ANALYSIS OF ORGANIC COMPOUNDS IN MARS ANALOG SAMPLES. P. R. Mahaffy[1], W. B Brinckerhoff[2], A. Buch[3], M. Cabane[4], P. Coll[5], J. Demick[3], D. P. Glavin[3]. [1]Code 915, Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, paul.r.mahaffy@nasa.gov, [2]The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, [3]Code 915, GSFC, [4]Service d'Aéronomie, IPSL, Université Pierre et Marie Curie, Paris, [5]LISA, Université de Paris VII et XII, Créteil.

Introduction: The detailed characterization of organic compounds that might be preserved in rocks, ices, or sedimentary layers on Mars would be a significant step toward resolving the question of the habitability and potential for life on that planet. The fact that the Viking gas chromatograph mass spectrometer (GCMS) did not detect organic compounds should not discourage further investigations since (a) an oxidizing environment in the near surface fines analyzed by Viking is likely to have destroyed many reduced carbon species; (b) there are classes of refractory or partially oxidized species such as carboxylic acids that would not have been detected by the Viking GCMS; and (c) the Viking landing sites are not representative of Mars overall. These factors motivate the development of advanced *in situ* analytical protocols to carry out a comprehensive survey of organic compounds in martian regolith, ices, and rocks. We combine pyrolysis GCMS for analysis of volatile species, chemical derivatization for transformation of less volatile organics, and laser desorption mass spectrometry (LDMS) for analysis of elements and more refractory, higher-mass organics. To evaluate this approach and enable a comparison with other measurement techniques we analyze organics in Mars simulant samples.

Pyrolysis GCMS: The pyrolysis approach is to heat a few milligrams of sample from ambient temperature to approximately 1200^{o}C using a linear temperature ramp. Gases are rapidly removed from the sample by an inert helium carrier gas. They are first analyzed directly by a mass spectrometer and then again after completion of the pyrolysis by rapid release of organic molecules trapped on a high surface area adsorbant into a GC column. The controlled sample heating also enables analysis of simple inorganic gases, such as CO_2, H_2O, SO_2 that provide information on mineral type and the degree of mineral alteration by weathering. **Figure 1a** shows a gas chromatogram and an example mass spectrum of molecular species released from a Mars simulant JSC HWMK101 Palagonitic Tephra from Hawaii of the type that has been widely used as a mineralogical [1] and spectral [2] analog. Numerous organic molecules are released. Species that are not resolved with the single GC column, in this example, can be separated by other columns and by selecting only a segment of the evolved organics for analysis at one time.

Derivatization: The transformation of reactive or less volatile organic molecules extracted from solid samples into chemical species that are sufficiently volatile to be stable in the GC column allows entirely new classes of compounds to be analyzed [3]. Single step reactions with a derivatizaton reagent that produces volatile species for a range of amino acids and nucleobases are the most useful candidates for *in situ* applications. **Figure 1b** illustrates transformation of all the 15 amino acids in a standard mixture by the reagent N,N-Methyl-tert.-butyl (dimethylsilyl) trifluoroacetamide, in our laboratory, into species that can be readily processed by a GC capillary column suitable for space use. Other such columns are well suited for separation of the D- and L-enantiomers of the derivatized amino acids.

Laser Desorption Mass Spectrometry: Both elemental and refractory organic analysis can be realized with the LDMS technique, wherein a laser pulse on a solid sample produces prompt ions for a time-of-flight (TOF) mass spectrometer. Features of this technique are a very high mass range, fine *grain-scale* spatial resolution enabled by the focused laser beam, and the ability to enhance refractory organics relative to atomic species by controlling the energy of the laser pulse. PAHs, hydrocarbon oligomers, and kerogen-like compounds whose pyrolysis spectra may be difficult to interpret are readily identified by the LDMS technique. **Figure 1c** shows an LDMS spectrum obtained from HWMK101 Mars simulant.

Summary: Pyrolysis GCMS, derivatization GCMS, and LDMS provide complementary data sets that enable a quite comprehensive survey of organics in a solid phase sample. The evolved gas analysis and LDMS also provide chemical data that can complement the organics analyses. We continue to develop these methods for *in situ* analysis at Mars.

