PROCESSING AND SYNTHESIS OF PRE-BIOTIC CHEMICALS IN HYPERVELOCITY IMPACTS.

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Introduction: Hypervelocity impacts (HVIs) may have played a significant role in establishing the initial organic inventory for pre-biotic chemistry on the Earth and other planetary bodies. In addition to the delivery of organic compounds intact to planetary surfaces, generally at velocities below ~20 km s^{-1}, HVIs also enable synthesis of new molecules. The cooling post-impact plasma plumes of HVIs in the interstellar medium (ISM), the protosolar nebula (PSN), and the early solar system comprise pervasive conditions for organic synthesis. Such plasma synthesis (PS) can operate over many length scales (from nm-scale dust to planets) and energy scales (from molecular rearrangement to atomization and recondensation). HVI experiments with the flexibility to probe the highest velocities and distinguish synthetic routes are a high priority to understand the relevance of PS to exobiology. We describe here recent studies of PS at small spatial scales and extremely high velocities with pulsed laser ablation (PLA). PLA can simulate the extreme plasma conditions generated in impacts of dust particles at speeds of up to 100 km s^{-1} or more. When applied to carbonaceous solids, new and pre-biotically relevant molecular species are formed with high efficiency [1,2].

Background: The relevance of HVIs to molecular evolution, whether from dust-dust impacts in dense clouds or from truly catastrophic impacts during heavy bombardment (HB), is of great interest. HVIs are high in energy density, transient, and complementary to ultraviolet (UV), cosmic ray, and other processing. Such interest in HVIs has encouraged their experimental study, such as for the survivability of organics in large impacts [3,4] or for the post-KT impact poisoning of the atmosphere [5]. However, measuring the chemical effects of HVIs is challenging, especially at cometary and dust particle velocities well above 20 km s^{-1} where impact guns cannot easily reach.

Pulsed laser ablation (LA) is a promising experimental tool to study the plasma processes in HVIs [6-9]. The correspondence of high-irradiance PLA ($\varepsilon > 1$ GW cm^{-2}) with HVIs up to ~10^2 km s^{-1} has recently been confirmed [10,11]. Irradiances up to $\varepsilon \sim 10^{13}$ W cm^{-2} are readily achieved by focusing a 10-100 millijoule-class Nd:YAG laser to a diameter d ~ 10-10^3 μm. However, one must take care when interpreting the laser irradiance $\varepsilon = \Delta E/At$, with pulse energy ΔE, spot area A, and duration t, in terms of the kinematic impact irradiance $\varepsilon_{HVI} = KE/\pi r^2 t \sim \pi r^2 h \rho v^2/(2\pi r^2 t) \sim \rho v^3/2$ associated with a cylindrical body of height h, radius r, density ρ, and velocity v. A laser pulse couples quite differently to the target than does a solid impactor: its energy is absorbed much more efficiently and over a shallower region. Furthermore, much of the laser pulse is absorbed above the surface in the expanding plume, rapidly energizing volatilized atoms. As such, cratering, solid shock, and ejecta patterns are qualitatively different between the laser and impact cases. However, the vapor plume itself, during expansion, cooling, and recombination, may be simulated with a pulsed laser at irradiances two to four orders of magnitude lower than the "equivalent" micrometeorite impact irradiance.

Experiment: Our experimental setup, described previously [2], is based on a laser time-of-flight mass spectrometer (TOF-MS) technique originally developed for *in situ* space probes [12]. Runs were conducted in the Hypervelocity Impact Simulation Microprobe (HISM) facility recently developed at JHU/APL and on similar apparatus at IKI. HISM utilizes field-free extraction and a band-pass reflectron to analyze the undisturbed prompt ions formed in the PLA plasma. We distinguish these compounds from those desorbed from the target intact by examining mass spectra over a range of initial kinetic energy (IKE) pass bands. In HISM, a postionization system also permits analysis of the neutral plume. Several laser sources and target-detector geometries are available.

Laser Analyses: We have begun to perform a comprehensive first analysis of PS as a function of impact conditions and target composition. In preliminary studies [1], high purity, non-graphitized (semi-amorphous) electrode carbon has served as a starting material for test targets. It contains volumetric hydrogen as verified by a surface stripping method. Spectra included singly-ionized methane, acetylene, ethylene, etc., as well as other C_NH_M oligomers with N = 1 to 40 and M = 1 to 4. Additional analyses revealed even higher N hydrocarbons. A few points support the PS route for these molecular ions (cf. [13,14]):

1. The dense plasma produced from carbonaceous targets at these irradiances atomizes its constituents with very high efficiency [15].
2. The experiment essentially excludes the detection of ions produced outside the plasma. Without an

extraction field, any ions formed from desorbed species do not generally attain sufficient kinetic energies to be seen in the analytical window.

