PLUME COLLECTION STRATEGIES FOR FUTURE ICY BODY SAMPLE RETURN MISSIONS. D. P. Glavin[1], P. Tsou[2], A. D. Anbar[3], J. Baross[4], L. W. Beegle[2], D. E. Brownlee[4], R. Dissly[5], C. Glein[6], I. Kanik[2], C. McKay[7], A. A. Monroe[3], M. Neveu[3], J. Schmidt[8], K. Takai[9], Y. Takano[9], P. Williams[3], and H. Yano[10]. [1]NASA Goddard Space Flight Center, Greenbelt, MD, USA (daniel.p.glavin@nasa.gov), [2]Jet Propulsion Laboratory, Pasadena, CA, USA, [3]Arizona State University, Tempe, AZ, USA, [4]University of Washington, Seattle, WA, USA, [5]Ball Aerospace & Technologies Corp., Boulder, CO, USA, [6]Carnegie Institution of Washington, Washington DC USA, [7]NASA Ames Research Center, Moffett Field, CA, USA, [8]University of Oulu, Oulu, Finland, [9]Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Tokyo, Japan, [10]Japan Aerospace of Exploration Agency (JAXA), Institute of Space and Astronautical Science, Tokyo, Japan.

Introduction: The discovery of plumes of water vapor and ice particles emanating from cracks near the south pole of Saturn's moon Enceladus [1] and more recent Hubble observations suggesting possible transient water vapor plumes at Jupiter's moon Europa [2] provide important opportunities to search for organics and possibly evidence for life in these unique, potentially habitable sub-surface ocean environments. The Cassini Ion and Neutral Mass Spectrometer (INMS) instrument measured the gas composition of the Enceladus plume and detected primarily water ice with trace levels of simple hydrocarbons that could be fragments of larger, more complex organics (Fig. 1, [3]). Since habitable environments on Earth exist when liquid water, organics and energy co-exist, laboratory analyses of the structure, distribution, isotopic composition, and chirality of the chemical components (including biomolecules) of plume materials returned from these icy moons would provide a unique opportunity to search for evidence of extraterrestrial life in our solar system.

In this paper we discuss approaches for the collection of dust and volatiles from the Enceladus plume flyby based on Cassini observations and results and lessons learned from the Stardust comet sample return mission. We also highlight areas where sample collector and containment technology development and testing may be needed for future Enceladus and Europa sample return missions.

Enceladus Plume Composition and Density: The Cassini INMS, Cosmic Dust Analyzer (CDA), and Visual and Infrared Mapping Spectrometer (VIMS) detected and characterized the nature of the Enceladus plume. The INMS measured the gas composition of the plume to be primarily water (90%), CO_2 (5%) and CO or N_2 (4%) with trace (< 1%) amounts of C_1-C_6 hydrocarbons, H_2CO and HCN [3]. In addition, the *in situ* detection of Na, K and other elements by the CDA indicates that a salty Enceladus subsurface ocean likely exists [4]. Model estimates of the amount of water ice and dust that could be collected during a 20 km altitude south polar Enceladus plume flyby based on CDA measurements of the total number density of particles [5] and composition [4] find that ~10^{-3} g of ice and ~10^{-5} g of refractory material could be captured per m^2 of collector surface area. This estimate is valid for particles > 0.2 μm, which was the size threshold for measuring particle composition [4]. Additional mass will be captured in the form of nano-sized ice grains present in the plume [6,7]. If hydrocarbons represent <1% of the total water-ice captured [3], only ~10 μg of total organics per m^2 would be collected after a single 20 km altitude flyby. Assuming the abundance of glycine in the ice is similar to the levels of formaldehyde (0.3 wt%) detected in the Enceladus plume [3], we calculate that 100 nmol glycine per m^2 would be captured after a single 20 km flyby. It is interesting to note that this estimate is similar to the glycine concentrations measured on Stardust flight foils exposed to comet Wild 2 [8].

