

A GCMS Instrument for the In-situ Detection of Organics on Mars. J. H. Waite¹, R. Dissly², R. Sacks¹, and B. Block¹, ¹University of Michigan (Dept. of Atmospheric, Oceanic, and Space Sciences, The University of Michigan, Space Research Bldg., 2455 Hayward, Ann Arbor, MI 48109-2143, hunterw@umich.edu), ²Ball Aerospace & Technologies Corp. (1600 Commerce St., Boulder, CO 80301).

Introduction: Future missions to Mars will offer the opportunity to continue the search for organic molecules accessible from the surface. This paper describes an analytical instrument suite that is designed to measure potential organic and isotopic signatures contained in near surface reservoirs on Mars, using a pyrolysis/extraction system coupled to a gas chromatograph (GC) and time-of-flight mass spectrometer (TOF-MS).

Motivation: The design of new techniques to look for biomarkers on Mars is largely driven by the results of the 1976 Viking mission. Viking results are interpreted to be inconsistent with the action of life, rather explained by simple inorganic chemical processes and an oxidizing upper regolith. However, organic degradation products from meteoritic infall should be present and detectable, at a minimum. Benner *et al* [1] suggest that the Viking GCMS experiment was not sufficiently hot to yield volatile products from such material. In addition, measurements that can preserve the structure of organic molecules and include isotopic information would be ideal. Increasing the concentra-

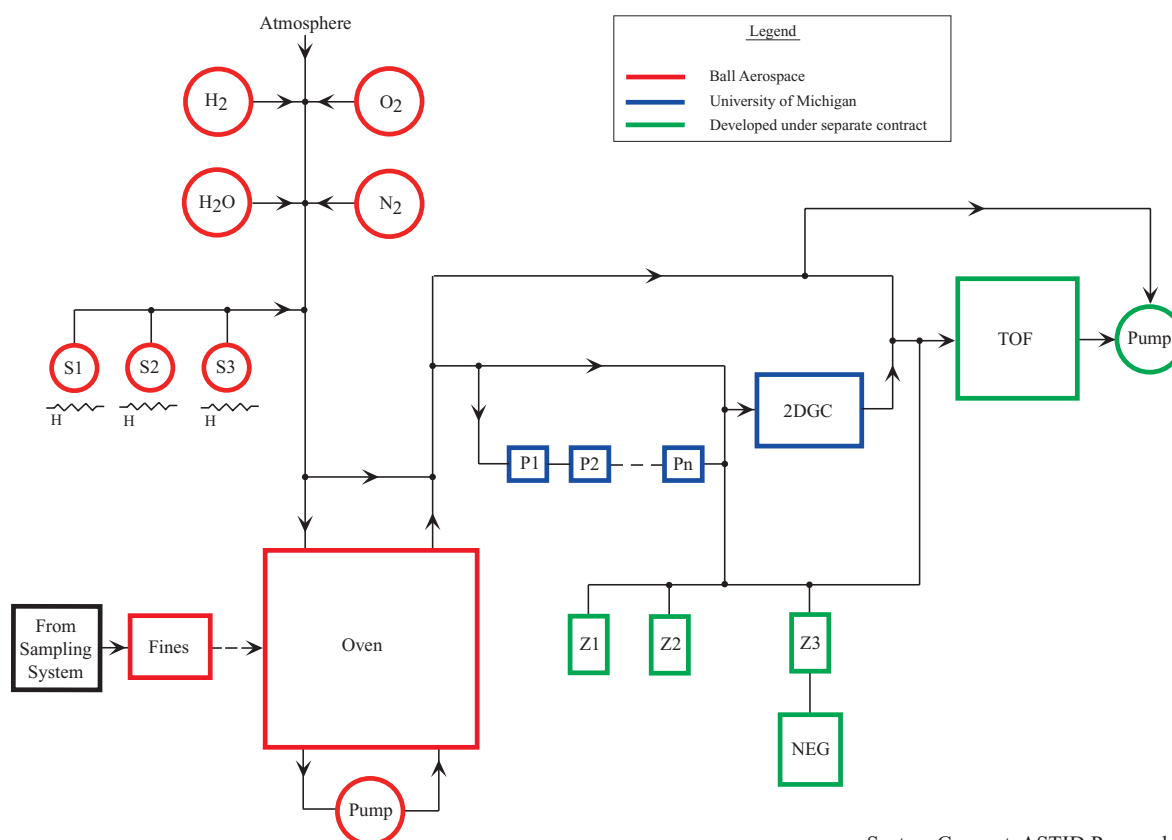
tion of potential organic material in samples would also be very desirable.

Proposed Instrument: The analytical suite described here includes an organic extraction system incorporated into a pyrolysis oven, followed by a two-dimensional gas chromatograph and mass spectrometer. A block diagram of the system is shown below.

Multiple carrier gases and solvents (labeled S_n) can be implemented. Preconcentration of evolved gases is included prior to analysis with either the GC or MS. Gas or liquid phase samples from the solvent extraction step can be introduced into the GC. The subsystems of this instrument are each described in more below.

