable. A possible disadvantage to pile driving is effectiveness vs. small size when trying to penetrate difficult regolith situations. More study of pile driving systems is desirable.

Application of terrestrial drilling and excavation techniques to planetary settings is often useful, but not without technical difficulty. The electromechanical and control elements of emerging planetary sample acquisition and sample transfer systems are resulting in clever new devices. The current generation of planetary sample acquisition and transfer mechanisms require miniaturization, must posses a very low mass, and must use very low power. These systems are constrained with respect to penetration torque and thrust reactions and require that all sample acquisition and transfer operations be autonomous. Such requirements, taken as a group, are the chief reason why existing terrestrial regolith drilling and penetration technologies are transferable only in a very narrow sense to planetary applications. On the Earth, even for portable drilling systems, there are (almost always) no obstacles to providing drilling operations with large drilling force and drilling torque reaction masses. Terrestrial powered hand drills or augers (as well as the manually operated Apollo drill) leverage sophisticated human control so as to instantly perform complex adjustments in thrust, torque reaction, feed rate jamming prevention, etc., as changing penetration conditions are encountered. Classical terrestrial coring technology is particularly troublesome to transfer to planetary operations. Meter-long cores (for instance) are difficult for precise autonomous manipulations, particularly with respect to instrument transfer or interface operations. Classical coring is also uncertain with respect to bringing an intact core to the surface; unconsolidated material is often lost and cores with bottom "covers" either partially lose material or require failure-prone, overly mechanistic means to achieve retention.

In the future, technology for regolith investigations in three dimensions will need to converge with mature knowledge of the target regolith. Today, a small sample analyzed from a comet is appropriate, whereas for lunar science, scientific interests seek to expose large regolith structure and stratigraphy to analyses. For more information to be gained from targets such as lunar regolith, innovative approaches will have to be put forward. For example, on a lunar rover mission, it should be possible to recover a sample of regolith and analyze it on board as the rover travels to another location (*Korotev et al.*, 1995); this may not be possible with rocks. A scoop in combination with a simple sieve mechanism (a single 1- or 2-mm mesh) would serve two purposes: (1) providing fines devoid of large "clasts" for bulk compositional analysis and (2) a source of granule- or gravel-sized particles. High-resolution imaging of the particles would provide valuable information about the components of the regolith. Another possibility would be to map large cross sections of regolith (1 m × 1 m or larger) with continuous wall penetration or trenching systems combined with instrumentation or sensors that go down into the excavation (instead of transporting small samples to the instruments located on the surface). Loss of definition from this trenching approach may be offset in the future by advances in sensor or instrumentation miniaturization. These efforts might be accompanied by remote evaluation of the shallow subsurface adjacent to excavations using an instrument like a ground-penetrating radar (*Grant and Schultz,* 1994).

## 8.6. INSTRUMENTATION AND TECHNOLOGIES—EXAMPLES

On different planetary surfaces, the measurements to be undertaken during investigation of regoliths will generally evolve in a logical sequence as exploration proceeds from one phase to the next. Such studies will typically begin with investigations of global issues and then move on to more detailed studies of local issues that may yield regional to global implications. A form of this phased approach to exploration was employed successfully during the Apollo program where remote sensing, Lunar Orbiter, and Surveyor data were followed by the series of manned landings. An additional example of how this phased approach might apply to investigations of regoliths on different solar system bodies follows.

Evaluation of regolith on Mercury would probably begin with a reconnaissance study, whereas the Viking results and analyses of SNCs permit a more comprehensive survey study on Mars. By contrast, on the Moon, analytical studies would serve as a capstone for understanding regolith properties and evolution on a global scale. Goals of each step in this process might overlap in some investigations of other bodies. In other studies, some steps might be skipped. Such decisions would be based on assessment of the difficulty or simplicity of goals, or by occurrence of analog regoliths. A resultant strategy of considering measurements and goals can be developed for any body and will consist of logical sequences of investigations for scientific studies of solar system regoliths. Table 8.3 lists a particular sequence of measurements that is not necessarily appropriate for any specific body, but serves to illustrate the concept.

Choices of instruments selected for a mission will depend on the measurement accuracies required to address specific science objectives at the body in question, as well as available resources for the mission and the environmental characteristics of the body. Relevant mission resources include weight, volume, and power; data storage, processing, and transmission rates; degree of mobility; and sample acquisition, storage, and manipulation capability. Relevant environmental characteristics include atmospheric density, ambient temperature, and surface gravity. As noted in Table 8.3, some instruments can operate in air or in a vacuum, but some require a vacuum. Some instruments have specific requirements for placement relative to a target and some impose requirements on sample handling such as placement of a sample within an analysis chamber. Technical issues that are universal—such as weight and power—are not specifically called out in Table 8.3 unless an instrument imposes unusual requirements. Table 8.3 is not intended to be exhaustive, but merely an illustration of the scientific and technical considerations.

Table 8.4 shows, for the same investigation types listed in Table 8.3, our estimate of the level of technical maturity. In some cases, investigations are rated at a low level of maturity simply owing to a lack of development, even though no specific technical difficulties are expected (e.g., microscopic imager). In other cases (e.g., sample acquisition and handling systems), investigations are rated as having flight heritage, even though considerable development may be required for accommodation on a specific future mission because of miniaturization or other technical requirements that would not be met by previously flown versions.

Table 8.5 gives examples of design considerations relevant to a particular investigation type (imaging) with a long flight history, emphasizing aspects peculiar to regolith investigations. Examples of imaging instruments that might accompany each stage of a phased investigation include a relatively simple device at the reconnaissance phase that could be used to constrain knowledge of the regolith environment and determine whether regolith exists and what its mechanical properties are (e.g., of a cometary surface). Such an imager could also be used in support of experiments for determining bulk chemistry. At the more advanced survey stage a multispectral imager might be used to further constrain bulk chemistry and would result in the ability to make

TABLE 8.3. Mission phases and examples of possible instruments.

| Phase | Instrument | Comments, Key Issues, Questions |
|---|---|---|
| Reconnaissance | Orbital survey/descent imager | Multispectral? Polarization? Stereo? |
| | Stereo panoramic imager | Zoom? Active focusing? |
| | Microscopic imager | Multispectral? Polarization? Focusing? |
| | Sampler for grab samples | Cores |
| Survey | Physical properties investigation | Sample handling? |
| | Gamma-ray densitometer/ spectrometer | Emplacement or sample handling? |
| | Neutron activation | Operates in atmosphere |
| | Heat flow experiment handling | Emplacement or sample |
| | Laser ablation/TOF mass spectrometer | Vacuum, sample handling |
| | Alpha-proton-X-ray | Placement close to sample |
| | X-ray diffraction/fluorescence | Vacuum? Sample handling |
| | Laser Raman spectroscopy | Sample handling or placement |
| | Mössbauer spectroscopy | Sample handling or placement |
| | Thermal emission spectroscopy | |
| | Thermal analyses | Sample handling or placement |
| | Mass spectrometer | Several types require vacuum |
| | Evolved gas analyzer | Sample handling |
| Analytical | 3-D regolith investigation | Trenching and analyses, high power context, may require ground truth (e.g., seismic), emplacement data |
| | Ground penetrating radar | |
| | High-density global network | |

* Sensitivity, accuracy, precision, and calibration of each instrument is highly dependent on the science goals of the mission and the nature of the target body (e.g., Moon vs. comet).

