Measurement of Organic Molecules and D-H Ratios in Laboratory Mass-Spectra of Hypervelocity Dust Impacts into Ice. Zach Ulibarri[1](zachary.ulibarri@colorado.edu), Tobin Munsat[1], Bernd Abel[2], Richard Dee[1], David James[1], Sascha Kempf [1], Zoltan Kupihar[3], Zoltan Sternovsky[1], [1]IMPACT, University of Colorado, Boulder, Colorado, United States, [2]Leibniz Institute of Surface Engineering, Leipzig, Germany, [3]University of Colorado, Dept. of Chemistry and Bio-chemistry, Boulder, Colorado, United States.

Introduction: Water ice is prevalent in the solar system, and there have been numerous studies of the effects of radiation and charged particle bombardment of water ice in laboratory settings [1-6]. However, many questions yet remain concerning the effect of interplanetary dust particle (IDP) bombardment on icy surfaces and bodies, as IDP impacts into ice have not been heavily investigated. This is despite the fact that IDP impacts are expected to be at least as important as radiation and charged particle bombardment [7].

Since liquid water is regarded as a prerequisite for life, icy ocean worlds such as Europa and Enceladus are the focus of several planned NASA and ESA fly-by missions [8-9]. Water plumes erupting from Enceladus's surface have been observed [10], and analysis of the plume using impact ionization time of flight (TOF) mass spectrometry from the Cosmic Dust Analyzer (CDA) on the Cassini spacecraft strongly indicate that the plume originated from the subsurface ocean [11]. There have also been observations of what appear to be similar water plumes on Europa [12-14]. These observations indicate that the environment around these bodies is rich with dust from both the ice surface and the subsurface oceans, and that fly-by spacecraft with TOF spectrometers will be able to study surface and subsurface chemistry in situ without landing.

Isotopic ratios have been used as metrics for solar system formation and evolution models, and the deuterium-hydrogen (D-H) ratio is of particular importance in studying the formation of planetary bodies. Temperature-dependent chemical processes result in deuterium-enrichment of water ice relative to hydrogen at low-temperatures [15]. Such enrichment processes enable measurements of D-H ratios in outer solar system bodies to be used to constrain the time and location that planetary bodies formed in the solar system as well as other geophysical phenomena [16-18].

While laboratory work has been performed to match CDA flight spectra, these studies have used laser ablation of flowing liquid sources rather than actual dust impact into actual ice surfaces [19]. However, the University of Colorado dust accelerator at the Institute for Modeling Plasma, Atmospheres, and Cosmic Dust (IMPACT, *impact.colorado.edu*), paired with a cryogenic target capable of creating H_2O ice mixtures, allows for unique and tightly controlled experiments to study hypervelocity dust impact into ice. Such experiments will answer significant questions about the long term chemical evolution of icy bodies under dust bombardment as well as the survivability and detectability of certain types of chemistry in icy dust grains, be they isotopic ratios or complex organics, studied by impact ionization TOF instruments on flyby spacecraft.

Experimental Setup: The IMPACT dust accelerator at the University of Colorado uses a 3 MV linear electrostatic potential to launch micron-sized dust particles at velocities up to 100km/s [20]. The accelerator features non-destructive inline beam detectors that record particle mass, velocity, charge, and radius. Active particle down-selection is provided by an FPGA-controlled particle selection unit. This unit prevents impact of particles outside of a user-defined mass, velocity, radius, or radius parameter space. Selected particles are impacted onto the ice target, shown in Fig. 1.

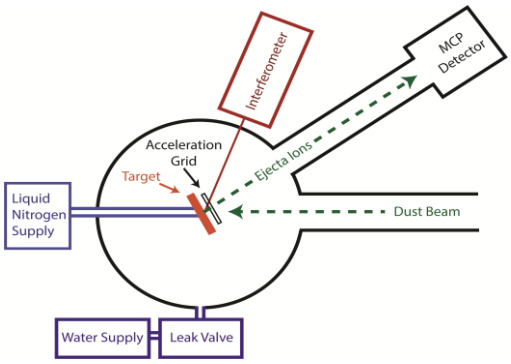

Figure 1. Diagram of the cryogenic ice target. Dust particles are impacted onto the ice surface and the ejecta plume is measured using impact ionization TOF mass spectrometry.

