THE MARS ORGANIC ANALYZER: INSTRUMENTATION AND METHODS FOR DETECTING TRACE ORGANIC MOLECULES ON MARS AND ELSEWHERE IN OUR SOLAR SYSTEM. Amanda Stockton[1,2], Jungkyu Kim[3], Peter Willis[2], Robert Lillis[4], Ronald Amundson[5], Luther Beegle[2], Anna Butterworth[4], David Curtis[4], Pascale Ehrenfreund[6], Frank Grunthaner[6], Robert Hazen[7], Ralf Kaiser[8], Michael Ludlam[4], Maria Mora[2], James Scherer[5], Paul Turin[4], Kees Welten[4], Kenneth Williford[2], and Richard A. Mathies[5*] [1]Georgia Institute of Technology, Atlanta, GA. [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA. [3]Texas Tech University, Lubbock, TX. [4]University of California Berkeley Space Science Laboratory, Berkeley, CA, [5]University of California, Berkeley, CA. [6]George Washington University, D.C. [7]Carnegie Institution of Washington, George Mason University, VA. [8]University of Hawaii, Honolulu, HI. *Corresponding author: Richard A. Mathies, College of Chemistry, University of California, Berkeley, CA.

Introduction: *In situ* organic analysis especially on Mars has been clearly proven to be a powerful and cost effective approach for detecting molecules of relevance for chemical evolution in our solar system. As miniaturized analytical systems become even more powerful, these capabilities and accomplishments will surely expand our knowledge of the chemistry and perhaps biochemistry of our solar system even further. Many missions, especially to exciting outer Solar System targets like the icy moons of Saturn and Jupiter are best approached with *in situ* instruments because of the formidable risks and costs of sample return.

The Mars Organic Analyzer (MOA), developed for Mars 2020, was designed to meet the *in situ* organic analysis needs of this mission by providing it with the capability characterize the martian ground-truth organic content of samples. The identity and concentration of a wide range of organic molecules including amines, amino acids, aldehydes, ketones, organic acids, thiols and polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial samples can be determined with sub-part-per-billion sensitivity using the MOA. An overview of the MOA operational scheme is shown at the top of Figure 1. The MOA concept is also applicable to many other planetary explorations to characterize in situ oranic content because of its sensitivity and its ability to detect many compound classes. For example this instrumentation is being utilized to develop the Enceladus Organic Analyzer (EOA) concept that samples *in situ* the water plumes from Enceladus in a fly-by mission. An overview of the EOA operational scheme is shown at the bottom of Figure 1. This illustrates how the MOA technology can be used to develop planetary organic analyzer instruments with the analytical sensitivity needed to characterize the habitability of environments, to characterize biosignature preservation potential, to search for chemical signs of past and present life.

