INSTRUMENT FOR CAPTURING AND ANALYZING TRACE ORGANIC MOLECULES FROM PLUMES FOR OCEAN WORLDS MISSIONS. Anna Butterworth[1], Jungkyu Kim[2], Amanda Stockton[3], Paul Turin[1], Michael Ludlam[1] and Richard A. Mathies[4] [1]Space Sciences Laboratory, University of California, Berkeley, CA. [2]Texas Tech University, Lubbock, TX, [3]Georgia Institute of Technology, Atlanta, GA. [4]College of Chemistry, University of California, Berkeley, CA (ramathies@berkeley.edu).

Introduction: Enceladus Organic Analyzer (EOA) is an innovative miniaturized microfluidic organic chemical and biochemical analysis instrument that will sample and determine trace organic content from plumes or comas. *In situ* organic analysis is a powerful and cost effective approach for detecting molecules of relevance for chemical evolution in our solar system. Furthermore, biologically important classes of compounds, such as amino acids, show a strong chiral bias on Earth, and are ideal for probing the presence of extraterrestrial life. The goal of the EOA is to sample the Enceladus south pole plumes and perform sensitive organic measurements and probe for indications of life.

Heritage: A miniature lab-on-a-chip approach for detection and chirality determination of trace organic compounds has been developed extensively over 15 years at UC Berkeley College of Chemistry and the Berkeley Space Sciences Lab [1-3]. Portable prototypes have been field tested in the Panoche Valley, CA and in the Atacama Desert in Chile, where amino acid biomarkers of ancient life were detected and dated based on their chiral ratios [1].

The technique employs an integrated microfluidic device (typically 10-cm diameter) to analyze microliter aqueous volume samples for a wide variety of molecular species with part-per-million sensitivity. The projection of a typical microfluidic chip is shown in Fig. 1. First, organic compounds are automatically labeled according to their chemical functional groups with specific fluorescent reagents in a Programmable Microfluidic Analyzer (PMA). Next, the labeled organic species are separated by high-resolution electrophoretic separation in a microfabricated capillary electrophoresis (µCE) device. Finally, high sensitivity laser-induced fluorescence detection results in molecular identification and chirality (by separation time) and quantitation (by peak intensity). This miniaturized instrument is ideal for deployment for *in situ* organic analysis of multiple and varied planetary science targets. We describe here the use of this technology to solve the challenging problem of acquiring samples from the Enceladus plumes by an orbiter or fly-by and analyzing for organic components.

Enceladus Organic Analyzer (EOA) Instrumentation: The icy plumes arising from Enceladus provide an outstanding opportunity to look for organic rich life or potential for life [4]. This sampling opportunity suggested a novel design for a flight-ready Lab-on-a-Chip organic analyzer instrument, where we capture elusive volatile samples such as comet comae or Enceladus plumes and analyze them operating an integrated microfluidic device in a low gravity environment.

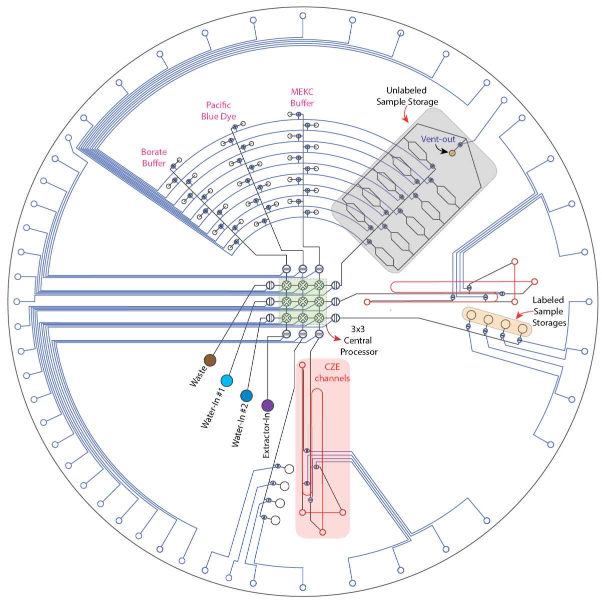

Figure 1: Microdevice at the heart of the Enceladus Organic Analyzer instrument. The processing core is a rectilinear array of valves at the center of the microdevice highlighted green. Reagent storage for multiple samples radiate from the center along spokes towards the top, and sample storage has been highlighted grey. The capillary electrophoresis channel is highlighted red.