TABLE 8.4. Mission phases and instruments: Maturity.

| Phase | Instrument* | Maturity |
|---|---|---|
| Reconnaissance | Orbital survey/descent imager | Flight |
| | Stereo panoramic imager | Flight |
| | Microscopic imager | Commercial/terrestrial |
| | Sampler for grab samples | Brassboard/breadboard |
| Survey | Physical properties investigation | Flight |
| | Gamma-ray densitometer/spectrometer | Flight |
| | Neutron activation | Commercial/terrestrial |
| | Heat flow experiment | Flight |
| | Laser ablation/TOF mass spectrometer | Flight |
| | Alpha-proton-X-ray | Flight |
| | X-ray diffraction/fluorescence | Commercial/terrestrial |
| | Laser Raman spectroscopy | Commerical/terrestrial |
| | Mössbauer spectroscopy | Brassboard/breadboard |
| | Thermal emission spectrometer | Flight |
| | Thermal analyses | Commercial/terrestrial |
| | Mass spectrometer | Flight |
| | Evolved gas analyzer | Flight |
| Analytical | 3-D regolith investigation | Concept |
| | Ground-penetrating radar | Commercial/terrestrial |
| | High-density global network | Brassboard/breadboard |

* Sensitivity, accuracy, precision, and calibration of each instrument is highly dependent on the science goals of the mission and the nature of the target body (e.g., Moon vs. comet).

TABLE 8.5. Issues related to instruments at each mission phase: Imagers as an example.

| | |
|---|---|
| Imager | IFOV—resolution |
| | Depth of view—Active focusing? |
| | Field of view |
| | Stereo coverage |
| | Radiometric requirements and dynamic range |
| Multispectral Imager | Wavelength coverage? |
| | Spectral resolution/bandpass? |
| | Polarization measurement? |
| | Detector technology weak in UV and IR |
| | Active detector cooling required? |
| Hyperspectral Imager | Data volume? |
| | Loss image compression? |

statements concerning regolith properties and evolution that can be applied over at least a local area. At the capstone analytical phase, a hyperspectral imager would ideally result in solutions to the remaining regolith issues over the entire surface of the body.

Design characteristics of instruments at each phase of a study are also critical. For design of orbital and descent cameras in the reconnaissance phase, it is implied that there is a high interest in high spatial resolution as well as a desire for stereo imaging to provide information about the third dimension. Polarization measurements are also desirable to constrain regolith textures. For panoramic and microscopic imagers in the survey or analytical phases, depth of field becomes an additional consideration that may or may not drive requirement of an active focusing mechanism. Wavelength range, spectral coverage, and spectral resolution become issues, particularly in the later phases where we envision the possibility of hyperspectral imaging on very small, possibly microscopic scales; nevertheless, large data volumes will result. Finally, coverage of mid- to far-IR wavelengths may require active cooling of instruments.

Table 8.6 lists technical and environmental issues of particular relevance for regolith studies, leaving aside universally important considerations like power or ambient pressure and temperature. Mechanical properties of regolith are essentially unknown for all bodies except for the Moon and, to some extent, Mars. Properties such as bearing strength and cohesiveness are of scientific as well as operational importance because of implications for mobility and sampling. Transport of fine regolith particles, whether as eolian dust, collisional ejecta, or electrostatically levitated dust on airless bodies, is likewise scientifically and operationally important. The likelihood that abrasive particles will be deposited on spacecraft mechanisms, optical surfaces, or sensitive sensors and electronic components is an additional important design consideration.

TABLE 8.6. Technical and environmental issues.

| | |
|---|---|
| Microgravity | How to deal with reaction forces from sampling, drilling, emplacement operations |
| Atmosphere | Winds and eolian dust if present; operation in vacuum otherwise |
| Mechanical and distribution properties of regolith | Bearing strength, penetration resistance, cohesive strength |
| Abrasiveness/cohesiveness of regolith | Lifetime, reliability of mechanisms |
| Mobility of lander | How far over terrain with what relief? |
| Sample acquisition | From where, how deep, how strong is material to be sampled, preservation of stratigraphy, texture, physical phase? |
| Emplacement of instruments | How accurate, is thermal/mechanical contact critical, depth |

Relative accuracies of the instruments described at each phase of study are dependent on what information is required to address pertinent questions related to the regolith. Accuracy and instrument capabilities at each phase of a mission also becomes dependent on how the instrument is deployed (e.g., in contact with surface or not) and what the results of the preceding phases of the study are.

## 8.7. SUMMARY AND RECOMMENDATIONS

Science objectives and measurement goals for regoliths can be stated in terms of a variety of critical science questions related to the exploration of solar system bodies (e.g., *COMPLEX,* 1994). Such objectives and measurement goals need to be distinguished, however, on the basis of whether they will contribute to a better understanding of overall body evolution, specific issues of regolith development, the ability of regolith to serve as a "tape recorder" of endogenic and exogenic processes, or a combination thereof. Because regolith properties are largely unknown for many bodies it is important to assure the success of sampling devices in order to achieve mission goals. Therefore, "smarter" sampling instruments should be developed that can assess regolith properties *in situ* and adjust accordingly. A sampler might begin with a simple push into the regolith and evolve into rotary drilling, percussion, and finally pile driving. Given the highly variable state of knowledge regarding the existence and character of regoliths on solar system bodies and the fundamental observation that regolith properties and settings will vary considerably, a flexible, phased approach toward investigations is suggested. For example, an initial stage might presently require a reconnaissance phase at some bodies (e.g., Mercury), a survey phase at others (e.g., Mars, based on the results of Viking and analyses of the SNCs), and a capstone analytical phase at others (e.g., the Moon). Although general statements can be made regarding measurement requirements in the context of resolving critical science questions, variable physical properties and levels of understanding of regoliths require assemblage of differing instrument arrays for differing bodies. Finally, investigation of the subsurface properties of regoliths is crucial and provides critical context for interpreting data from instruments investigating surface properties. Suggested methods of accomplishing this are varied, but include the deployment of ground-penetrating radar and a regolith trenching/sampling device.

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# 9: Field Geology/Processes

***—Carlton Allen, Petr Jakeš, Ralf Jaumann, John Marshall, Stewart Moses, Graham Ryder, Stephen Saunders, and Robert Singer***

The field geology/processes group examined the basic operations of a terrestrial field geologist and the manner in which these operations could be transferred to a planetary lander. We determined four basic requirements for robotic field geology: geologic context, surface vision, mobility, and manipulation. Geologic context requires a combination of orbital and descent imaging. Surface vision requirements include range, resolution, stereo, and multispectral imaging. The minimum mobility for useful field geology depends on the scale of orbital imagery. Manipulation requirements include exposing unweathered surfaces, screening samples, and bringing samples in contact with analytical instruments. To support these requirements we recommended several advanced capabilities for future development. Capabilities include near-infrared reflectance spectroscopy, hyperspectral imaging, multispectral microscopy, artificial intelligence in support of imaging, XRD/XRF, and rock chipping.

