QUANTITATIVE CAPTURE OF ORGANICS FROM ICE IMPACTS FOR CHEMICAL BIOSIGNATURE ANALYSIS OF ENCELADUS PLUME ICE. A. L. Butterworth[1], J. S. New[1,2,3], B. Kazemi[2], V. Spathis[3], M. Golozar[2] and R. A. Mathies[2], [1]Space Sciences Laboratory and [2]Chemistry Department, University of California, Berkeley, CA 94720, [3]University of Kent, Canterbury, Kent, CT2 7NH

Introduction: Enceladus ice and vapor plumes, discovered venting directly from its sub-surface ocean, provide direct access to interrogate the icy moon's chemical evolution, habitability and potential biochemical signatures. *Cassini* completed 23 flybys of Enceladus through the plumes with a closest approach altitude of ~50 km. This tantalizing look found salts, organic molecules, evidence of a rocky core in contact with a global ocean and a dynamic chemical system. Making a return to Enceladus with next generation sensitive, high–resolution instrumentation is an exciting prospect for ocean world and astrobiology exploration [1]. Collecting a plume sample would enable a wider range of more powerful *in situ* measurements and set the stage for sample return science [2].

A critical step in designing a mission for trace organic biosignature detection is developing and deploying a capture system that efficiently gathers intact organic molecules while transecting the plume [3]. We present here results of a novel series of ice shot experiments that quantify capture of intact organic molecules from <10 µm diameter ice projectiles impacting metal foils in the 0.8 to 3.0 km/s velocity range [4]. The capture efficiency of several soft metal capture surfaces is explored; soft metals allow efficient extraction of the collected sample while minimizing trace organic contamination. The capture efficiency of a doped fluorescent organic tracer molecule is quantified using epifluorescence microscopy of the craters in the metal foil targets. We then model the total sample that may be captured during a mission and relate this to an achievable amino acid detection sensitivity [5].

Ice Particle Impact Experiments: The "cold" Light Gas Gun (LGG) at the University of Kent, UK [6] was used to fire organic doped ice projectiles with high precision velocity into vertical metal foil targets [7]. We developed methods to perform particle–crater size calibration of ice projectiles for the different metal target materials and controlled background contamination. Pacific Blue (PB) fluorescent dye ($C_{10}H_4F_2O_7$, Thermo Fisher Scientific) was added as an organic tracer (100 µM) in a pH 9.5 buffered solution, frozen into 90 µL cylinders. The ice sabots were fired in the cold LGG, releasing the rapidly accelerating ice projectile through a frozen (−100 °C) and evacuated (50 mbar) launch tube. The sudden acceleration causes the ice to fragment creating a plume of small (micrometers to millimeters in diameter) ice particles, which impacted vertically mounted metal targets. Ice shot experiments were carried out at 0.8, 1.2, 1.7, 2.2, 2.7, and 3.0 km/s velocities (±0.05 km/s) impacting Au, Al, In foil targets (Goodfellow).

Organic Capture Measured by Epifluorescence: A calibrated epifluorescence microscope method was developed to quantify the amount of unmodified fluorescent PB dye detected on a capture surface target on a crater-by-crater basis [8]. PB fluoresces only when hydrated, providing an elegant separation method of shot residue from background gun contamination. The foils were mounted in a humidifying chamber and UV images taken dry (under dry N_2) to subtract background and at 70% humidity to highlight the captured PB. The fluorescence intensity and area were calibrated to the number of intact PB molecules detected. A bright field image was also taken at each field of view to identify and measure the crater dimensions, which were calibrated to impactor sizes. Using the ice particle size, the expected PB impacting each crater could be determined. Organic capture was calculated as the ratio between the number of PB molecules captured on the foil and the number of PB molecules in an impacting particle.

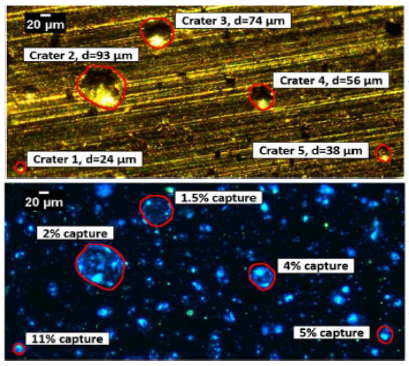

Figure 1: Comparison of bright light and epifluorescence images of organic residue captured in micron-sized ice impact craters in Al at 1.7 km/s [5]