Pyrolysis/Extraction. The pyrolysis module functionality is designed to include the capability for 1) pyrolysis under various carrier gas compositions, 2) solvent extraction under elevated pressures to increase solvation efficiency, and 3) automated sample handling to introduce new samples and remove spent samples from the oven chamber.

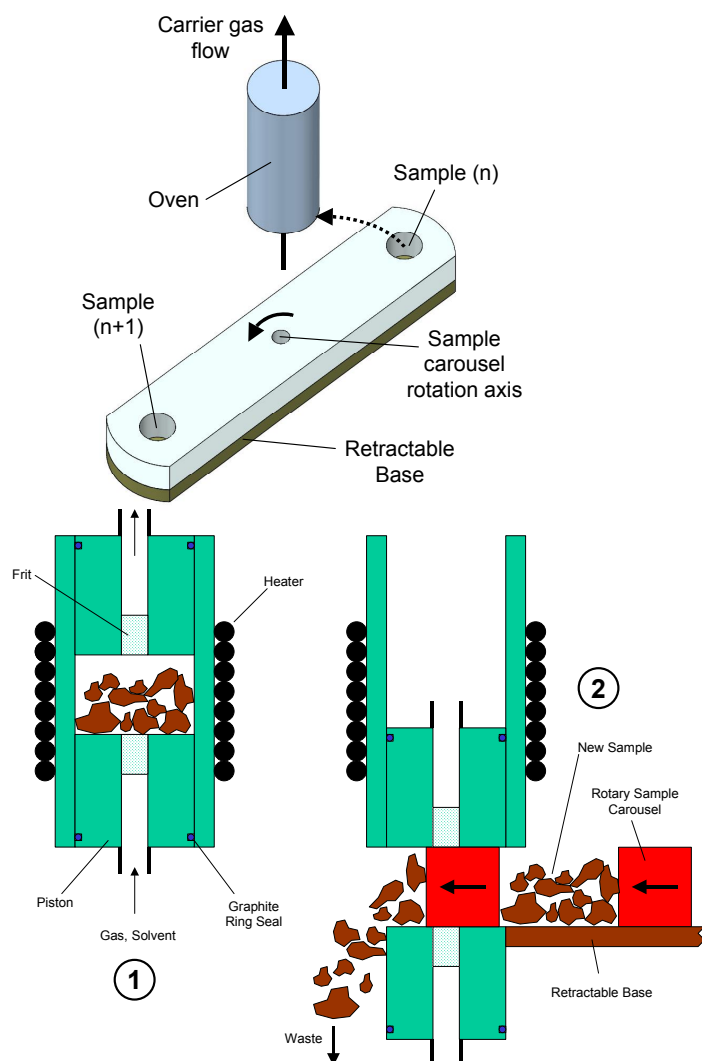
Pyrolytic heating of a given sample under differing at-



mospheric compositions can produce very different product distributions. If the sample is a complete unknown, multiple data sets from a suite of carrier gases can provide much more insight into the sample composition than a single analysis. Oxidative pyrolysis, or combustion, of all carbonaceous and organic compounds in the oven will produce a combination of simple oxide gases. Inert pyrolytic heating is required to preserve the elemental and isotopic state of samples that could potentially contain a trace abundance of oxidants, as have been hypothesized in the upper few cm of the Martian soil. Both hydro-pyrolysis, or pyrolytic heating under an atmosphere of H_2 , and hydrous-pyrolysis, under an atmosphere of H_2O , have been shown to be effective in preserving structural and stereo-chemical features compared to other pyrolytic methods, and additionally show high yields of preserved products from characteristically difficult materials such as kerogens [2].

The pyrolysis oven, pictured below, will nominally be designed to meet the following operational requirements:

1. Max temperature of 1200C to enable quantitative pyrolysis of organics
2. Max pressure of 5 bar to enable solvent extraction at elevated pressures



3. Hermetic sealing to prevent loss of evolved gases
4. Reusable for multiple samples
5. Automated sample handling
6. Low thermal mass to minimize power draw and enable calorimetry

The pyrolysis oven will be incorporated into a plumbing scheme that allows for optional organic solvent extraction prior to pyrolytic heating. This option adds a unique capability to this analytical system, and is particularly valuable as an initial separation step for potentially complex organic mixtures. A variety of organic solvents can be used (e.g., methanol, benzene, dichloromethane), depending on the functionality of the component that is to be extracted.

Two-Dimensional Gas Chromatograph (2DGC)
2DGC is a standard separation technique used in the petroleum industry [3]. In this technique, the entire chromatogram eluting from a primary column is transferred to a secondary column for a separate, orthogonal separation. The resulting 2D chromatogram has a peak capacity equal to the product of the two dimensions, and has peaks scattered in a plane rather than along a line. Component identifications are likely to be more reliable, as distinct structural patterns will be expressed as two independent characteristics (e.g., polarity and molecular size).

References: [1] S. A. Benner et al, (2000) *Proc. Nat Acad. Sci.* 97, 2425-2430. [2] G. D. Love (1995) *Org. Geochem* 23, 981-986 [3] J. Blomberg et al, (1997) *J. High Resol. Chromatogr.* 20, 539-544. (1996).