## 9.1. INTRODUCTION

The maturity of our geologic knowledge of bodies in the solar system varies dramatically. All the planets except Pluto, many of the satellites, and several of the smaller bodies have been imaged at resolutions of a few kilometers. Higher-resolution orbital imagery, as well as site-specific analytical data, are available for the Moon, Mars, and Venus. We have identified undocumented samples (meteorites) from the Moon, Mars, and some asteroids. The Moon is the only solar system body other than Earth on which studies approaching classical field geology have been conducted.

Planetary field geology, for at least the near future, will be conducted by robotic spacecraft. The goals of these field studies will vary depending on the planet or satellite. An overarching goal will always be exploration, discovering basic facts about worlds that are almost unknown. Much effort may be put toward providing ground truth for interpretations based on orbital imagery, for example, the extent of basin ejecta or the reality of massive flooding. Planetary field studies may be targeted to answer specific questions, such as the presence or absence of lake deposits or permafrost. Finally, field work will certainly be called upon to support sample analysis and return by selecting samples and providing geologic context. These goals illustrate both the similarities and the differences between planetary studies and classical field geology that has been developed for over 200 years on the Earth.

## 9.2. TERRESTRIAL FIELD GEOLOGY

Field geology comprises the sensory and cognitive methods used to examine and interpret materials and structures at scales appropriate to outcrops at the Earth's surface. This scale is dominantly that of meters, but includes scans over distances as far as the horizon as well as close-up inspection. Extrapolation must be made to include the subsurface. These observations are synthesized to larger scales by correlating among outcrop-scale inferences, another cognitive step. Some of these inferences can be synthesized in the form of geologic maps and cross sections. The field geologist attempts to characterize rocks and their identifiable units, the nature of the contacts or gradations between them, their spatial relationships, their origins, their structures, and their histories. Choice is required in defining useful rock units, and is dependent on both the scale of observation and the purposes of the geologist. Geologic history comprises the formation of rocks and rock units themselves and subsequent changes, such as weathering, metamorphism, burial, folding, faulting, and erosion. The geologist has a purpose before starting field work, ranging from derivation of an overall geologic history to a detailed accounting of some particular feature.

For some inferences, information not obtainable (or only obtainable with great difficulty) in the field must be acquired. These include rock chemistry, petrographic character, ages, and isotopic measurements. Thus the field geologist commonly needs to select and remove small samples for later laboratory analysis. However, field geology is much more than a sample-collecting expedition. In some cases the sample collecting is for investigation of deep-seated characteristics and processes (rather than near-surface events), such as isotopic studies of magmas or their xenoliths for mantle investigations. In any case, geologic context and characterization are prerequisites.

The main sensory tool of the terrestrial field geologist is a visual one. This visual tool is largely cognitive, rather than simply sensory, and its use is learned. However, human evolution has had influences that do not include the distinction of rhyolite from basalt, nor dolomite from calcite. Thus the geologist's senses are expanded by including a hand lens and some chemical and mineralogical indicators such as acids and streak plates. A common piece of equipment is the hammer, used to obtain fresh unweathered surfaces that are diagnostic of rock type and to obtain samples for laboratory analysis. The human visual system uses only a small part of the electromagnetic spectrum. In some circumstances the field geologist may use equipment that expands that range into the ultraviolet or infrared.

The geologist needs to relate an outcrop to other outcrops and to its surrounding terrain, and therefore requires base maps or images, and some means of accurately determining positions. Orientation and means of measuring angles for dips and strikes are also needed. On Earth this is generally done with a compass.

The geologist has to record observations, selecting from an infinite input those features considered relevant for the study. Field geology, like good writing, requires critical thinking. Experience going back more than 200 years shows that field geology is an iterative process of observation, hypothesis, testing, and synthesis. How this can be accomplished by telepresence is a topic of continuing debate (*Spudis*, 1992).

## 9.3. PLANETARY FIELD GEOLOGY

The main objectives of planetary field studies mirror those of terrestrial field geology: (1) identification and distribution of geologic units; (2) discrimination between primary rocks, sediments, and secondary weathering products; (3) estimation of the distribution, size, shape, texture, deposition, and erosional features of solid rocks; (4) estimation of the distribution, texture, deposition, and erosional features of soils and weathering products; (5) estimation of the three-dimensional orientation of features and samples; (6) estimation of the local topography and slopes; (7) identification and characterization of tectonic features; (8) estimation of tectonic orientations and local stress fields; (9) identification of layered materials and stratigraphic sequences; (10) identification of temporal and spatial variations of surface features; (11) preselection of samples for detailed analysis and definition of their geologic context; and (12) comprehensive geologic studies including the interrelation between compositional and structural/tectonic features as well as comparisons among sample analysis, local landing site data, and regional orbital data.

A robotic field geologist on a planetary surface will require a number of basic capabilities: **Geologic context** is knowledge of the lander's location and its relation to features recognizable from orbit. **Vision** is the ability to return recognizable images of the local area to Earth. **Mobility** implies significant movement of a rover away from the landing site. **Manipulation** is the ability to physically handle samples. Our group has attempted to develop requirements in these basic areas for any planetary lander (Table 9.1).

TABLE 9.1. Requirements for robotic field geology.

| | |
|---|---|
| *Geologic Context* | |
| Orbital imaging | 100-m to 1-km pixel resolution |
| Descent imaging | 10-m-pixel resolution |
| *Vision* | |
| Range | Infinity to centimeters |
| Local horizon | 100 m |
| Resolution | 1 mrad (10 cm at 100 m) |
| Stereo | Far field and close-up |
| Spectroscopy | UV-VIS-NIR to 2.5 µm, optimized for specific local conditions |
| *Mobility* | |
| Minimum range | 1–10 km (10 pixels of orbital imaging) |
| *Manipulation* | |
| Transport analytical instruments to samples or samples to instruments | |
| Expose fresh (unweathered) surfaces | |
| Screen samples based on chemistry or mineralogy | |

## 9.4. MARS PATHFINDER—THE CURRENT STATE OF PLANETARY FIELD GEOLOGY

Robotic field geology on planetary surfaces is in its infancy. Mars Pathfinder, due to be launched in 1996, will be the first planetary mission to include, albeit at a minimal level, our four basic capabilities of geologic context, vision, mobility, and manipulation. The geologic context was determined from Viking orbital imaging, but will not be supplemented by descent imaging. The capabilities of the lander camera are close to those required by our group, though the Pathfinder camera is not sensitive to wavelengths as long as 2.5 µm. The Pathfinder rover, named Sojourner, has minimal capabilities for field geology. It moves extremely slowly, and will probably cover only a fraction of the area that can be seen from the lander. The rover will carry an α-proton-X-ray spectrometer that can produce semiquantitative elemental analyses of the rocks and soil. Fresh surfaces may be exposed by scraping rocks with the rover wheels.

Mars Pathfinder represents a first step toward true robotic field geology. It will demonstrate both the current state of the art and the very real need for advancements in this area of planetary science.