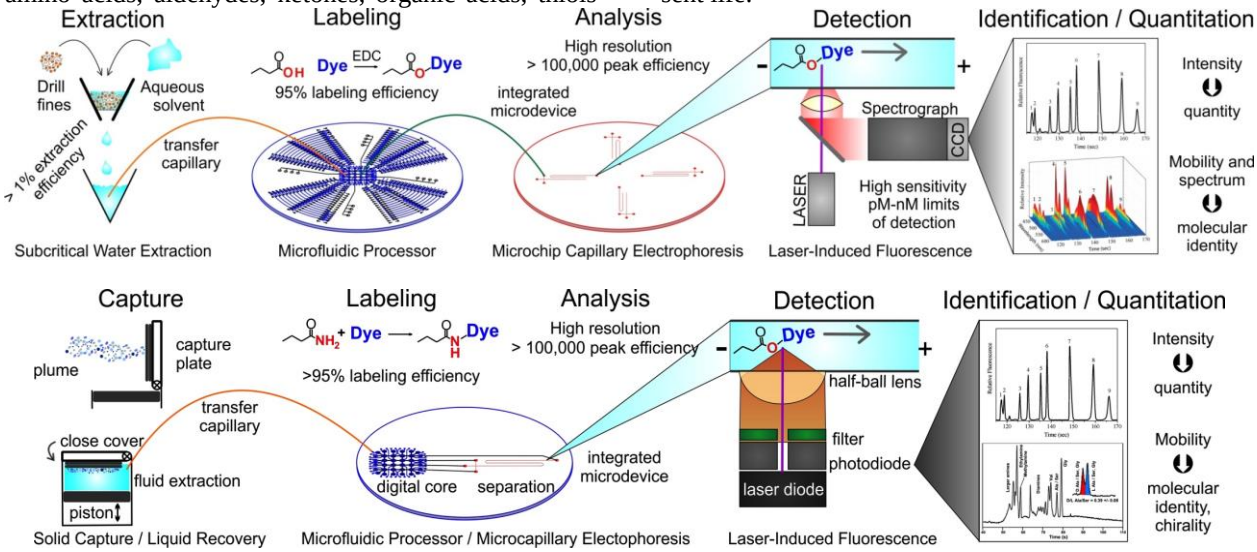

Figure 1*: (Top) MOA investigational schematic. (Bottom) EOA investigational schematic. In the MOA, the solid samples are extracted with subcriticial water, labeled with a functional group specific dye in the Microfluidic Processo,r and analyzed by size and charge in the capillary electrophoresis system that is detected by laser induced fluorescence. The EOA captures and similarly analyzes only a single sample that is acquired from the Enceladus water plumes using a capture plate.*

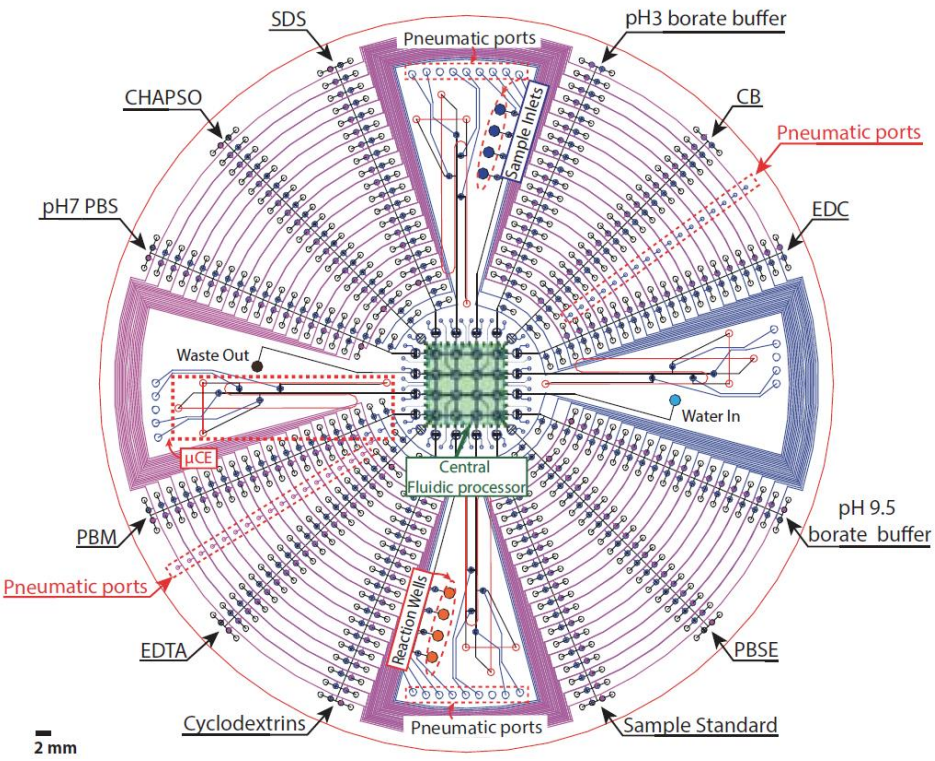

Figure 2: *MOA Programmable Microfluidic Analyzer layout. This 100-mm diameter multilayer glass-PDMS device with 516 multiplexed valves contains the dried reagents needed to perform all MOA chemical analyses upon 38 separate sample extracts. A similar, lower-complexity microdevice has been designed for the EOA instrument.*

