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Introduction: The next landed missions to Mars, such as the planned Mars Science Laboratory and ExoMars, will require sample analysis capabilities refined well beyond what has been flown to date. A key science objective driving this requirement is the determination of the carbon inventory of Mars, and particularly the detection of organic compounds [1]. While the gas chromatograph mass spectrometers (GC/MS) on the Viking landers did not detect any indigenous organics in near surface fines [2], it is possible that these measurements were not representative of Mars on the whole. That is, those compounds to which the GC/MS was sensitive would likely not have survived the strong oxidative decomposition in the regolith at the landing sites in question. The near surface fines could very well contain a significant quantity of refractory compounds that would not have been volatilized in the sample ovens on Viking [3]. It is also possible that volatile organics exist on Mars in sedimentary, subsurface, or polar niches.

The detection of any organic compounds on Mars would be of enormous interest. Certainly the detection and careful confirmation of higher molecular weight compounds in large numbers would be the most exciting possibility. Such a discovery, particularly in samples derived from a protected environmental niche, could indicate the presence of an extant (though possibly dormant) Martian biosphere. More probable would the the near-surface detection of less-complex marker organics at relatively lower densities. Such compounds could suggest any number of scenarios, including a subsurface biosphere, long-extinct life, or an arrested pre-biotic chemical process. The intepretation of such evidence would require a detailed understanding of the geological, geochemical, and atmospheric context in which it was found. Moreover, such compounds would have to be distinguished from those that may have been delivered by meteoritic infall, and even from those brought from Earth as spacecraft contaminants. The meteoritic component may have survived as refractory degradation products at up to several hundred parts per billion by weight (ppbw), depending on gardening depth [3]. Due to their shared oxidation environment, the remnants of meteoritic and indigenous near-surface marker molecules may be quite similar. However, highly-localized "niches" could support much more complex, fragile, and probably trace biosignatures written into sedimentary rock over a strong meteoritic background. In the extinct life scenario, or at least one in which near-surface materials do not contain living organisms, such signatures would likely range spatially from sub-micron to tens of microns in diameter, and would likely be strongly affiliated with certain mineralogical microenvironments.

To understand the results of a highly-sensitive *in situ* search for indigenous Martian organics, positive or negative, clear contextual data are required. Microscopic imaging, elemental, and mineralogical analyses are of high priority in this regard. A broad compositional assay of individual samples, with very low detection limits, would help define the host microenvironment of any detected organic species, as well as further our understanding of the origins of the solid samples obtained at the site. Of course, if organics are found in a sample, it would be desirable to apply a suite of measurements to fully characterize their properties. These may include measuring their molecular weights, their spatial distribution in the sample, their carbon isotope ratios, and the degree to which they exhibit homochirality. In the absence of organic compounds, the analysis of possible oxidation agents such as H_2O_2 and the detection of any water ice would be especially important. In all cases, mineral phases of high interest include hydrates, carbonates, nitrates, sulfates, and clays, which are indicative of the presumed milder and wetter Martian surface and atmosphere in the past. In addition, a thorough analysis of the abundances and isotope ratios of trace atmospheric gases will significantly advance our understanding of the early environment of Mars, mechanisms of atmospheric loss, and the origin and fate of Martian water.

Overview of SAM: An effort is underway to develop a complementary set of definitive experimental tools that would greatly enhance our understanding of the organic and chemical composition of Mars. The Sample Analysis at Mars (SAM) suite consists of a group of tightly-integrated experiments that would analyze samples delivered directly from a coring drill or by a facility sample processing and delivery (SPAD) mechanism. SAM consists of an advanced GC/MS system and a laser desorption mass spectrometer (LDMS). The combined capabilities of these tech-

niques can address Mars science objectives with much improved sensitivity, resolution, and analytical breadth over what has been previously possible *in situ*. The GC/MS system analyzes the bulk composition (both molecular and isotopic) of solid-phase and atmospheric samples. Solid samples are introduced with a highly flexible chemical derivatization/pyrolysis subsystem (Pyr/GC/MS) that is significantly more capable than the mass spectrometers on Viking. The LDMS analyzes local elemental and molecular composition in solid samples vaporized and ionized with a pulsed laser. As described below, each of these capabilities has particular strengths that can achieve key measurement objectives at Mars. In addition, the close co-development of the GC/MS and LDMS along with a sample manipulation system enables the the sharing of resources, the correlation of results, and the utilization of certain approaches that would not be possible with separate instruments. For instance, the same samples could be analyzed with more than one technique, increasing efficiency and providing cross-checks for quantification. There is also the possibility of combining methods, such as by permitting TOF-MS analyses of evolved gas (Pyr/EI-TOF-MS) or GC/MS analyses of laser evaporated gas (LD-GC/MS).

