2: Precise Chemical Analyses of Planetary Surfaces

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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

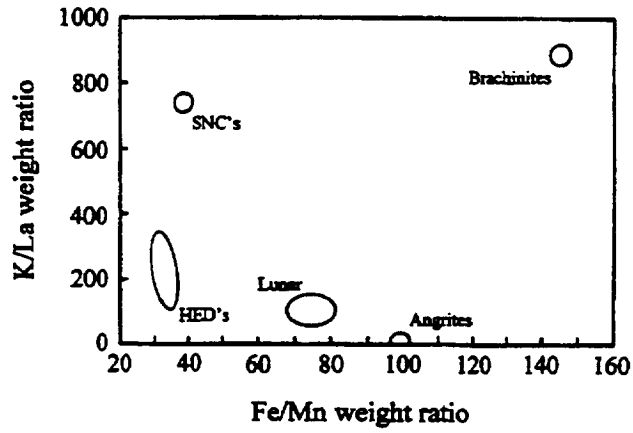

Fig. 2.1. K/La vs. Fe/Mn in several types of achondritic material in the solar system. The SNC samples may represent material on Mars and the HED samples may represent material on Vesta.

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 composi-

tion 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 γ 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.

		Peridotite (PCC-1)		Basalt (W-1)		Basalt (BCR-1)		Carbonate (Type 4)	
Element	Mass Range	α	Conventional Analysis	α	Conventional Analysis	α	Conventional Analysis	α	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 γ-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 γ-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 γ-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 γ-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 γ-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: α 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 (α) radiation (*Perry*, 1986; *Henrich*, 1987). Such Mg and Al K (α) 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.

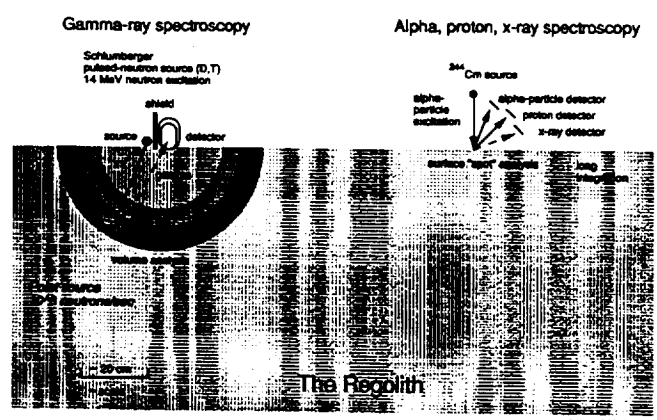

Fig. 2.2.

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