

On the Genesis and Detectability of Organic Chemistry in Hypervelocity Impact Ice Spectra. Zach Ulibarri¹ (zachary.ulibarri@colorado.edu), Tobin Munsat¹, Bernd Abel², Richard Dee¹, David James¹, Sascha Kempf¹, Zoltan Kupihar³, Zoltan Sternovsky¹, ¹IMPACT, University of Colorado, Boulder, Colorado, United States, ²Leibniz Institute of Surface Engineering, Leipzig, Germany, ³University of Colorado, Dept. of Chemistry and Biochemistry, 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 effects 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.

While laboratory work has been performed to match CDA flight spectra, these studies have laser ablated flowing liquid sources rather than impacting actual dust into ice surfaces [15]. 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 H₂O ice mixtures, allows for unique and tightly controlled experiments to study hypervelocity dust impacts 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 complex organic chemistry in icy dust grains 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 100 km/s [16]. The accelerator features non-destructive inline beam detectors that record particle velocity and charge, from which mass and effective radius can be derived. 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, or radius parameter space. Selected particles are impacted onto the ice target, shown schematically in Fig. 1.

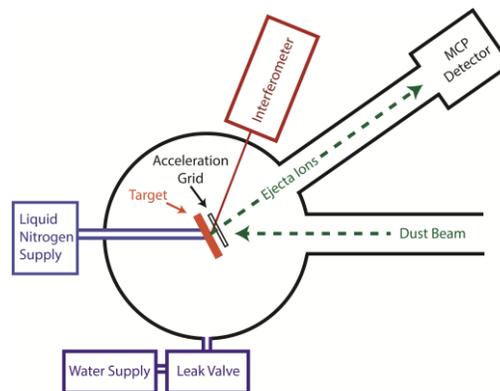


Figure 1. Diagram of the cryogenic ice target. Dust particles are impacted onto the ice surface and the ejecta plume is measured using impact ionization TOF mass spectrometry.

The target is held at high potential (up to 5 kV) and a grounded planar grid 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 CO₂ 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 a uniform accelerating potential. A heating system based on [17] allows ice to be grown at temperatures between 80 and 200 K.

More complicated ice mixtures, such as water ice doped with salts, 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 air and installed into the ice target, which is then pumped to vacuum. This allows for ho-

mogeneous 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 [18]. 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.

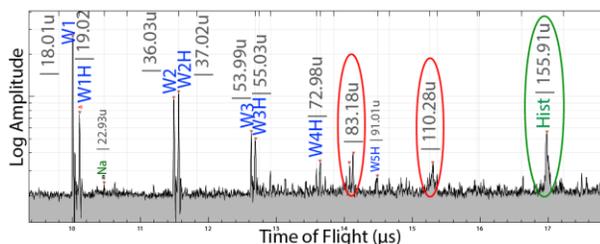


Figure 2. Spectrum produced by a 3.2 km/s iron dust impactor into water ice doped with histidine. In addition to direct detection of the parent molecule (highlighted in green), breakup products related to the NIST electron impact ionization breakup products [18] are observed (highlighted in red).

In experimental investigations into the long term chemical evolution of icy bodies under dust bombardment, gaseous CO₂ was doped into water ice and bombarded by iron dust. CO₂ was detected at velocities >3 km/s, and at high velocity (>15km/s), CO was produced and a strong line at mass 32 AMU was occasionally observed. An example spectrum is shown in Fig. 3. While mass 32 could merely represent O₂ molecules, O₂ would be expected to charge negative and thus would not be measured in this positive ion spectrum. More importantly, such strong lines at mass 32 are not observed in high velocity dust impacts into pure H₂O ice, and thus far they have only been detected in spectra produced by impacts into these CO₂ and H₂O ice mixtures.

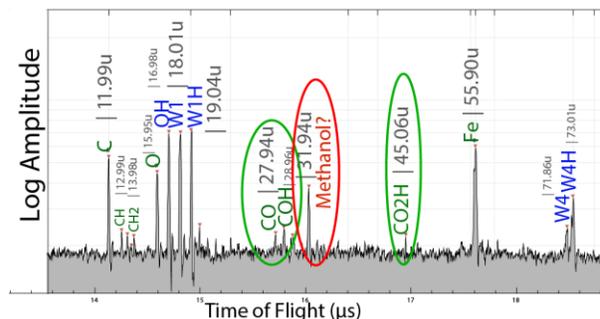


Figure 3. Spectrum produced by a 17 km/s iron dust impact into H₂O ice doped with CO₂. The strong line at mass 32 has only been observed in this dataset, which suggests that it is not created by O₂ molecules.

It is therefore possible that the lines at mass 32 are methanol, CH₃OH. If this is the case, then these results may indicate that simple inorganic carbon chemicals is being converted by dust impact into organic chemical products. Ongoing experiments are using isotopic carbon-13 CO₂ in an otherwise similar experiment to break the ambiguity between O₂ and CH₃OH. If the line at mass 32 is in fact methanol, the carbon-13 will shift the line to 33 AMU. Such a result would be an important first step in understanding chemical processing of icy moons and ice surfaces throughout the solar system as a result of dust bombardment.

Future experiments will further probe the creation of organic chemistry from inorganic sources. Other experiments will determine if relative concentrations of amino acids can be inferred from impact ionization TOF spectra.

References: [1] J. F. Cooper et al. (2001) *Icarus*, 149(1), 133-159. [2] T. Cassidy et al. (2010) *Space Science Reviews*, 153(1-4), 299-315. [3] M. J. Loeffler et al. (2010) *J. of Chem. Phys.*, 132(5). [4] R. A. Baragiola et al. (2010) *Planetary and Space Science*, 51(14-15), 953-961. [5] M. J. Loeffler et al. (2006) *Icarus*, 180(1), 265-273. [6] R. A. Baragiola et al. (2008) *Nuc. Instr. and Methods in Phys. Research*, 266(12-13), 3057-3062. [7] D. Nna-Mvondo et al. (2007) *Icarus*, 194(2), 822-835. [8] C. B. Phillips et al. (2014) *EOS, Transactions from AGU*, 95(20), 165-167. [9] J. Lunine et al. (2015) *Geophys. Research Abstracts*, 17. [10] C. J. Hansen et al. (2006) *Science*, 311(5766), 1422-1425. [11] F. Postberg et al. (2009) *Nature*, 474, 620-622. [12] L. Roth et al. (2014) *Science*, 343, 171-174. [13] W. B. Sparks et al. (2016) *The Astrophysical J.*, 829, 121. [14] X. Jia (2018) *Nature Astronomy*, 2, 459-464. [15] F. Postberg (2009) *Nature*, 459(7250), 1098. [16] A. Shu et al. (2016) *RSI*, 83(7), 075108. [17] J. T. Cosier (1986) *J. App. Crystallography*, 19(2), 105-107. [18] NIST (2018) *NIST Chem. Webbook*.