The target is held at high potential (up to 5 kV) and a grounded plane provides an accelerating potential for ions within the dust impact ejecta plume. These ions are accelerated towards a TOF mass spectrometer to analyze the chemical composition of the impact plume.

Simple ices, such as pure water or mixtures of water and CO_2 are vapor deposited onto a gold-coated sapphire substrate which is actively cooled by flowing liquid nitrogen. The reflective gold surface allows the use of Fabry-Perot interferometry to measure the thickness of the ice as it is grown. The conductivity of the surface also maintains the accelerating potential. A

heating system based on [21] allows ice to be grown at temperature between 80 and 200 K.

More complicated ice mixtures, such as water ice doped with amino acids or other types of complex organic chemistry, are created either by flash-freezing aqueous solutions of desired composition or by spraying droplets tens of microns in radius in a nitrogen environment. These prepared ices are then isolated from ambient pressure and installed into the ice target, which is then pumped to vacuum. This allows for homogeneous ices of known compositions to be studied in the ice target without atmospheric contamination.

Initial Results: In experiments assessing the survivability and detectability of complex organic chemistry in impact ionization TOF mass spectra, water ice was doped with various amino acids and bombarded with dust. Chemical analysis of the impact plume shows that amino acids and even the more fragile dipeptide dual amino acid chain lysine-glycine survive the impact process and can be measured directly. Furthermore, spectra from impacts into water ice doped with the amino acid histidine show that fragmentation products are related to but not identical to those found in the NIST electron impact ionization mass spectra of histidine [22]. This indicates that even in the event of breakup, it may be possible to use the breakup products as a means to identify the parent molecule. Fig. 2 shows such a spectrum, produced by a 3.2 km/s iron dust impact, with the parent histidine molecule highlighted in green and the breakup products highlighted in red.

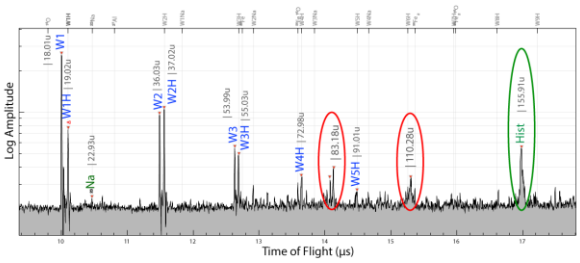

Figure 2. Spectrum produced by a 3.2 km/s iron dust impactor into water ice doped with histidine. In addition to direct detection of the parent molecule (highlighted in green), breakup products related to the NIST electron impact ionization breakup products [21] are observed (highlighted in red).

Previous generations of impact ionization TOFs have operated only in the positive ion mode. However, in this regime, the 2 AMU deuterium aliases to molecular hydrogen, H_2, and thus a direct measurement of the ratio of these two species cannot be made. However, modern impact ionization instruments are capable of both positive and negative ion measurements, and the H_2 anion does not exist.

Figure 3 shows the summed negative ion-spectra from water ice containing an 80.6% D2O:H2O mixture. By integrating the ion content of the D and H lines, a measurement of 82.0% was made, indicating that impact ionization TOFs operating in the negative ion mode can successfully measure the D-H ratio of icy dust grains, and thus the D-H ratio of their parent bodies.

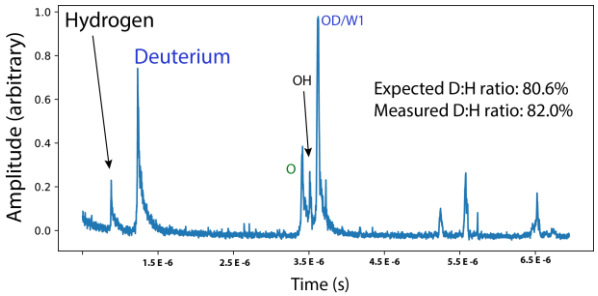

Figure 3. Summed negative ion spectra of dust impacts into an 80.6% D2O:H2O water ice. The D:H ratio was measured as 82.0%

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