UV IRRADIATION OF CARBONACEOUS METEORITES MAY SYNTHESIZE SMALL ORGANIC ACIDS ON MARS

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Introduction: Organics are required for life as we know it and are ubiquitous to primitive abiotic exogenous materials, including carbonaceous chondrites [1,2]. Since biotic and abiotic synthesis mechanisms differ, organics bear molecular structures, distributions, and isotopic signatures that can indicate biological vs astrochemical/geological origin, making organics high-priority targets in astrobiological exploration of Mars [1]. Deconvolving the origin of Martian carbon is complex: multiple sources are expected, including exogenous delivery [2], abiotic *in situ* production [3], and potentially life [1]. Post-depositional alteration via ionizing cosmic radiation and UV can complicate the signal [4]. Photochemical reactions can destroy, transform, or synthesize organics; radiolysis rates vary by molecule, functional group, and mineral associations [5].

Meteoritic organics are well-understood on Earth [2], but their evolution on Mars has not been constrained: characterizing UV alteration of exogenous organics is key to deconvolving the abiotic background for Mars life detection, especially compared to cosmic radiation, which alters organics differently [4,5]. Toward this goal, we exposed powdered Aguas Zarcas (AZ) meteorite and SiO_2 blanks to Mars-like UV under analog conditions in the Planetary Atmospheres Chamber (PAC) [6] for ~100 sols equivalent. Post-irradiation, we extracted and measured carboxylic acid (CA) molecules and compound-specific C isotopes, then analyzed bulk C, N, and D/H isotopes in residues.

Methods: Powdered samples of AZ (Meteorite Marketplace) and combusted (550 °C/12 h) SiO_2 were divided into aliquots (~50 mg each, <1 mm thick). Triplicate sets of AZ and SiO_2 samples comprise lab controls (no treatment), PAC controls (remained in the PAC during experiment, shielded from UV), and PAC UV experimental (~100 sols UV, Mars-like conditions). PAC conditions: Mars-normal VC-VIS-NIR calibrated to Mars fluence rates for UVA, UVB, and UVC, at 6.9 mbar, at -10 °C, Mars atmospheric mixture (95.3% CO_2, 2.7% N_2, 1.7% Ar, 0.2% O_2, & 0.03% v/v H_2O) [6]. For CAs, samples were H_2O-extracted (100 °C for 24h), derivatized, and analyzed with GC-TQMS and GC-MS/IRMS [2]. For bulk isotopes, extracted residues were freeze-dried, homogenized, and measured with TC/EA-MS [7].

Results: We observe both synthesis and degradation of CAs for irradiated AZ samples, compared to controls; effects vary by molecule (Fig. 1). Synthesis of formic and acetic acid is observed for all PAC samples (greatest increase for UV sets), resulting in net increase of tot. CA abundance. Decreases (<5- ~25 nmol/g) of longer-chained meteoritic CAs is observed. Compound-specific $\delta^{13}C$ for formic and acetic acids vary with treatment. Bulk N, C, D/H display minimal change.

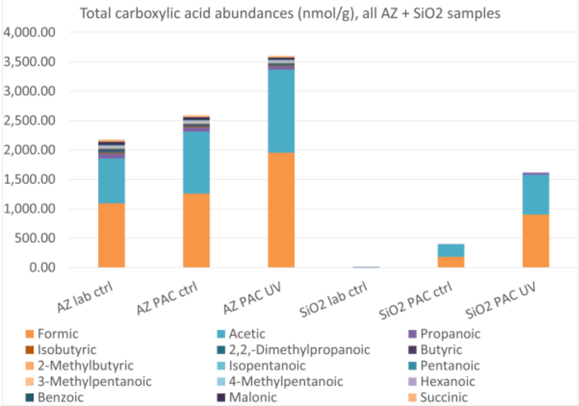

Figure 1. Total CA abundances (nmol/g) for all AZ and SiO_2 samples, subdivided by abundances (nmol/g) of individual CAs measured in each sample.

Discussion: Results indicate that Mars-like UV irradiation of carbonaceous chondrites is an abiotic organic synthesis mechanism that may be operating on Mars, producing C_1 and $C_{2:0}$. Meteoritic or atmospheric (e.g., CO_2) carbon are hypothesized precursors. Past experiments with proton irradiation of the Murchison meteorite and SiO_2 also report short-chain organic acids synthesized radiolytically, likely catalyzed by metal oxide minerals from indigenous C [4]. Our experiments highlight the importance of laboratory studies of natural samples to better constrain expectations for organics Mars [1]. Additionally, we hypothesize photochemical alteration of exogenous material producing short-chain organic acids may be an abiotic organic synthesis mechanism on Mars.

Acknowledgments: Funding provided via a 2023 NASA Ames Research Innovation Award, Florida Space Grant travel award, and 2021 Space Research Initiative (UF-led). D.F. acknowledges the support of the NASA-EW grants 80NSSC20K0344 and 80NSSC21K0654.

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