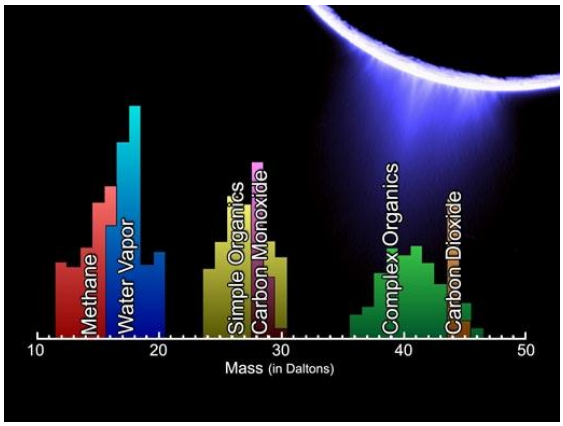

Figure 1. *Water vapor and a range of low molecular weight organics were detected in the plume by the Cassini ion and neutral mass spectrometer during a flyby of Enceladus. Image credit: NASA/JPL.*

To ensure that sufficient quantities of plume materials are collected and returned to Earth to search for biosignatures, multiply low altitude plume flybys using a collector with a large surface area containing multiple surface adsorbent and substrate types optimized to capture and retain silicate grains, water, and a range of other key species including noble gases, organics and biomolecules will be required. In addition, the collec-

tor hardware and sample return capsule will need to be cleaned (and protected from recontamination) to minimize terrestrial volatile and organic contributions to the plume sample, including spacecraft outgassing products. To help distinguish between plume components and terrestrial contamination, multiple witness materials that are not directly exposed to the plume, but are exposed to the spacecraft environment during all phases of the mission will need to be included in the design of the collector and sample return capsule.

Sampling Strategy for Organics and Biomolecules: An Enceladus plume sample collector could consist of different volatile adsorbent and particle capture assemblies that would be exposed to multiple samples (e.g. Enceladus plume and Saturn E ring) during multiple flybys *via* a rotating cover. In order to reduce the plume particle impact speed on the collector (Stardust was 6.1 km/s) and maximize the preservation of complex organics, including biomolecules, spacecraft trajectory simulations have shown that Enceladus plume encounter speeds of less than 2 km/s can be achieved for a spacecraft in Saturn orbit with gravity assists from Titan [9]. Such low encounter speeds may not be required for the survival of organics and biomolecules. Even with the high Stardust collector comet encounter speeds, cometary glycine was identified in samples of aerogel and foil returned to Earth [8], demonstrating that amino acids can survive impact and be retained on these materials.

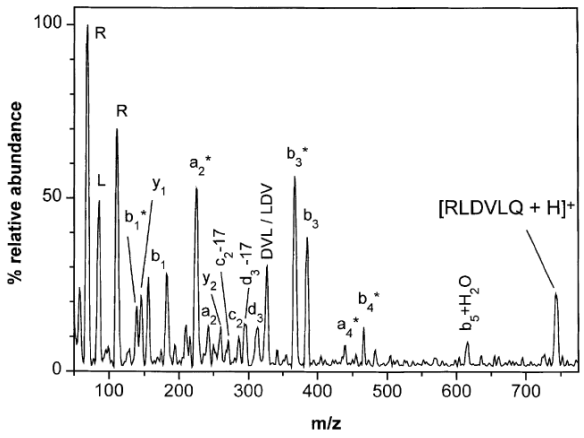

Figure 2. *Mass spectrum of the protonated polypeptide RLDVLQ (Arg-Leu-Asp-Val-Leu-Gln) after impact into a self-assembled monolayer of octadecanethiolate on gold with 4.6 km/sec (80 eV) collision energy showing survival of the parent ion [10].*

Laboratory experiments have demonstrated that ~95% of hexapeptide ions survive collision with a "soft" collision surface (coated with a self-assembled long-chain thiol monolayer) at 3.5 km/s and some parent ions and significant structural information survive collisions as fast as 4.6 km/s (Fig. 2 [10]). Ice-encased polypeptides and even short DNA oligomers (10-mers) have been shown to survive collisions with metal targets in vacuum at speeds that completely vaporize the ice [11]. Hypervelocity impact experiments at velocities over ~4 km/s using stearic acid and anthracene trapped in frozen dimethylsulfoxide at speeds up to ~4 km/s have also shown that complex organics in a frozen matrix can survive high shock pressures [12].

