THE CASE FOR AN ORBITAL MISSION TO CHARACTERIZE THE ORGANIC CONTENT OF THE ENCELADUS PLUMES

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SUMMARY: The icy moons of Saturn and Jupiter are high priority nearly ideal locations in which to search for biomarkers and possible life in our solar system. In particular, Enceladus is begging us to visit her by providing an ice plume sample from its under-ice ocean that extends many km into space. We now know that these organic rich ice particles can be efficiently captured at fly-by velocities below 2 km/s without organic destruction. Furthermore, an Enceladus orbiter with from 1-100 successful plume encounters will gather sufficient ice material to enable very valuable scientific measurements. The results from such an Enceladus plume orbiter will complement and support the development of subsequent landed missions to icy moons.

1. The search for biomarkers and possible life in our solar system is one of NASA's most important and highest priorities. Follow the water is a great guide in this quest but so far we have not looked where we know there is or was recently liquid water in an environment presently conducive to habitability and to life. The outer solar system moons and especially Enceladus offer that opportunity. It is time to transcend this gap. Nature and Cassini have conspired to provide us with a very obvious opportunity to sample a liquid ocean at Enceladus without many of the issues of planetary protection and special regions. It is imperative that we exploit this opportunity with a high capability organic biosignature analysis mission.

2. Icy moons such as Enceladus and Europa are now recognized as most promising locations to look for habitability and for life. Our primary focus is on Enceladus that has a global water ocean (Postberg et al. 2009; Thomas et al. 2016) and (1) lies under an ice sheet, (2) is in contact with a rocky core (Iess et al. 2014), (3) is understood to have significant salinity (Postberg et al. 2011) and (4) experiences hydrothermal activity at the ocean-core boundary that appears to supply adequate thermal energy to support microbial life forms (Hsu et al. 2015; Sekine et al. 2015; Waite et al. 2017). The Enceladus ocean is thought to have significant organic content, which taken together with the geological context and the observation of molecular hydrogen suggests high habitability potential (McKay et al. 2008; Glein and Zolotov 2020). Pristine samples from the sub-surface ocean are ejected through warm fractures in the icy crust (Porco et al. 2006; Spencer et al. 2006) forming plumes that extend thousands of kilometers above the surface (Spahn et al. 2006; Lunine 2017). Simple organic compounds have been observed in the plume material (Waite et al. 2006, 2009; Postberg et al. 2008) and, more recently, concentrated and complex macromolecular organics have also been detected (Postberg et al. 2018; Khawaja et al. 2019). Thus, Enceladus presents us with a remarkable opportunity to conduct in-depth astrobiological investigations to probe for organic and bioorganic molecules residing in the sub-surface ocean that are indicative of at least habitability, but perhaps also extinct or extant life.

3. Advancing our knowledge about the identity and concentration of organic molecules in the Enceladus plume will advance our knowledge of the boundaries of habitability and life in our solar system and will compliment and facilitate more detailed landed missions to the icy moons. While significant amounts of fragmented

organic material have been detected in the Enceladus plumes, exploring the organic content of the plumes was not the intended goal of the Cassini mission and instruments. Now that we know the plumes are there and now that we have some knowledge of their organic content, there is much to be learned about habitability and life by sending a focused plume characterization and high sensitivity organic detection suite of instruments to Enceladus analogous to the proposed ELF mission (Reh et al., 2016). Maximum science return would be provided by first entering a Saturn orbit with high velocity 4-6 km/s transits through the Enceladus plume to enable impact ionization MS sampling as proposed in the white paper by Cable et al. (2020) providing 1 micromolar biomarker detection limits. The orbital transit velocity past Enceladus could then be lowered into the 1-2 km/s range to enable accumulation of intact organic molecules and their detection by chemical analyzers with from 10-100 nanomolar detection limits. Finally, entry into Enceladus orbit would enable a large number of plume encounters and sample accumulation that would raise the science measurement capabilities to the level needed to fully assess habitability and biomarker potential (1 nanomolar, Hand et al., 2017). Plume density varies temporally and thins at increasing altitude, which boosts the case for a multi-collection approach, rather than attempting to perfectly time a transect. To thoroughly characterize Enceladus' ocean, we need to analyze pristine samples of the plume and its entrained gases together with measurements of processed surface and snow in-fall (Porco et al., 2017). Missions are being proposed to both Enceladus and Europa whose design would be facilitated by having more detailed information about the organic content of these ices. A full understanding of the Enceladus surface samples requires also analyzing the chemical content of the emitted ice particles before they land on the surface and are subject to environmental processing.

4. There are a variety of mission profiles ranging from high velocity fly-bys to an orbiter that can provide opportunities to make individual and multiple samplings of the Enceladus plume with sufficient sample gathered to make very meaningful measurements by MS and by organic analyzers. Figure 1 presents a critical comparison of various approaches for sampling the Enceladus ice plumes with a fly-by, an orbiter and a landed mission. The biomarker analyte concentration is presented on the y-axes while the volume/mass of total gathered ice sample is on the x-axis. The blue shaded region highlights the ice mass that can be gathered ranging from a single pass to an Enceladus orbiter with 100 passes through the plume (Hedeman et al., 2009; Porco et al., 2017). The red region indicates the region of this graph that is enabled by a lander that gathers and presents from 10 mg to 1 gm of material for analysis. The data space that is accessible by TOF-MS is all above 100 ppb because typically no sample accumulation is required; this is also true for the impact ionization mass spectrometer. The biosignature detection limits in the plume are limited to ~100 ppb (~1 micromolar) for impact ionization (Klenner et al., 2020). The indicated GCMS approaches like MOMA are more sensitive reaching 10 ppb but require a multi-mg surface sample and processing (Goesmann, 2017).