MOA Instrumentation: Extensive instrument and method development and field testing has been used to develop the basic MOA capabilities [1]. Sub-part-per-billion sensitivity is achieved with an integrated instrument that first efficiently extracts organic molecules from soils or drill fines using subcritical aqueous extraction (SCAE) [2]. The molecular extracts are passed to a multilayer integrated microdevice (Figure 2) that consists of a Programmable Microfluidic Analyzer or PMA and a microfabricated capillary electrophoresis (μCE) device. In the PMA [3], the organic compounds are automatically labeled according to their chemical functional groups with fluorescent reagents specific for amines, aldehydes, ketones, organic acids and thiols. As indicated in the figures, the labeled molecules (or naturally fluorescent PAHs) are then passed to the μCE system for high-resolution electrophoretic separation followed by high sensitivity laser-induced fluorescence detection on one of the four independent CE channels [4]. The dye-labeled organics are identified by their electrophoretic mobility (Figure 3) and the PAHs are identified by their mobility and their fluorescence spectrum detected on one quadrant of a CCD spectrograph. The coupling of efficient non-perturbative SCAE, high sensitivity labeling and detection results in sub-part-per-billion detection limits that dramatically enhance our ability to perform in situ detection and characterization of organic molecules on Mars and other solar system bodies including moons and comets.

Heritage: The instrumental concepts and technologies described here are based on over 15 years of development work at UC Berkeley and JPL [1-4]. Portable prototypes, particularly of the MOA concept, have been field tested in the Panoche Valley, CA and in the Atacama Desert in Chile, where amino biomarkers of

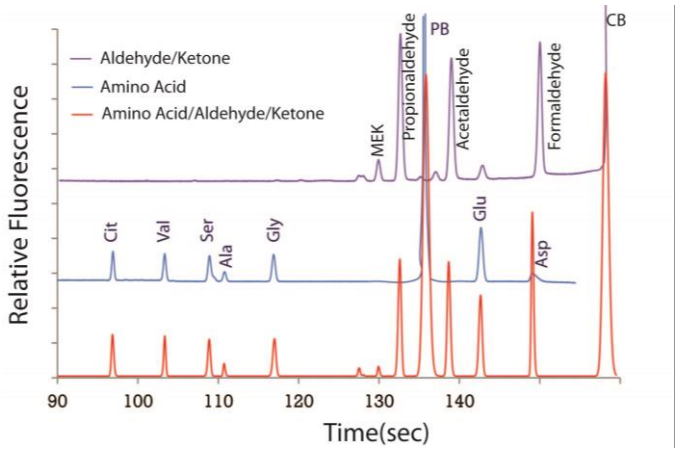

Figure 3*: Exemplary analysis of a mixture of various amino acids, aldehydes and ketones. High sensitivity labeling, CE separation and detection enables sub-part-per-billion sensitivity and high resolution.*