## 9.5. ADVANCED CAPABILITIES TO SUPPORT FIELD GEOLOGY REQUIREMENTS

The field geology/processes group recognized that comprehensive planetary field geology studies will require significant advances over current capabilities. We strongly endorse the development of the following technologies to support the next generation of robotic planetary landers:

- near-infrared reflectance spectroscopy to 2.5 µm
- hyperspectral imaging
- multispectral microscopy
- artificial intelligence in support of imaging
- XRD/XRF
- rock chipping

### 9.5.1. Near-Infrared Reflectance Spectroscopy to 2.5 µm

Visible and near-IR reflectance spectroscopy are important techniques for remotely determining and mapping the compositions of planetary surfaces (including the Earth). The subject is reviewed in various publications, e.g., *Goetz et al.* (1983), *Elachi* (1987), *Vane and Goetz* (1988), and *Pieters and Englert* (1993). To summarize, spectral properties ("color") in the near-UV and visible (~0.35–0.7 µm) are generally controlled by crystal-field electronic transitions within transition series cations (most commonly Fe), electronic charge transfers between cations, and electronic charge transfers between cations and anions (*Burns*, 1970). Other sources of color in this wavelength region include conduction bands and color centers. Further into the near-IR (0.7–2.5 µm), overtone absorptions of vibrational fundamentals begin to dominate reflectance spectra. Water, OH, various carbonates, and other salts have diagnostic signatures in the near-IR. An additional capability of near-IR sensing is its ability to "see through" thin layers of certain materials and analyze the material(s) underneath. Examples include thin ferric-oxide stains (e.g., *Buckingham and Sommer,* 1983; *Singer and Roush,* 1983).

Beyond 2.5 µm, reflectance observations of planetary surfaces and their interpretations are increasingly complicated by signal contributions from thermal effects, both from the object observed and within the instrumentation itself. For these reasons, 2.5 µm is a logical and productive long-wavelength limit for the type of compositional discrimination and identification tasks proposed here.

These diagnostic near-IR vibrational features are all beyond the range of human vision, and many are beyond the range of silicon detectors such as CCD cameras. The development of reliable near-IR detectors suitable for planetary landers is an important area for support.

### 9.5.2. Hyperspectral Imaging

The canonical ideal instrument for remote sensing is an imaging or mapping spectrometer (also called a hyperspectral imager) that obtains complete spectral information for every spatial pixel of an image. The practical value of such data has been well demonstrated with prototype airborne instruments studying the Earth (e.g., *Vane and Goetz,* 1988; *Farrand and Singer,* 1991; *Farrand et al.*, 1994). In the past such instruments have been quite large and expensive, with inherently large data rates. Recent developments in hardware technology, however, have reduced the weight and size, while software technology has also advanced to make these instruments more flexible and programmable. Special image compression software is being developed to manage the large flow of data.

The breakthrough in hyperspectral imaging is the ability to provide tens to hundreds of wavelength bands simultaneously for each pixel, whereas multispectral systems relying on filter wheels usually obtain no more than about a dozen bands. Since the spectral data are obtained simultaneously, there is no problem of co-registration of pixels taken with different filters at different times. The basic system passes light through a slit and onto a grating before illuminating a two-dimensional CCD array. In this manner, one axis of the array corresponds to the spatial dimension and the other to the spectral. The second spatial dimension of the image is obtained by scanning the slit across the scene in the direction orthogonal to the slit axis, thus producing an image "cube" with two spatial dimensions and one spectral dimension. In general, one can get hundreds of pixels in each of the three dimensions.

With this image cube stored in memory (either on the spacecraft or on the ground), one can now perform detailed analyses of the environment by searching for specific spectral features. For example, the instrument can be programmed to search for the telltale absorption features of ferric oxides at 0.85–0.9 µm and highlight their presence in the image. In current systems, the spectral resolution is 5–10 nm, which allows one to distinguish among mineral types with similar reflectance spectra. The high programmability of the instrument lends itself to data processing on board to lessen the amount of data downlinked. The processed data can be made to consist of a false-color image tinted according to mineral type.

A hyperspectral imager on a planetary lander will be able to achieve all and more of the science objectives normally associated with conventional imaging systems. A hyperspectral image of a landing site would enable investigators to efficiently select interesting locations, based on their mineralogy, for close-up examination and retrieval of samples by a rover. The stratigraphy exposed in a vertical surface would be readily discernable by the different spectral characteristics of each layer. Hyperspectral imaging would also enhance the information in geologic maps of a landing site by correlating morphology and topography with mineralogy.

The hyperspectral imager that will be flown on the Lewis spacecraft has the capability of imaging in 384 bands between 0.4 and 2.5 µm. This instrument has a mass of 21 kg and a power requirement of 75 W. A smaller and simpler instrument called the Ocean Color Sensor (OCS) will fly on a Korean satellite and has a mass of only 6 kg. The OCS requires 20 W, but only images in 64 spectral bands between 0.4 and 1.0 µm. Both instruments employ the orbital motion of the spacecraft to obtain the second spatial dimension. (An analogous system on a lander would require a scanning mechanism.) This technology continues to evolve and will undoubtedly become a standard tool of planetary exploration.

### 9.5.3. Multispectral Microscopy

Our understanding of the evolution of the Earth, Moon, and meteorite parent bodies has increased enormously due to sample studies at the millimeter to submillimeter scale. Evaluation of rock textures and mineral particles, their shapes, sizes, and distributions are critical to interpreting processes acting on planetary surfaces. Even without data on large-scale features, microanalytical studies have led to models of planet and asteroid formation, magmatic history, and interactions with the space environment. Petrologists, mineralogists, and experimentalists have developed criteria to identify processes such as magmatic crystallization, sedimentation, impact, and weathering through the studies of particle morphologies and compositions. A number of such criteria rely on the observation of rocks through hand lenses and microscopes. For loose samples, morphology and particle size distribution can often distinguish among impact, volcanic, eolian, aqueous, or evaporite origins. Rock textures, even at low resolution, indicate volcanic, plutonic, sedimentary, and metamorphic environments. Magmatic textures and compositions provide information on the nature of the source, ascent of the magma, and possible modification during emplacement.

A compact television microscope has been designed and constructed to obtain mineralogical and morphological information *in situ* on planetary surfaces (*Jakeš and Wänke,* 1993). This microscope can image an area of several square centimeters. The microscope uses a CCD chip and a TV camera, combined with lenses, mirrors, internal light, and fiber optics to image in visible, near-IR, or IR wavelengths. The magnification is changed by varying the optics. The best results have been obtained with magnifications of 10–100× on the TV screen, providing images with sufficient depth of focus and good resolution (better than 5 μm). The images can be digitized and saved to computer memory for later processing.

An internal "visible" light source has proven necessary for higher magnifications because the short working distance prevents sunlight from illuminating the area. Independent illumination allows the use of light of known spectral characteristics and sufficient intensity. With "white" light and color filters, multispectral images can be obtained. Multispectral images can also be obtained using monochromatic sources such as LEDs. Computer combination of images taken at different wavelengths can provide color images. Ultraviolet illumination providing "visible light" effects can be added to detect fluorescent phases. The use of near-IR or IR illumination enlarges the analytical capabilities.

The use of image processing makes the microscope camera an identification tool that can be used in planetary exploration (*Jakeš,* 1992). The value of mineralogical and chemical analysis increases if the analyzed object is "visually" known. It is imperative to exploration geology and geochemistry that analyzed surfaces are also imaged, at least in visible light.