Figure 1. Plot of the detection space for the analysis of organic biomarkers in ice samples from icy moons such as Enceladus. The detection limit of impact ionization MS is fixed independent of sample size at ~ 100 ppb. The detection limit of wet chemical analyzers is determined by analyte concentration and can be improved by gathering more sample and by placing it in a smaller analytical volume. The grey shaded region indicates where the CE-LIF system is limited by too few analyte molecules in the sample. The blue region is accessible by 1-100 Enceladus passes after sample dissolution in 10 microliter of solvent.

In complementary chemical analyzers, the limits of detection are determined by aggregate concentration so if you accumulate more ice sample and present it to the analyzer in a small volume, the detection limits are improved. For example for the Microcapillary Electrophoresis Laser Induced Fluorescence CE-LIF system represented by the Enceladus Organic Analyzer (Mathies 2017, <http://eoas.ssl.berkeley.edu>) the limit of detection in a 10 microliter analysis volume is 100 picomolar (Chiesl et al., 2009). Thus for a single pass through the Enceladus plume, 10 nL of ice are gathered producing a detection limit of 100 nM for biosignatures. However if one performs 100 passes through the plume gathering 100-times more material, the detection limit improves to 1 nanomolar (0.1 ppb). For reference this is the detection limit specified for organic molecules in the Science Trace Matrix in the Europa Lander SDT report (Hand et al., 2017). This detection limit provides very valuable information about the presence and identity of biomarkers in the Enceladus plume. For completeness, once a sample larger than 10 mg is provided, the wet chemical analyzer detection limit is determined by the intrinsic properties of the CE-LIF format at 100 pM, a sensitivity ~ 4 orders of magnitude better than TOF MS. Since we do not know *a priori* the level of individual organic molecules in the plume, it is imperative to study it with the most sensitive analytical instruments.

5. There are capture surfaces that enable the capture of organic containing ice particles in the velocity range from 3 to less than 1 km/s for intact organic molecular analysis. For biosignature analyses, we desire to capture intact organic molecules in the ice particles, dissolve them in the smallest volume of solution to maintain high concentration and then subject them to chemical analysis. To this end New et al. have performed light gas gun experiments at the University of Kent, UK (Burchell et al., 2014) where they shot micron sized ice particles containing an organic tracer into soft metal capture surfaces and then quantitatively analyzed the percent capture and survival of a fluorescent test molecule (New et al., 2020a, New et al., 2020b). Representative images of impacts at 1.3 and 1.7 km/s into indium foils are presented in Fig. 2 showing the craters produced and the fluorescence of the captured intact fluorescent tracer. These experiments enabled quantitative evaluation of capture and survival percentages in hypervelocity impacts. A summary plot of all the observed impacts at 1.7 km/s is presented in Figure 3 showing that the mean capture efficiency is $\sim 10\%$ and can be as high as 50% for some impact events. The targets were mounted vertically so that loosely bound material may fall off, therefore these measured efficiencies may be regarded as conservative estimates. The capture efficiency is generally higher at lower velocities and for smaller particles; additional studies are in process to study smaller particles. Other groups and studies are developing alternative formats for hypervelocity particle capture; however, to our knowledge they have not published or talked about these instruments or results. Our results inform the Committee that it is feasible to capture intact organic molecules on these capture surfaces in hypervelocity impacts in at least the 1-2 km/s range and likely also at lower velocities.

Figure 2. Bright-field and fluorescence images of craters on indium foils following 1–2 km s⁻¹ velocity ice impacts. Fluorescent dye residue, which was doped into the initial ice projectile, is observed in the circled craters and the corresponding particle diameters and organic capture efficiencies are indicated. The integrated fluorescence intensity in the craters is a direct measure of the capture and survival of the organic tracer molecule.

Figure 3. Representative organic capture efficiency (%) plotted on logarithmic scale against particle diameter (μm) for impacts at 1.7 km/s ($N=173$). Power functions fit to the organic capture efficiency data (dashed red line) enable extrapolation to smaller particle sizes.

6. We conclude that a mission to sample the Enceladus plumes with a focused suite of organic analysis and plume gas characterization instruments should be a priority for the next Decadal Survey. The reasons for this recommendation are:

(1) Cassini revealed a remarkable new opportunity to probe for biosignatures in a likely habitable environment at Enceladus that demands a rethinking of our sequential priorities. Detailed analysis of the chemical content of the Enceladus plumes for potential intact bioorganic molecules and for molecules that characterize the ocean redox chemistry will dramatically advance our understanding of the limits of habitability and of the potential for life in our solar system by directly probing one of the most interesting likely alternative gestation sites currently available.

(2) A large number of scientists agree that Enceladus is one of the best places to look for biosignatures and habitability so there is a consensus that its priority should be raised since it directly addresses one of NASA's primary goals (*Astrobiology*, **17**, 2017).

(3) Improved measurements of the identity and amounts of organic material and of the redox environment in icy moon oceans will provide valuable information for the selection of instruments to improve science return for landed missions to Enceladus and Europa.

(4) A complete understanding of Enceladus' ocean will require measurements of the plume and the surface – this proposed mission addresses one of these mission goals making the landed mission more focused and less complex. Measurements of the pristine plume content must be made for a complete scientific understanding of the habitability of Enceladus' ocean and its organic content so why not do it well with a focused mission?

(5) It has now been experimentally determined that there are efficient capture surfaces for harvesting Enceladus ice particles without organic destruction and fragmentation. Furthermore, an Enceladus orbiter can gather sufficient ice sample through multiple passes to enable a scientifically very valuable 1 nM sensitivity (Hand et al., 2017).

(6) The Planetary Protection challenges of an Enceladus orbiter are easier to solve since the plume is out in space and there is no need to directly contact this clearly special ice surface region while making scientifically valuable measurements.

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