Results: New et al. [4] presented 1,200 individual crater analyses of ice impacts into Au, Al and In foils. The results of impacts of ice particles <10 µm diameter, encompassing likely Enceladus plume ice particle dimensions [9], are summarized in Figure 2. The median capture efficiency of PB organic molecules is shown as a function of impact velocity. Aluminum was the best target at intermediate speed (17 ±4% captured at 2.2 km/s) and indium was the best

target at lower speed (efficiency was 17 ±4 % at 0.8 km/s). Gold did not perform well capturing organics from ice impacts at any speed tested. This result contrasted with earlier ice analog experiments [10] demonstrating the critical need for actual ice particle impact studies. We note that the reported capture efficiencies are lower estimates because (1) targets were mounted vertically so that weakly bound impactors might drop off due to gravity, and (2) particle size calibration assumed a sphere, overestimating the number of impacting PB molecules.

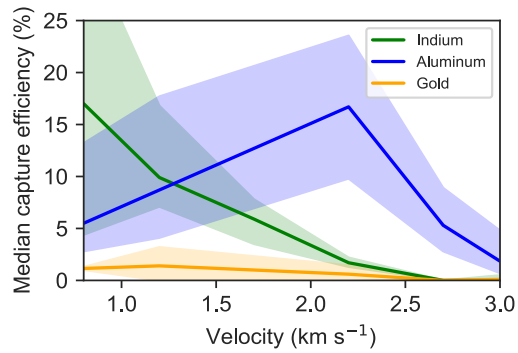

Figure 2: Median capture efficiency vs. impact velocity for small (dia. ≤ 10 µm) ice particles representative of the Enceladus plume. Al (blue), In (green) and Au (gold) capture surfaces are shown with 95% confidence bands. From New et al. [4].

Evaluating Plume Sample Analysis: We can use our capture efficiency results together with the Enceladus plume particle size and density data from *Cassini* at 50 km altitude [11] to quantitatively estimate the amount of ice that can be gathered in a variety of possible flight scenarios. The blue shaded region in Figure 3 indicates the range of ice particle volume (3.4 nL to 0.34 µL) that can be gathered in one pass using collectors from 100 cm^2 to 1 m^2 in area. In each case the total amount of ice gathered can be increased by repetitively passing through the plume with the collector open with a likely practical limit of 10-100 passes.

The ability of an analytical instrument to detect biosignatures from the gathered ice depends on the instrument sensitivity and the volume that the sample is dissolved in. Post capture, by using microfluidics the sample can be dissolved in as little as 10 µL volume for transport and manipulation. The modeling in Figure 3 is based on the amino acid sensitivity that can be achieved with the EOA [3] instrument, featuring Capillary Electrophoresis–Laser Induced Fluorescence detection (CE-LIF). This instrument has a current limit of detection of ~60 pM (S/N=3) [12]. Figure 3 shows the detection space for trace analytes (amino acids) where the vertical axis is the biomarker concentration in the ice sample and the horizontal dashed line is the desired biomarker measurement capability of 1 nM. For example, with a 1 m^2 capture area, it would take 29 accumulating passes to reach the desired biomarker sensitivity with a 1 nM limit of detection; only a single pass is needed with the current 60 pM EOA CE-LIF sensitivity. We conclude that there are a variety of mission profiles that can achieve very powerful *in situ* science measurements at Enceladus.

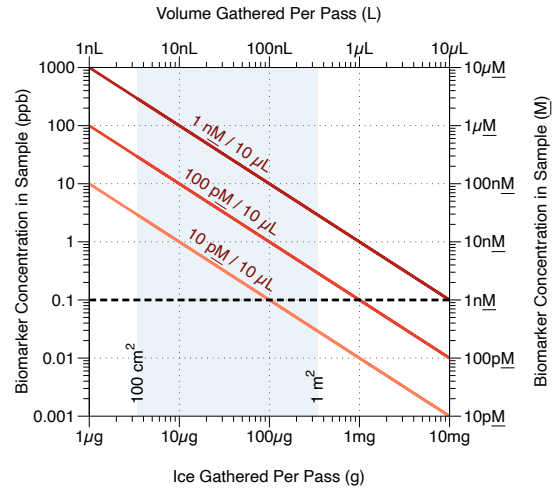

Figure 3: Detection space for the analysis of organic biomarkers in ice samples nondestructively gathered from the Enceladus icy plume. The blue shaded region indicates the range of ice volume that can be gathered in a single pass with capture system areas ranging from 100 cm^2 to 1 m^2. The diagonal lines provide the reference relating gathered ice volume to the biomarker detection limits with a processed volume of 10 µL and detection sensitivity ranging from 1 nM to 10 pM which is feasible with the EOA system.

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