Collector Enhancements from Stardust: One of the primary advantages of silica aerogel is that it is flight proven and has been shown to be exceptional at capturing and preserving both silicate grains and volatile organic molecules [13], including amino acids and amines [14,15]. However, the relatively high Stardust particle impact speeds coupled with a significant background of terrestrial carbon (primarily Si-CH_3 groups) and organics (including amino acids and amines) within the silica aerogel itself [16] can complicate the identification of some extraterrestrial organic compounds. Moreover, laboratory impact experiments of meteorite particles in aerogel at ~6 km/s and subsequent analysis of the impact grains showed some chemical transformation of the indigenous polycyclic aromatic hydrocarbons during aerogel capture [17].

The first significant improvement to the collector would be to reduce the silica aerogel density from 10 mg/cc to 2 mg/cc which would effectively reduce the background carbon found in Stardust aerogel. In addition, the factor of 5 reduction in aerogel density coupled with a reduced Enceladus plume encounter speed results in a 50-fold reduction in ice particle impact energy. The reduced impact energy could help preserve the original structure of any plume organics in the gas, ice or particulate and reduce the likelihood of formation of organics (e.g. low molecular weight polycyclic aromatic hydrocarbons) from aerogel carbon as a result of particle impact heating [16].

Another key improvement to the Stardust collector would be inclusion of multiple adsorbent and particle assemblies that can be exposed individually to the plume during multiple passes *via* a rotating cover (Fig. 3, bottom). Since surface area determines the abundance of adhered atmospheric contaminants on any surface, the relatively large internal surface area of aerogel reduces its efficacy as a collector for trace organics. Metallic surfaces on the other hand, such as aluminum, gold or stainless steel, could be used to collect and retain both silicate particle impacts and less-volatile organic compounds. Organic contamination on metallic surfaces is more easily removed chemically or thermally compared to aerogel which is typi-

cally hydrophobic and cannot be heated to temperatures high enough to completely remove organics without damaging the aerogel structure.

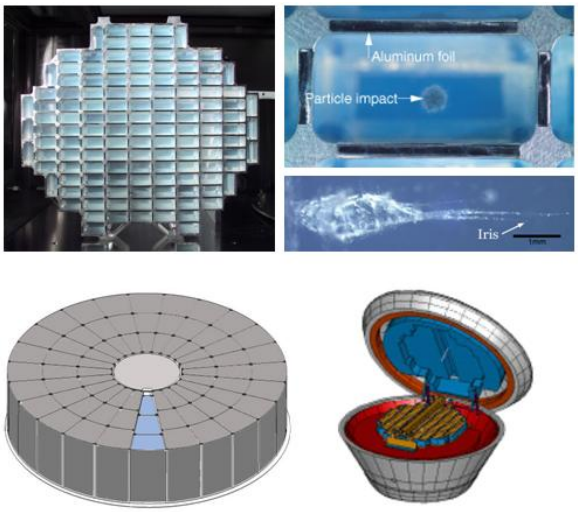

Figure 3. *TOP: Stardust sample collector tray with aerogel cells separated by aluminum foil ribs and a cross section of one of the comet dust impact tracks. BOTTOM: Rotating plume collector tray capable of exposing different substrates for multiple flyby samplings and return to Earth via a Stardust-like return capsule. Image credits: NASA/JPL-Caltech/University of Washington.*

Ice grain impacts on solid surfaces will result in shock-driven explosion of the ice and volatilization of entrained biomolecules, which will deposit on secondary collector surfaces [11]. For biomolecule analysis these secondary collectors could be configured for direct, robotic insertion into mass spectrometers for matrix-assisted laser desorption-ionization (MALDI) analyses upon return, minimizing exposure to terrestrial contaminants. The collector surfaces can be hydrophobically-patterned so that the diffuse capture layer of biomolecules and organics can be dissolved and concentrated into small surface spots prior to analysis.