3. Purely elemental mass spectra are seen at higher IKEs (essentially elemental C in the pure carbon electrode case). Pure metal and other non-C-bearing targets did not produce significant molecular species, in contrast to gas-mediated cluster formation.
4. Multiply-charged hydrocarbons (e.g., CH_4^{4+}) were observed at $\varepsilon > 5$ GW cm^{-2} with singly-charged ions and increased in number as ε increased.

Some of the most intriguing data obtained so far in the current research effort have been from physical mixtures of C-rich matrices with dilute inorganic substances such as NH_4NO_3. With proper controls, any compounds with species from *both* sources can be primarily assumed to have formed in the gas phase. An example HISM spectrum from such a mixture is shown in **Figure 1**. Molecular mass peaks were observed to at least mass-to-charge (m/z) 180 Da. As with most simulations using carbonaceous targets, the C_NH_M "carbon comb" dominates the spectrum. However, numerous additional hetero-species, not present in pure-C target spectra, are seen. We can rule out elemental assignments for most of these because their abundance pattern is far removed from that of the atomic isotopes. Monoisotopic elements (e.g., ^{27}Al) cannot be ruled out in this way, but can certainly be limited to trace interferences on other grounds. Peaks at m/z 26, 27, 30, 41, 44, and 46 were also highly reproducible over many laser pulses. The presence of N^+ and N^{2+} in spectra suggests that N participates in PS as well, although for any single instance we cannot unambiguously identify CN bonding due to the isobaric interference between ^{14}N and $^{12}CH_2$. Peaks at m/z 26 and 27 are likely CN and HCN, not C_2H_2 and C_2H_3, by comparison with pure C spectra and separate experiments using spiked $^{15}NH_4{}^{15}NO_3$. Moreover, we hypothesize that the marked masses m/z 75, 115, and 126 are cationized amino acids. We are currently undergoing a systematic dilution series run with both standard and isotopically-spiked adducts to observe the variation of key peaks in this experiment as a function of concentration. Due to the limited mass resolving power of HISM (several hundred), this approach is likely to be more productive than an attempt to discriminate C-N and non-C-N organics directly from their isotope patterns ($^{13}C/^{12}C \sim 1.1 \cdot 10^{-2}$ while $^{15}N/^{14}N \sim 3.7 \cdot 10^{-3}$). However, the ultimate determination of PS-formed amino acids, if it occurs, should come from an unambiguous isomeric separation such as offered by gas chromatography (GC). GCMS-based analyses are planned.

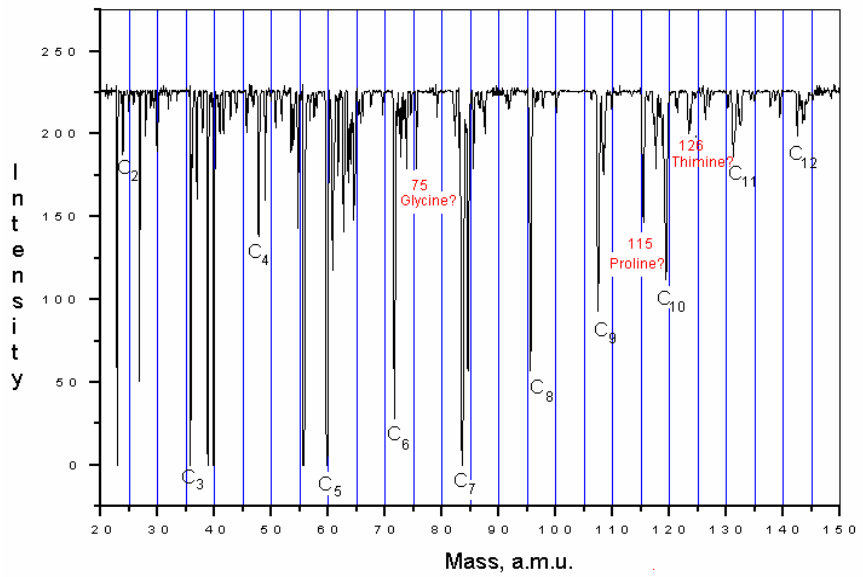

Fig. 1 Example HISM spectrum from simulated impact involving high-purity carbon and NH_4NO_3 target materials in a physical mixture. $\varepsilon > 1.5$ GW cm^{-2}

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