The SAM measurement objectives fall into six categories that are aligned with high-priority science goals of Mars exploration. These include measuring (1) abundances of trace atmospheric species such as noble gases and certain small molecules (CH_4, H_2S, etc.); (2) high-precision isotope ratios in key atmospheric species, such as the noble gases, C in CO_2, N in N_2, and D/H in H_2O; identities, isotope ratios, and possible chirality of (3) relatively volatile organics and (4) pyrolyzable inorganic species, characteristic of specific mineralogies, in solid phase samples; (5) identities of moderate to high mass refractory organics; and (6) relative abundances of refractory elements, to trace levels, in solid phase samples. The technical approaches for categories (1) and (2), which involve sampling the atmosphere at the outset of Mars surface operations, and performing static mass spectrometry with a clean system, have been discussed in the context of the Galileo and Cassini missions by Niemann *et al*. [4], Israel *et al*. [5], and Mahaffy *et al*. [6]. The techniques used for measurement categories (3), (4), and portions of (5) have been recently reported by Cabane *et al*. [7,8] and Rodier *et al*. [9]. Here we focus on aspects of categories (5) and (6) relating to the LDMS technique. The LDMS provides an approach to sample analysis that is highly complementary to that of the Pyr/GC/MS system. LDMS provides spatially local composition, compared to the bulk analysis of Pyr/GC/MS. LDMS is also biased to the ionization of

more refractory compounds (elements and organics) than is the Pyr/GC/MS system. Ions of relatively volatile organics are not likely to survive laser desorption from neat geological surfaces because their formation energy is above that needed for dissociation. However, more refractory species such as PAHs, kerogens, and other classes of hydrocarbons do survive even at high mass without excessive fragmentation.

The local analysis capability arises from the small spot size of the focused laser (about 50 microns), and is enabled within SAM by the sample manipulation system (SMS). The SMS is briefly described here before descriptions of the LDMS methods for categories (5) and (6) are given below.

Sample Manipulation System (SMS). The SMS enables the laser analysis of any spot on the surface of a delivered sample, with a spatial resolution comparable to the focal diameter of the laser. An automatic laser "raster" of the sample would permit a rough chemical map of the sample to be generated. The map would be correlated to a full-field microscopic image of the sample surface recorded with a color CCD imager. In one possible SMS positioning scheme, shown in **Fig. 1**, sample cups are brought to the laser analysis position in a carousel. By rotating the sample cup on its spindle at positions slightly off axis from the laser, the full sample surface may be addressed.
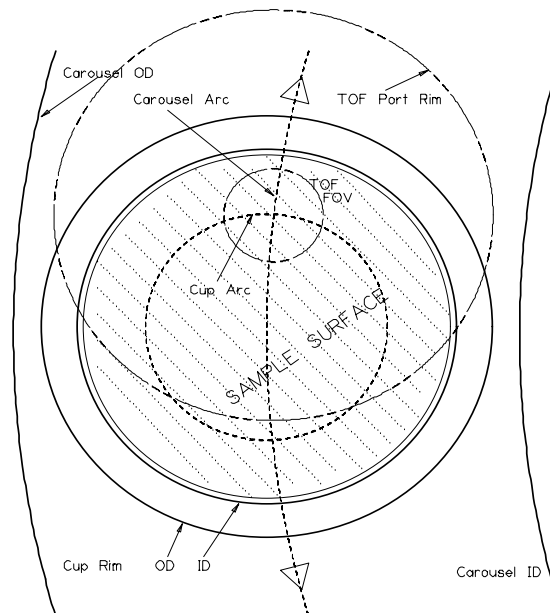

Fig. 1 Schematic diagram of a possible arrangement of a sample cup relative to the inlet port of the LDMS, top view. Any of several hundred points on the few-mm diameter sample surface may be accessed by the laser by rotating and moving the holder.

Prototypes of this and other SMS schemes are under development at Honeybee Robotics. In all designs, the SMS must be able to permit the mass spectrometric analysis of a relatively large number of samples, obtained from various sites and depths over the course of Mars surface operations. In the case of the LDMS, an unlimited number of samples could be analyzed in principle, as the effects of cross contamination that might occur during automated sample removal are less problematic. Each mechanism, however, must be carefully studied and justified within the overall risk portfolio of the system. A major driver in this regard is the requirement for careful insertion of solid samples into a vacuum enclosure. The limited scale of vacuum pumping available *in situ* favors the minimization of the volume to be maintained at low pressure. This tendency must be balanced by the need to utilize as little mass and as few vacuum sealing events as possible to assure feasibility and reliability. These considerations are being examined within the SAM operational and assurance models, and are being tested with prototype SMS hardware.