Free molecules impacting a solid surface at the projected spacecraft velocity will not adsorb directly but also will rebound and scatter. For example methane or ammonia molecules impacting at 4-5 km/s have kinetic energies ~ 1-2 eV, too high for direct adsorption even on a cooled surface. Capture will require multiple surface scattering events to greatly reduce the kinetic energy. On a highly porous capture surface such as aerogel most impacts could result in scattering and capture into internal pores; however the high internal surface area and difficulty of outgassing aerogel will result in very high background levels. Honeycomb metal or graphite collectors with high depth/cross-section ratios for the channels should be significantly easier to outgas. In addition to an onboard power supply, significant outgassing might be achieved by heating the capture assemblies by exposure to solar radiation during the initial phase of the mission.

After return of the Stardust collector, the tray was stored at room temperature in an ISO Class 5 cleanroom at the NASA Johnson Space Center (JSC). During the analysis of Stardust foils for the presence of glycine at NASA Goddard Space Flight Center, it was observed that the glycine levels on the Stardust flight foils dropped by a factor of ~6 to 10 from the glycine levels originally measured on the foils over a period of ~1000 days during storage under ambient conditions at JSC. One possibility for the observed decrease in glycine abundances is the loss of more volatile glycine precursors (e.g. formaldehyde and aminoacetonitrile) from the Stardust foils. To avoid a similar loss of volatile species from an Enceladus or Europa plume collector, the temperature of the sample collector should ideally be maintained below the *in situ* sample temperature at capture (~270K) to Earth return. Active collector cooling and phase change materials inside the sample return capsule will likely be required in order to maintain the cold sample collector temperatures during Earth entry. Since a cold sample collector would obviously serve as a cold trap for volatiles during atmospheric entry, one challenge will be to ensure that the returned sample tray is shielded from terrestrial volatiles and organics from the atmosphere and ablation/outgassing of the sample return capsule.

References: [1] Spencer J. R. et al. (2006) *Science 311,* 1401–1405. [2] Roth L. et al. (2013) *Science 343,* 171-174. [3] Waite J. H. Jr. et al. (2009) *Nature 460,* 487-490. [4] Postberg F. et al. (2011) *Nature 459,* 1098-1101. [5] Spahn F. et al. (2006) *Science 311,* 416-418. [6] Jones G. H. et al. (2009) *Geophys. Res. Lett. 36,* L16204. [7] Hill T. W. et al. (2012) *J. Geophys. Res. 117,* A05209. [8] Elsila J. et al. (2009) *Meteorit. Planet. Sci. 4,* 1323-1330. [9] Tsou P. et al. (2012) *Astrobiology 12,* 730-742. [10] Gu C. et al. (1999) *Anal. Chim. Acta 397,* 247-256. [11] Aksyonov S. A. and Williams P. (2001) *Rapid Comm. Mass Spec.* 15, 2001-2006. [12] Burchell M. J. et al. (2014) *Astrobiology 14,* 473-485. [13] Tsou P. et al. (2003) *J. Geophys. Res. 108,* E108113. [14] Sandford S. A. et al. (2006) *Science 314,* 1720-1724. [15] Glavin D. P. et al. (2008) *Meteorit. Planet. Sci. 43,* 399-413. [16] Sandford S. A. et al. (2011) *Meteorit. Planet. Sci. 43,* 399-413. [17] Spencer M. K. et al. (2009) *Meteorit. Planet. Sci. 44,* 15-24.