A small microscope system has been designed for use in conjunction with α-proton, X-ray fluorescence (XRF), and Mössbauer spectrometers (*Rieder et al.*, 1995). The microscope is built to image the same area as the chemical analyzer, approximately 40 × 40 mm. In this system, the microscope camera can also image a smaller area (approximately 4 × 4 mm) with resolution better than 10 μm in order to identify mineral phases. Fixed focus optics connected to two chips and different color illuminations (0.470, 0.565, and 0.635 μm) are used. The size of the microscope camera system is 70 × 40 × 30 mm, and the weight is 150 g.

A microscope that provides mineralogical information together with reflectance spectra can be an extremely important tool for planetary field geology. Such an instrument offers the ability to directly correlate data collected *in situ* with those obtained by multispectral imaging through telescopes or from orbit.

### 9.5.4. Artificial Intelligence in Support of Imaging

While multispectral remote sensing is usually thought of as measurements made from a great distance, similar observations can be equally important for near-field characterization of surroundings. Spectroscopic machine vision provides a wealth of compositional information compared with monochrome or three-color systems. The approach is to develop a suite of practical capabilities for autonomous noncontact optical compositional determination in a spatial context, i.e., determining "what is it and where is it?"

Much, if not most, of the new work required to demonstrate such practical autonomous geologic exploration systems is in artificial intelligence and other software. The information returned from an autonomous sensor system should be a targeted, context-sensitive, high-level extract of the more voluminous data obtained by the system. This is true whether the recipient is another machine or a human. The sensor system must be able to adaptively decide what data to take, how and when to take it, and how to process and analyze it to suitably return the desired information about local geology. Such a system requires automated "intelligence," onboard processing and analysis, and adaptive decision-making capabilities.

The real-world environments in which an intelligent spectroscopic imaging system needs to operate are intrinsically unstructured, and data collected will contain noise that can degrade the certainty of identification. After initial classification using multispectral image panoramas, the system must decide which image regions or cluster groups have classifications and/or identifications that are unacceptable and require spectral sampling. The decision that a cluster is unacceptable and requires new information must be based on the context in which the spectral data were taken, such as the complexity of the geologic setting, image acquisition parameters, and knowledge from previous spectral data. This information is often imprecise, vague, and uncertain.

Humans have the ability to make good decisions using this quality of information. Fuzzy logic seems to provide an ideal tool for transferring human decision knowledge into a computer-based control system, where decisions are made based on imprecise, incomplete, and uncertain information. A fuzzy-logic rule-based approach therefore seems an attractive avenue to explore in developing the necessary autonomous sensing systems. However, a number of such pilot systems must actually be built, tested, and rigorously assessed by geoscientists (who are understandably conservative when it comes to machines messing with their data) before the community at large can be expected to welcome (or even accept) such high levels of automation.

### 9.5.5. X-Ray Diffraction and X-Ray Fluorescence (XRD/XRF)

In the field setting, a geologist automatically attempts to identify mineral suites in hand samples. In fact, this "suite recognition" (as opposed to recognition of individual minerals) is conducted mentally as a rapid-scan operation that subconsciously selects samples of interest while rejecting samples deemed irrelevant. It is a method of rapidly assessing samples that can be returned to a lab for more thorough analysis. If an instrument is to replace this human capability in robotic planetary exploration, the instrument should have the capability for both rapid assessment and intensive analysis. Given the requirements to identify mineralogy and select only a limited sample number for intensive study, there are few instrument concepts currently available, particularly as field-deployable units.

A potential instrument concept that may satisfy this type of field requirement is a portable X-ray diffractometer capable of rapidly fingerprinting mineral suites. As depicted in Fig. 9.1, this concept utilizes a CCD detector and a multiwavelength X-ray generator that enable Bragg angles to be satisfied for the detection of forward-scattered diffraction cones (a traditional single wavelength source will also suffice if placed close enough to the surface under investigation). Most noteworthy about such a design is the potential ability of the device to examine the rock or soil without the need to acquire or process a sample. Laboratory experiments (*Marshall et al.,* 1994; *Keaten et al.,* 1995) have indeed demonstrated that solid, rough-textured rock surfaces can be satisfactorily examined without powdering the samples for signal randomization.

The CCD can be interrogated for the position each photon strikes, thus providing diffraction information, or it can be interrogated for photon energy, thus providing elemental information via X-ray fluorescence. This combined XRD/XRF capability (*Kerner et al.,* 1995) enables geochemical augmentation of the diffractometric data, a capability that is particularly useful when there are complex mixtures of minerals or the presence of amorphous compounds with diffuse diffraction signatures. Certainly in the planetary exploration context, a technique such as XRD/XRF is needed to provide calibration or "ground truth" for other analytical methods such as spectroscopic mineralogy or elemental analysis.

### 9.5.6. Rock Chipping

Planetary surfaces are exposed to myriad processes that alter the chemical and mineralogical nature of the topmost layer. On airless bodies, micrometeorites and solar wind atoms produce thin amorphous coatings of glass (patina) on exposed rock surfaces. On bodies with corrosive atmospheres like Mars ($CO_2$) and Venus ($SO_2$), thick weathering rinds may form. In order to measure the chemical and mineralogical properties of fresh rocks one has to first remove these altered surface layers.

An early version of the Mars minirover (Rocky IV) was equipped with a pecking tool run by a small cam (Fig. 9.2). As the rover drove up to a rock the pecking action chipped the surface much like a woodpecker until the wheels of the rover provided sufficient force to stop the pecking action. The rover then automatically backed up and started over. This sequence continued until the weathering rind was removed.

Another approach is the miniature rock chipper/sampler (MRCS), a reduced-size, lightweight version of a large rock sampler developed at the Applied Physics Laboratory (*Cheng,* 1994). The large rock sampler has demonstrated extraction and acquisition of 40-g samples from solid basalt rock, reinforced hardened concrete, and loose unconsolidated sand. The miniaturized version is designed to remove the weath-