References: [1] Ming, D.W. et al., "The search for water and other volatile-bearing phases on Mars: Mauna Kea volcano as an analog", LPSC XXXIV, 1800 (2003). [2] Bell, J.F., et al., "Thermally altered palagonitic tephra: A spectral and process analog to the soils and dust of Mars", JGR 98, 3373 (1993). [3] Rodier, C., "Detection of martian amino acids by chemical derivatization coupled to gas chromatography in situ and laboratory analysis", Adv. Space Res. 27, 195 (2001).

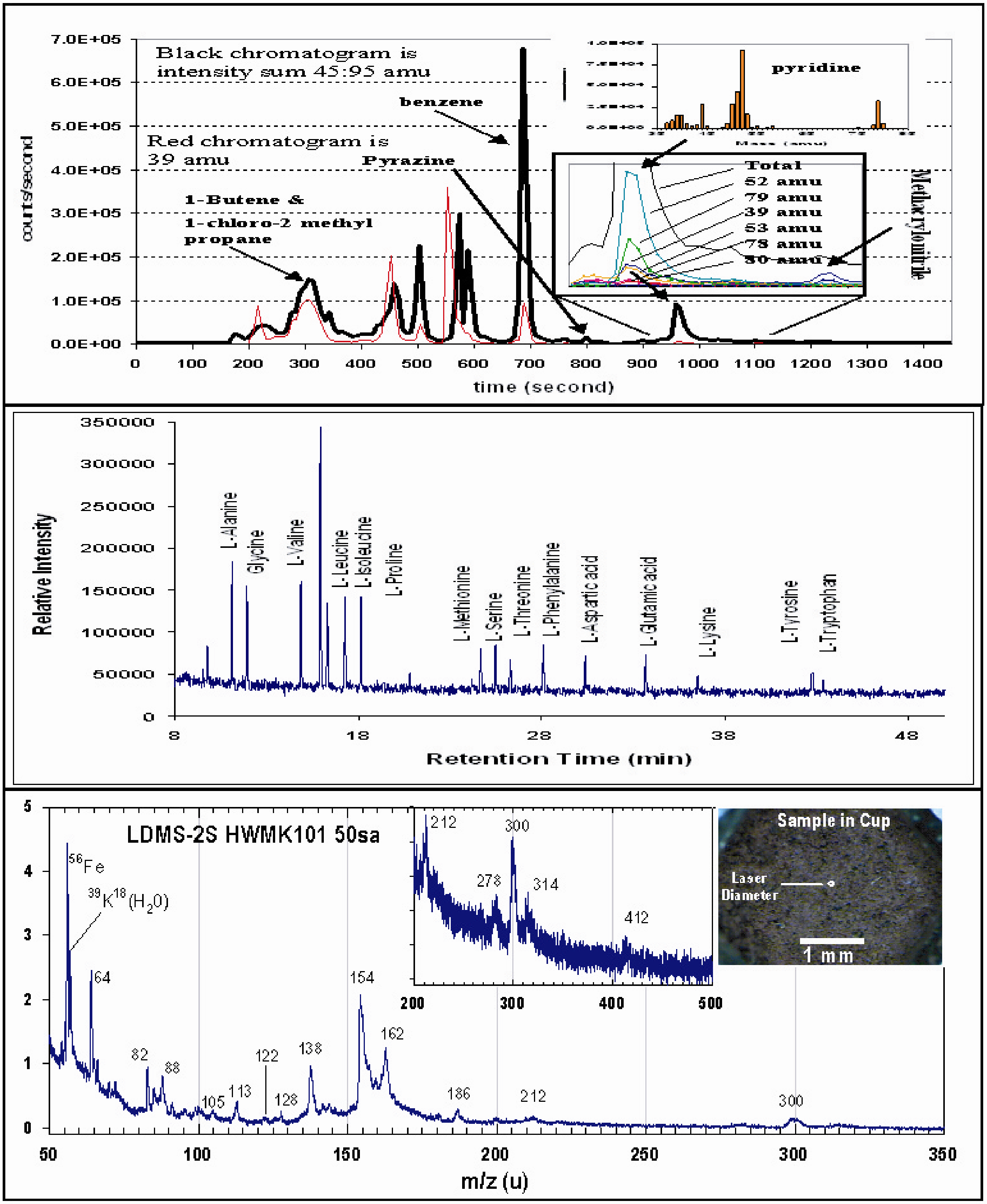

Figure 1. (a) GCMS analysis of organic molecules released on pyrolysis of palagonitic tephra, (b) derivatization of 15 amino acids with a single reagent, (c) laser desorption TOF mass spectrum of palagonitic tephra (right inset: LDMS imager view of sample).