

PRESERVATION AND PRODUCTION OF SUGAR MOLECULES DURING COMET

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Introduction: The debate over whether or not impacts of extraterrestrial bodies with an early Earth can affect biologically relevant molecules has been ongoing since the arrival of the Murchison meteorite in 1969 [e.g. 1, 2]. In an early study, Chyba et al. [3] calculated that organic molecules were being delivered at a rate of 10^6 to 10^7 kg/year approximately 10^9 years ago. Impact experiments conducted on many of these biologically relevant molecules show that impact pressures do not totally destroy them. For example, amino acids subjected to pressures of 5 to 20 GPa [e.g., 4, 5, 6] demonstrated that not only will a portion of the molecules remain intact, but that they also undergo a series of polymerization and racemization reactions.

Since 2012, over 200 molecules [e.g., 8, 9] have been detected in multiple extra-terrestrial environments, most likely having formed in those environments and then incorporated into interstellar ice and grain mantles [e.g., 10, 11] and comets [e.g., 12]. Comet spectra [e.g., 13, 14, 15, 16] and samples [e.g., 7, 17] show evidence for complex compounds. In particular, glycolaldehyde (HOCH₂C(O)H) and ethylene glycol ((OH)CH₂CH₂(OH)) have been detected in the comae of Oort Cloud comets [e.g., 14-16] and in situ on the nucleus of a Jupiter-Family Comet [18].

Here we report on impact experiments using glycolaldehyde (GLA), a simple two-carbon sugar, that simulate asteroid or comet impacts with pressures from 4.5 GPa to 25 GPa, corresponding to incoming impact velocities of 2.4–5.8 km/s for typical silicate-silicate impacts on Earth [6]. Even if comets were just a small fraction of the impactors in the early Solar System, it is likely that they delivered a substantial amount of sugar compounds to habitable planets or moon, providing a starting material for the formose reaction that leads to ribose, the backbone of RNA.

Experiments: Impact experiments have been conducted at NASA Johnson Space Center's Experimental Impact Laboratory, using the Flat-

plate Accelerator [e.g., 19-21], building on previous work to understand how GLA is affected by impact conditions [22, 23]. Experimental material consisted of a 20:1 mass ratio of a montmorillonite (bentonite) clay to GLA. This clay, a weathered ash collected from Bell Fourche, SD, is a phyllosilicate, known to be abundant on various Solar System objects, including Mars [e.g., 24] and Europa [e.g., 25]. Importantly, it has been shown to catalyze the formation of phosphodiester bond linkages between activated nucleotides [26].

In all experiments, ~100 mg of the dry GLA + clay were packed into stainless steel sample wells as tightly as possible to minimize porosity that could affect localized reverberations and associated stress concentrations [4, 21]. The target chamber was evacuated to below 200 mTorr and the target was then impacted by either a Lexan projectile with no flyer plate, an aluminum (Al 2024) flyer plate, or a stainless steel (SS 304) flyer plate, depending on the desired shock stress. Given the composition of the projectiles and the flyer plates, with velocities averaging ~1.1 km/s, the samples experienced shock pressures of 4.6 GPa, 12.2 GPa and 25.1 GPa.

Analyses: Shocked samples (~25 mg) were placed in a small scintillation vial, and the organic materials were extracted from the clay by addition of 1 mL of tetrahydrofuran. The mixture was sonicated to completely dissolve the organic materials, and the solution containing the dissolved organics was decanted off and treated with 100 μ L of nitrogen-purged BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide; Fisher Scientific) to form the trimethylsilyl ethers prior to analysis by gas chromatography-mass spectrometry (GC/MS), as described in McCaffrey et al. [27].

Discussion: In all impact experiments, substantial amounts of GLA survived impact delivery and moderate amounts of threose, erythrose, glycolic acid, and ethylene glycol (EG) were produced (Table 1).

Recent detections of GLA and EG in comet comae [14-16] and *in situ* on a comet nucleus [17] provide evidence that these ribose precursors were likely to have been delivered during the bombardment era(s) in the early history of the Solar System. Based on impact experiments [e.g., 26], up to 97% of GLA could be delivered in tact to a habitable moon or planet. This means that, depending on the size of the comet and its initial inventory of GLA, up to billions of kilograms of GLA and millions of kilograms of EG (Table 1) could survive impact of a single comet.

Conclusion: The delivery, preservation, and/or formation of these simple and complex compounds is exciting in the context of the origin of life. As evidenced by experimental results, especially at low pressures, large amounts of GLA and impact-produced EG were available on habitable moons or planets. During the era of late heavy bombardment (~4.2 to ~3.7 billion years ago; 28) when life may have been developing on Earth, these biomolecules would have been readily available. Large amounts of GLA are particularly important, due to the suspected contributions of the formose reaction to the prebiotic production of sugars.

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Table 1. Estimated minimum masses of sugar molecules from four comets [14-17], assuming minimum nucleus radii, 30% H₂O in the comet, and an impact pressure of 4.6 GPa (e.g., low-inclination angle). NIC = Nearly Isotropic Comet, JFC = Jupiter Family Comet. **Values were determined assuming a 0.5% yield starting from GLA [27] and do not include EG already on the comet nucleus.

Comet Name (diameter, family)	Comet's GLA (kg)	GLA at Impact (kg)	Comet's EG (kg)	Impact- Produced EG** (kg)
Hale-Bopp (13.5 km, NIC)	2×10^{22}	2×10^{12}	6×10^{12}	9.4×10^9
Lenmon (1 km, NIC)	2.0×10^9	1.9×10^9	6.2×10^9	1.0×10^6
Love-Joy 2013 (1 km)	4.7×10^8	4.5×10^8	2.4×10^9	2.4×10^6
Love-Joy 2014 (0.25 km, NIC)	2.4×10^6	2.3×10^6	1.1×10^7	1.2×10^4
P/67 (2.15 km, JFC)	1×10^{14}	1×10^{14}	7×10^{13}	6.5×10^{13}