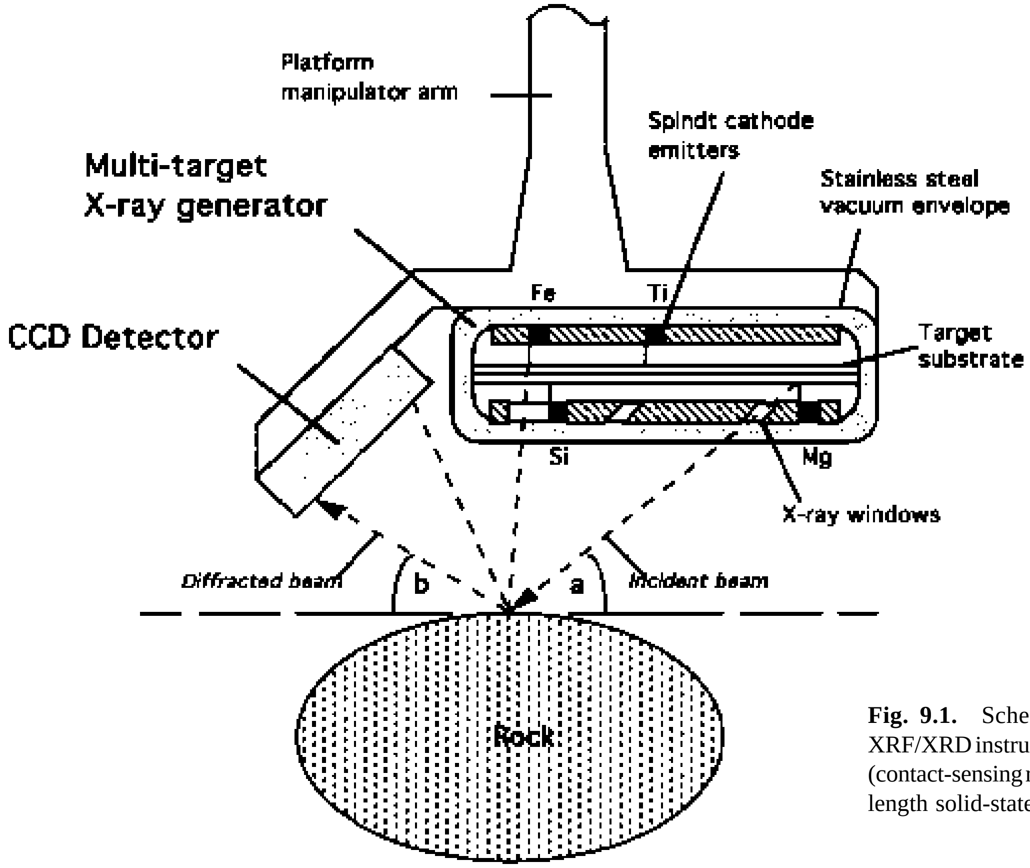

**Fig. 9.1.** Schematic design for combined XRF/XRD instrument based on a CCD detector (contact-sensing rock analysis using multiwavelength solid-state X-ray generator).

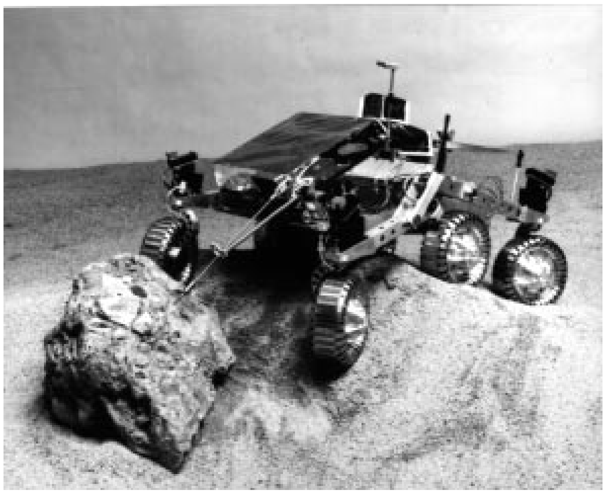

**Fig. 9.2.** Rocky IV illustrating the use of a rock chipper for removal of surface coatings (patina) from sample.

ered rind from a rock to allow access to the unaltered interior. It can also, as an option, collect small, separate samples of the rock, one sample containing weathered rind and the other containing rind plus interior material.

The MRCS uses a pyrotechnic device, similar to those used on spacecraft for cable cutters and bolt cutters, to drive a steel penetrator into the rock surface. The penetrator is retained within the MRCS and removed from the target surface after firing, and the propellant is vented away.

As a pyrotechnic device, MRCS operates rapidly, imposes no sustained force on the carrier vehicle, and has no sustained power requirement. It imposes a recoil and shock load on the carrier vehicle upon firing that is mitigated with appropriate shock mounting.

## 9.6. CONCLUSIONS

Planetary field geology, for at least the near future, will be conducted by robotic spacecraft. Basic requirements for robotic field geology include geologic context, surface vision, mobility, and manipulation. Geologic context requires a combination of orbital and descent imaging, with resolutions as fine as 10 m/pixel. Surface vision requirements include a local horizon at least 100 m from the lander, camera resolution of 1 mrad, stereo vision, and multispectral imaging in the ultraviolet, visible, and near-infrared. The minimum mobility for useful field geology depends on the scale of the orbital imagery, and ranges from 1 to 10 km. The robotic field geologist should be large enough to travel such a distance and tall enough to "see" geologic features in the area of interest. Manipulation requirements include exposing unweathered surfaces, screening samples, and bringing samples in contact with analytical instruments.

To support these requirements we recommend several advanced capabilities for future development. Capabilities include near-infrared reflectance spectroscopy to 2.5 µm, hyperspectral imaging, multispectral microscopy, artificial intelligence in support of imaging, XRD/XRF, and rock chipping.

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# List of Workshop Participants

Rachel E. Abercrombie
*Department of Earth and Space Sciences*
*University of California*
*Los Angeles CA 90095-1567*
*Phone: 310-825-3123*
*Fax: 310-206-3051*
*E-mail: rachel@coda.usc.edu*

James B. Abshire
*Mail Code 924*
*Experimental Instrumentation Branch*
*NASA Goddard Space Flight Center*
*Greenbelt MD 20771*
*Phone: 301-286-2611*
*Fax: 301-286-1761*
*E-mail: jba@eib1.gsfc.nasa.gov*

Carlton C. Allen
*Mail Code C23*
*Engineering and Sciences Company*
*Lockheed Martin*
*2400 NASA Road 1*
*Houston TX 77058*
*Phone: 713-483-2630*
*Fax: 713-483-5347*
*E-mail: allen@snmail.jsc.nasa.gov*

Bruce Banerdt
*Mail Stop 183-501*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-5413*
*Fax: 818-393-9226*
*E-mail: bruce.banerdt@ccmail.jpl.nasa.gov*

Patricia M. Beauchamp
*Mail Stop 168-222*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-0529*
*Fax: 818-393-6984*
*E-mail: patricia.m.beauchamp@ccmail.jpl.nasa.gov*

David Blake
*Mail Stop 239-4*
*NASA Ames Research Center*
*Moffett Field CA 94035*
*Phone: 415-604-4816*
*Fax: 415-604-1088*
*E-mail: david_blake@qmgate.arc.nasa.gov*

Diana L. Blaney
*Mail Stop 183-501*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-5419*
*Fax: 818-354-0966*
*E-mail: blaney@kookaburra.jpl.nasa.gov*

William V. Boynton
*Lunar and Planetary Laboratory*
*Space Sciences Building #92*
*University of Arizona*
*Tucson AZ 85721*
*Phone: 520-621-6941*
*Fax: 520-621-6783*
*E-mail: wboynton@lpl.arizona.edu*

Andrew Cheng
*Applied Physics Laboratory*
*Johns Hopkins University*
*Laurel MD 20723*
*Phone: 301-953-5415*
*Fax: 301-953-6670*
*E-mail: andrew.cheng@jhuapl.edu*

Ara Chutjian
*Mail Stop 121-114*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-7012*
*Fax: 818-393-1899*
*E-mail: ara.chutjian@jpl.nasa.gov*

R. Todd Clancy
*Space Science Institute*
*1234 Innovation Drive*
*Boulder CO 80303*
*Phone: 303-492-6998*
*Fax: 303-492-3789*
*E-mail: clancy@isidis.colorado.edu*