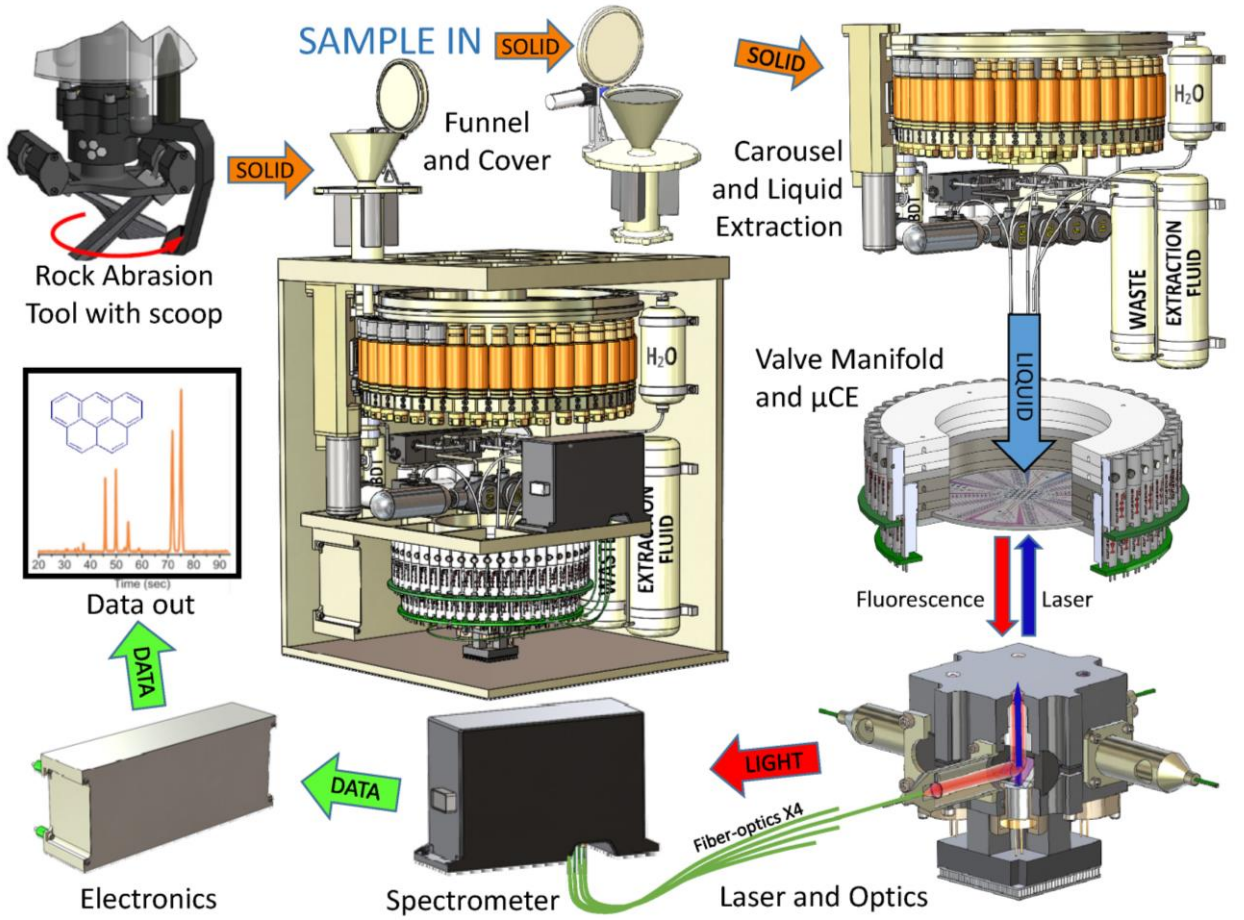

Figure 4*: In the MOA investigation, drill fines are passed through a funnel to the extraction cup and aqueous solvent at elevated T, P is forced through the drill fines, extracting organic molecules. This extract is then transported to a programmable microfluidic sample processing system for fluorescence labeling followed by injection, separation and high sensitivity detection on a microfabricated capillary electrophoresis channel to reveal the identity and concentration of a wide variety of organic molecules.*

ancient life were detected and dated based on their chiral ratios [1].

Organic Analyzer Technical Presentation: The laboratory development of the extraction, labeling, processing, separation and detection methods that make the MOA instrument possible will be presented. The engineering design that integrates all of these functions for the analysis of up to 38 samples on the surface of Mars including the fiber optic coupling of the four detection systems to a single spectrograph and CCD will be presented. Overall the MOA instrument is a compact 12 kg, 5 watt, 22 x 22 x 29 cm instrument (Figure 4) that only requires 25 MB of data return for the analysis of 38 samples.

The EOA instrument is a simplified version of MOA based on the core technology of the PMA-µCE microdevice. The EOA is simpler because of the lower sample number requirements and because it does not need to extract organics from a solid rock or dirt matrix. The high science return capability of MOA is preserved in EOA, including breadth of organic chemical class coverage, high sensitivity, and chiral analytical capabilities. Current EOA design is an ultra-compact 2.5 kg, 94 cm^3 package requiring only 2 watt (max) and producing 2 MB total data return.

While currently designed for Mars and Enceladus missions, our instrumentation could be easily repackaged for many other planetary science missions requiring highly sensitive in situ organic analysis.

References: [1] Skelley A.M., Scherer J.R., Aubrey A.D., Grover W.H., Ivester R.H.C., Ehrenfreund P., Grunthaner F.G., Bada J.L., Mathies R.A. (2005) *PNAS USA, 102*, 1041-1046. [2] Beegle L.W., Kirby J.P., Fisher A., Hodyss R., Saltzman A., Soto J., Lasnik J., Roark S. (2011) *Aerospace Conference*. [3] Kim J., Jensen E., Stockton A., Mathies R.A. (2013) *Anal. Chem.*, *85*, 7682−7688. [4] Mora M.F., Stockton A.M., Willis P.A. (2012) *Electrophoresis*, *33*, 2624–2638.