LDMS Analyses. One of the major goals of Mars surface missions will be to compare chemical and mineralogical compositions of a range of rocks and fines from within the mobility range of the spacecraft. Such data can help us understand the internal chemical structure and history of Mars, its volcanic activity, and its primitive inventory for biochemistry. Of particular interest are the absolute and relative abundances of the rock-forming elements Na through Ni. Abundances down to a few ppm by weight, and ratios such as Mg/Si, Mg/(Mg+Fe), Na/Ca, and (Na+K)/Si, may be used to differentiate between basaltic and andesitic compositions, and among various depositional mechanisms. Laser desorption analyzes these species equally well in rocks and fines. When applied to rocks, the laser probe also permits the rapid detection, characterization, and removal of thin surface layers, to access the bulk composition beneath. This is critical on Mars, where windblown dust has coated rock surfaces. Another priority for Mars rocks is the identification and spatial interrelationship of mineral grains. The 50 :m laser spot size can identify the species within and between grains, providing a tool that complements micro-imaging and mineralogy probes in a suite. The examination of materials thought to be formed by aqueous activity is needed to begin studying microenvironments that may have been conducive to life. Within these materials, large elemental fractionations (e.g., in H, C, N, O, P, and S), as well as trace organic compounds (in samples obtained at some depth), should be detected and spatially correlated. Particu-

larly significant would be the detection of larger organics (100-1000 amu and beyond), including various aromatic and aliphatic hydrocarbons. Pulsed laser irradiation is capable of desorbing many of these species from geological samples, and coupling this desorption to a TOF-MS may permit their detection down to extremely low levels. Furthermore, the mass spectrometer does not assume the presence of a particular analyte (and search only for that compound): all organic compounds ionized by the laser are sorted by mass and recorded.

The LDMS analyzes elemental and refractory organic composition on a fine spatial scale (approximately 0.05 mm resolution) with a focused laser [10-13]. By combining this information with a co-focused sample imager, a chemical map may be generated to permit studies of the heterogeneity and grain sizes of Mars samples, as well as to detect organic compounds that may be confined to small mineral inclusions. At higher laser powers, molecular compounds are dissociated into their atomic constitutents. The resulting elemental composition is instantly recorded by a TOF-MS, which provides a qualitative but complete mass spectrum (to ppmw detection levels) in a single laser pulse. By averaging the signals from multiple LDMS spectra, semi-quantitative elemental analyses (at the 5%-25% RSD precision level, depending on element) are available. Spectra are clear and unambiguous: the identification of elemental species at each spatial position needs no curve fitting. **Fig. 2** shows example elemental mass spectra from standard samples of Johnstown Hypersthene and VG-A99 glass.
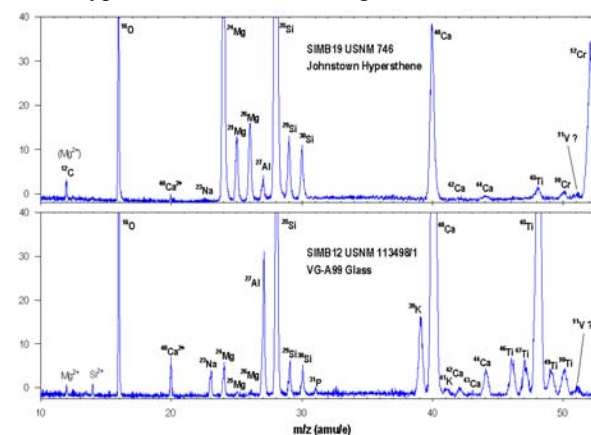
Fig. 2 Example elemental laser mass spectra from samples in a standard mineral mount, courtesy E. Vicenzi, NMNH.

At lower laser powers, molecular species increasingly survive, although the intrinsic ionization efficiency is somewhat lower than in the elemental analy-

sis mode. As such, for organic analyses, the LDMS instrument is operated in a mode where the formed molecular ions are accelerated and focused, providing a more concentrated beam for the TOF-MS. **Fig. 3** shows an example LDMS spectrum from an unprepared Allende meteorite chip. Allende is known to contain a component of refractory hydrocarbons (PAHs and kerogen-like compounds) at low levels. LDMS analyses have shown that these are readily detected at high signal-to-noise ratios, and that they are generally confined to localized "hot spots" within the matrix regions of the sample. Masses up to 1000 amu have been detected despite the lack of wet chemical sample preparation.
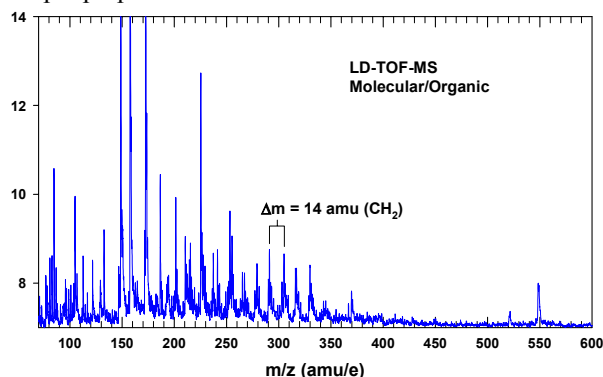
Fig. 3 LDMS spectrum of a sample of the Allende CV3 meteorite (courtesy T. McCoy, NMNH).

An intensive study of the elemental and organic analysis capabilities of the SAM/LDMS technique with a range of natural and synthetic Martian analog materials is underway.

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