Alan Delamere
*Ball Aerospace*
*P.O. Box 1062*
*Boulder CO 80304*
*Phone: 303-939-4243*
*Fax: 303-939-6177*
*E-mail: adelamere@ball.com*

David DesMarais
*Mail Stop 239-4*
*NASA Ames Research Center*
*Moffett Field CA 94035-1000*
*Phone: 415-604-3220*
*Fax: 415-604-1088*
*E-mail: david_desmarais@qmgate.arc.nasa.gov*

M. Darby Dyar
*Department of Astronomy and Geology*
*West Chester University*
*West Chester PA 19380*
*Phone: 610-436-2213*
*E-mail: ddyar@wcupa.edu*

Friedemann Freund
*Mail Stop 239-4*
*NASA Ames Research Center*
*Moffett Field CA 94035-1000*
*Phone: 415-604-5183*
*Fax: 415-604-1088*
*E-mail: friedemann_freund@qmgate.nasa.arc.gov*

Ghee Fry
*Mission Research Corporation*
*One Tara Boulevard, Suite 302*
*Nashua NH 03062-2801*
*Phone: 603-891-0070 ext. 299*
*Fax: 603-891-0088*
*E-mail: gfry@lanl.gov*

Stephen Gorevan
*Honeybee Robotics*
*204 Elizabeth Street*
*New York NY 10012*
*Phone: 212-966-0661*
*Fax: 212-925-0835*
*E-mail: gorevan@panix.com*

John Grant
*Department of Earth Sciences*
*State University of New York*
*1300 Elmwood Avenue*
*Buffalo NY 14222-1095*
*Phone: 716-878-5116*
*Fax: 716-878-4028*
*E-mail: grantja@snybufaa.cs.snybuf.edu*

Bo A. Gustafson
*Department of Astronomy*
*211 SSRB*
*University of Florida*
*Gainesville FL 32611*
*Phone: 904-392-7677*
*Fax: 904-392-5089*
*E-mail: gustaf@astro.ufl.edu*

Michael Hecht
*Mail Stop 302-231*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-2774*
*Fax: 818-393-4540*
*E-mail: Michael.H.Hecht@jpl.nasa.gov*

John H. Hoffman
*FO 22*
*University of Texas-Dallas*
*P.O. Box 830688*
*Richardson TX 75083-0688*
*Phone: 214-883-2840*
*Fax: 214-883-2848*
*E-mail: jhoffman@utdallas.edu*

Petr Jakeš
*Faculty of Science*
*Charles University*
*Albertov 6*
*128 43 Praha 2*
*CZECH REPUBLIC*
*Phone: 2939-419 ext. 2426*
*Fax: 42-2-296084*
*E-mail: jakes@prfdec.natur.cuni.cz*

Ralf Jaumann
*Institute for Planetary Exploration*
*DLR German Aerospace Research Establishment*
*Rudower Chaussee 5*
*12489 Berlin*
*GERMANY*
*Phone: 49-30-69545-400*
*Fax: 49-30-69545-402*
*E-mail: jaumann@terra.pe.ba.dlr.de*

Jim L. Jordan
*Department of Geology*
*Lamar University*
*P.O. Box 1003*
*Beaumont TX 77710*
*Phone: 409-880-8240*
*Fax: 409-880-1895*
*E-mail: jordanjl@lub001.lamar.edu*

Jeff Kargel
*Astrogeology Branch Laboratory*
*U.S. Geological Survey*
*2255 N. Gemini Drive*
*Flagstaff AZ 86001*
*Phone: 520-556-7034*
*Fax: 520-556-7014*
*E-mail: jkargel@iflag2.wr.usgs.gov*

Susan Keddie
*Science Applications International Corporation*
*400 Virginia Avenue SW, Suite 400*
*Washington DC 20024*
*Phone: 202-479-0750*
*Fax: 202-479-0856*
*E-mail: keddie#m#_susan@smtpgmgw.ossa.hq.nasa.gov*

John F. Kerridge
*Department of Chemistry/0317*
*University of California at San Diego*
*La Jolla CA 92093-0317*
*Phone: 619-534-0443*
*Fax: 619-534-7441*
*E-mail: jkerridg@ucsd.edu*

R. K. Khanna
*Department of Chemistry and Biochemistry*
*University of Maryland*
*College Park MD 20742*
*Phone: 301-405-1894*
*Fax: 301-314-9121*
*E-mail: rk13rajkkhanna@umd.edu*

Soon S. Kim
*Mail Stop 183-401*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-2477*
*Fax: 818-393-5039*
*E-mail: sam.s.kim@jpl.nasa.gov*

Gostar Klingelhöfer
*Institut für Kernphysik*
*TH Darmstadt*
*Schlossgartenstrasse 9*
*Darmstadt D-62489*
*GERMANY*
*Phone: 49-61-51-162-321*
*Fax: 49-61-51-164-321*
*E-mail: d184@hr2pub.th-darmstadt.de*

Randy Korotev
*Department of Earth and Planetary Sciences*
*Campus Box 1169*
*Washington University*
*One Brookings Drive*
*St. Louis MO 63130-4899*
*Phone: 314-935-5637*
*Fax: 314-935-7361*
*E-mail: rlk@wumooon2.wustl.edu*

Theodor Kostiuk
*Mail Code SL*
*NASA Headquarters*
*Washington DC 20546*
*Phone: 202-358-0297*
*Fax: 202-358-3097*
*E-mail: t.kostiuk@gsfc.nasa.gov*

David A. Kring
*Department of Planetary Sciences*
*Lunar and Planetary Laboratory*
*University of Arizona*
*Tucson AZ 85721*
*Phone: 520-621-2024*
*Fax: 520-621-4933*
*E-mail: kring@gammal.lpl.arizona.edu*

Carey Lisse
*Mail Code 685.9*
*NASA Goddard Space Flight Center*
*Greenbelt MD 20771*
*Phone: 301-513-7786*
*Fax: 301-513-7726*
*E-mail: lisse@stars.gsfc.nasa.gov*

Rocco Mancinelli
*Mail Stop 239-12*
*NASA Ames Research Center*
*Moffett Field CA 94035-1000*
*Phone: 415-604-6165*
*Fax: 415-604-0092*
*E-mail: rocco_mancinelli@qmgate.arc.nasa.gov*

John Marshall
*Mail Stop 239-12*
*NASA Ames Research Center*
*Moffett Field CA 94035*
*Phone: 415-604-4983*
*Fax: 415-604-0092*
*E-mail: john_marshall@qmgate.arc.nasa.gov*

Gene McDonald
*Cornell University*
*324 Space Sciences Building*
*Ithaca NY 14853*
*Phone: 607-255-6913*
*Fax: 607-255-9888*
*E-mail: mcdonald@astrosun.tn.cornell.edu*

Richard W. McEntire
*Applied Physics Laboratory*
*Johns Hopkins University*
*Johns Hopkins Road*
*Laurel MD 20723-6099*
*Phone: 301-953-5410*
*Fax: 301-953-6670*
*E-mail: richard_mcentire@jhuapl.edu*

David S. McKay
*Mail Code SN6*
*NASA Johnson Space Center*
*Houston TX 77058*
*Phone: 713-483-5048*
*Fax: 713-483-5347*
*E-mail: dmckay@snmail.jsc.nasa.gov*