EOA analysis schematic is shown in Fig 2 and the instrument design is shown in Fig. 3. The instrument is flown through the Enceladus plume where a capture plate is used for ice-particle collection; adsorbed organics are dissolved and transported to the PMA-µCE microfluidic device for analysis. The key question is the design and function of the capture plate that picks up the sample in a 1-5 km/s fly-by through the plume. It is important to dissipate the kinetic energy of impact in such a way that the organic molecules in the ice particles are not isomerized or significantly altered by the impact. We have performed detailed mechanical modeling calculations to determine the partitioning of

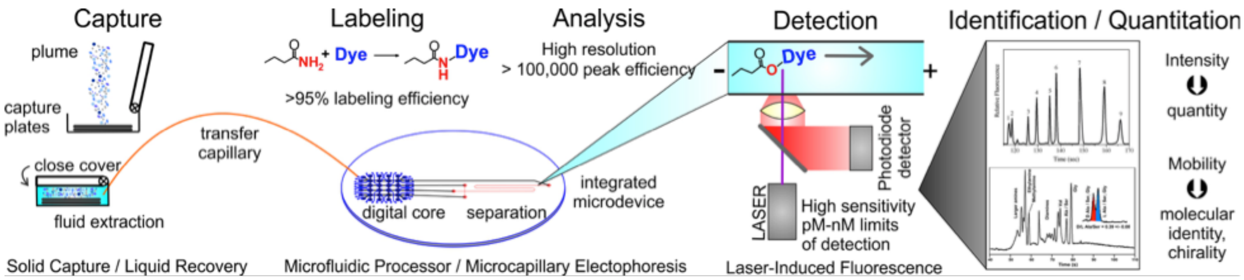

Figure 2. Schematic of functional elements and analysis process of Enceladus Organic Analyzer (EOA). The ice plume impacts the capture plate when the lid is open depositing organic molecules. After the lid is closed, the molecules are dissolved and, after passage to the microfluidic processor, the amine-containing molecules in the extract including amino acids are labeled with a fluorescent dye, separated by high resolution capillary electrophoresis, and detected with ppm sensitivity. Biologically significant molecules which may indicate life such as amino acids are identified by their unique mobility and their chirality is determined.

the input kinetic energy into the work of deformation of the target material, thermal transfer from the ice particle into the target material during the impact and heating of the projectile material. These calculations demonstrate that with the correct impact material, organic molecules in the incoming ice are not heated sufficiently to cause isomerization or thermal decomposition. A design that enables over 25% capture of the input material has also been developed providing micrograms of captured material for analysis by EOA.

EOA is a ~2.5 kg mass instrument, with a 16 cm by 16 cm footprint, and low power operation requirement. It is capable of ppm-organic species detection and chiral measurement of organic molecules such as amines and amino acids in 5 µg ice. Fluidic management is achieved by using pressured nitrogen. A microfluidic valve array, the Programmable Microfluidic Analyzer, is used to perform labeling of the sample with fluorescent dyes and to process the sample for high resolution electrophoretic analysis and sensitive fluorescence detection. In particular the measurement of amino concentration composition and chirality is especially important for probing for the potential for life or perhaps its actual existence on Enceladus.

Many missions, especially to outer Solar System targets like the icy moons of Saturn and Jupiter, or comets, are best approached with *in situ* instruments because of the formidable risks and costs of sample return. The identity and concentration of a wide range of organic molecules including amines, amino acids, aldehydes, ketones, organic acids, thiols and to polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial samples can be determined with sub-part-per-billion sensitivity using the EOA concept. The demonstration and deployment of such technology should dramatically advance our knowledge of molecular planetary science.

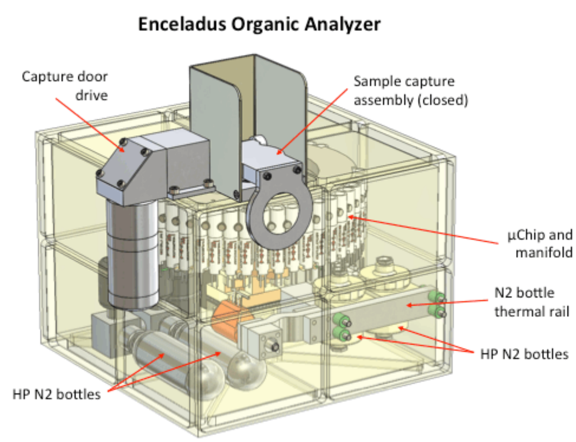

Figure 3: Schematic CAD of the EOA Instrument. The EOA is a 16x16x12 cm instrument with a mass of 2.5 kg that can be used for sensitivity part-per-million chemical analysis of organic molecules from plumes or comet tails that impact the capture plate assembly.

References: [1] Skelley A.M. et al. (2005) *PNAS USA, 102*, 1041-1046. [2] Kim J. et al. (2013) *Anal. Chem.*, *85*, 7682–7688. [3] Stockton A.M. et al. (2014) *Second International Workshop on Instrumentation for Planetary Missions*. [4] Porco C.C. (2006) *Science 311*, 1393-1401.