Greg Mehall
*Box 871404*
*Arizona State University*
*Tempe AZ 85287-1404*
*Phone: 602-965-3063*
*Fax: 602-965-1787*
*E-mail: mehall@tes.la.asu.edu*

Charles Meyer
*Mail Code SN2*
*NASA Johnson Space Center*
*Houston TX 77058*
*Phone: 713-483-5133*
*Fax: 713-483-2911*
*E-mail: meyer@snmail.jsc.nasa.gov*

Hitoshi Mizutani
*Institute of Space and Astronomical Science*
*Yoshino-dai 3-1*
*Sagamihara-shi*
*Kanagawa 229*
*JAPAN*
*Phone: 0427-51-3911*
*Fax: 0427-59-4237*
*E-mail: mizutani@planeta.sci.isas.ac.jp*

Thomas H. Morgan
*Southwest Research Institute*
*6220 Culebra Road*
*P.O. Drawer 28510*
*San Antonio TX 78284*
*Phone: 210-522-3985*
*Fax: 210-647-4325*
*E-mail: tom@image1.space.swri.edu*

Richard V. Morris
*Mail Code SN4*
*NASA Johnson Space Center*
*Houston TX 77058*
*Phone: 713-483-5040*
*Fax: 713-483-5347*
*E-mail: morris@snmail.jsc.nasa.gov*

Stewart Moses
*TRW*
*R1-2144*
*One Space Park*
*Redondo Beach CA 90278*
*Phone: 310-812-0075*
*Fax: 310-812-1277*
*E-mail: smoses@amelia.sp.trw.com*

Seiichi Nagihara
*Department of Geosciences*
*University of Houston*
*Houston TX 77204-5503*
*Phone: 713-743-3413*
*Fax: 713-748-7906*
*E-mail: nagihara@uh.edu*

Yosio Nakamura
*Institute for Geophysics*
*University of Texas*
*8701 North Mopac Expressway*
*Austin TX 78759-8397*
*Phone: 512-471-0428*
*Fax: 512-471-8844*
*E-mail: yosio@utig.ig.utexas.edu*

Zoran Ninkov
*Center for Imaging Science*
*Rochester Institute of Technology*
*One Lomb Memorial Drive*
*Rochester NY 14623*
*Phone: 716-475-7195*
*Fax: 716-475-5988*
*E-mail: zxnpci@mail.cis.rit.edu*

Laurence E. Nyquist
*Mail Code SN4*
*NASA Johnson Space Center*
*Houston TX 77058*
*Phone: 713-483-5038*
*Fax: 713-483-5347*
*E-mail: nyquist@snmail.jsc.nasa.gov*

Carlé Pieters
*Department of Geological Sciences*
*Box 1846*
*Brown University*
*Providence RI 02912*
*Phone: 401-863-2417*
*Fax: 401-863-3978*
*E-mail: pieters@pds.geo.brown.edu*

W. T. Pike
*Center for Space Microelectronics*
*Jet Propulsion Laboratory*
*4800 Oak Grove Drive*
*Pasadena CA 91109*
*Phone: 818-354-0662*
*Fax: 818-393-4540*
*E-mail: wpike@voyager.jpl.nasa.gov*

Filippo Radicati di Brozolo
*Charles Evans and Associates*
*301 Chesapeake Drive*
*Redwood City CA 94063*
*Phone: 415-369-4567 ext. 321*
*Fax: 415-369-7921*
*E-mail: rfilippo@cea.mhs.compuserve.com*

Jonathon Rall
*Mail Code 924*
*Experimental Instrumentation Branch*
*NASA Goddard Space Flight Center*
*Greenbelt MD 20771*
*Phone: 301-286-7397*
*Fax: 301-286-1761*
*E-mail: jarrall@aibl.gsfc.nasa.gov*

Graham Ryder
*Lunar and Planetary Institute*
*3600 Bay Area Boulevard*
*Houston TX 77058*
*Phone: 713-486-2141*
*Fax: 713-486-2162*
*E-mail: zryder@lpi.jsc.nasa.gov*

R. Stephen Saunders
*Mail Code SX*
*NASA Headquarters*
*Washington DC 20546*
*Phone: 202-554-6459*
*Fax: 202-554-6499*
*E-mail: saunders@hq.nasa.gov*

Harrison H. Schmitt
*P.O. Box 14338*
*Albuquerque NM 87191-4338*
*Phone: 505-823-2616*
*Fax: 505-821-2601*
*E-mail: schmitt@engr.wisc.edu*

Jeffrey S. Schweitzer
*Schlumberger-Doll Research*
*Old Quarry Road*
*Ridgefield CT 06877-4108*
*Phone: 203-431-5444*
*Fax: 203-438-3819*
*E-mail: Schwietzer@ridgefield.sdr.slb.com*

W. R. Sheldon
*Department of Physics*
*University of Houston*
*4800 Calhoun*
*Houston TX 77204-5506*
*Phone: 713-743-3544*
*Fax: 713-743-3589*
*E-mail: sheldon@uh.edu*

Robert B. Singer
*Lunar and Planetary Laboratory*
*Space Sciences Building #92*
*University of Arizona*
*Tucson AZ 85721*
*Phone: 520-621-4573*
*Fax: 520-621-9628*
*E-mail: singer@pirl.lpl.arizona.edu*

Ann L. Sprague
*Lunar and Planetary Laboratory*
*Space Sciences Building #325*
*University of Arizona*
*Tucson AZ 85721*
*Phone: 520-621-2282*
*Fax: 520-621-4933*
*E-mail: sprague@pirl.lpl.arizona.edu*

Timothy D. Swindle
*Lunar and Planetary Laboratory*
*University of Arizona*
*Tucson AZ 85721*
*Phone: 520-621-4128*
*Fax: 520-621-4933*
*E-mail: timswindle@ccit.arizona.edu*

Allan H. Treiman
*Lunar and Planetary Institute*
*3600 Bay Area Boulevard*
*Houston TX 77058*
*Phone: 713-486-2117*
*Fax: 713-486-2162*
*E-mail: treiman@lpi.jsc.nasa.gov*

Thomas J. Wdowiak
*Campbell Hall 310*
*University of Alabama at Birmingham*
*1300 University Boulevard*
*Birmingham AL 35299*
*Phone: 205-934-8036*
*Fax: 205-934-8042*
*E-mail: wdowiak@phy.uab.edu*

Albert S. Yen
*Mail Stop 170-25*
*California Institute of Technology*
*Pasadena CA 91125*
*Phone: 818-395-6447*
*Fax: 818-577-4875*
*E-mail: ayen@mars1.gps.caltech.edu*

J. C. Zarnecki
*Unit for Space Sciences*
*University of Kent*
*Canterbury*
*Kent CT2 7NR*
*UK*
*Phone: 44-227-764000*
*Fax: 44-227-762616*
*E-mail: jcz@uk.ac.ukc*

Michael Zolensky
*Mail Code SN2*
*NASA Johnson Space Center*
*Houston TX 77058*
*Phone: 713-483-5128*
*Fax: 713-483-5347*
*E-mail: zolensky@snmail.jsc.nasa.gov*