PHOTOCHEMICAL PRODUCTION OF SHORT-CHAIN CARBOXYLIC ACIDS FROM CARBONACEOUS CHONDRITIC PRECURSORS UNDER MARS-LIKE CONDITIONS.

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Introduction: In the search for life on Mars, deconvolving the origin of organic carbon (OC) crucial. A complex, mixed signal from multiple sources is expected, including exogenous infall [1], *in situ* abiotic synthesis [2], and potentially life [3]. Post-depositional processing, especially through radiation, can alter OC [4]. Meteoritic organics are well-understood [1], but their evolution in the Martian environment has not been constrained, where a thinner atmosphere allows a higher flux of solar photons to reach the surface, especially organics-damaging short-wavelength UVC (~190 nm+) [4,5]. UV can degrade, transform, and/or synthesize organics; effects vary by molecule/functional group and associations with photoprotective or catalytic minerals [4]. Constraining these processes is key to elucidating sources and sinks of carbon on Mars and predicting the abiotic background that must be deconvolved for life detection *in situ* and with future returned samples.

We conducted a ~154-sol exposure study experimentally irradiating crushed carbonaceous chondrites (CCs) and organically-clean SiO_2 blanks with Mars-like UV under relevant environmental conditions in the Planetary Atmospheres Chamber (PAC) [5]. Post-UV, changes to carboxylic acids (CAs), bulk and compound-specific ^{13}C, and insoluble organic macromolecules (IOM) were measured with spaceflight-like and lab techniques that include Deep UV (DUV) Raman & fluorescence spectroscopy with the Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) engineering model [6] and mass spectrometry.

Methods: An interior pre-rain fragment of the carbonaceous chondrite Aguas Zarcas (AZ) meteorite (Meteorite Marketplace) was powdered, homogenized, and divided into 50 mg aliquots (<0.5 mm thick) in individual borosilicate glass dishes covered with UV-transparent fused silica slips. Combusted (550 °C/12 h) SiO_2 was a witness and process blank. Sample sets include lab control (*no treatment*), PAC control (*in the PAC during experiment, shielded from UV but exposed to other conditions*), and UV experimental *(~154 sols UV + Mars conditions*). Mars conditions: UV-VIS-NIR with a 1000 W Xenon-arc lamp calibrated to Mars fluence rates for UVA/UVB/UVC, at 8.5 mbar, at -5 to -7 °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) [5]. For CAs, samples were H_2O-extracted at 100 °C for 24h, derivatized [1], and analyzed with GC-TQMS and GC-MS/IRMS (matched to the NIST database, quantified via standard calibration curves). For bulk isotopes and elemental abundances, H_2O-extracted residues were freeze-dried and homogenized, then measured with TC/EA-MS and quantified relative to standards [7]. For IOM, powders were pressed flat on wafers and analyzed with SHERLOC-like DUV Raman spectroscopy with a 248.6 nm NeCu laser (20 A, 38 µW avg, ~110 nm spot size, ambient temp/pressure) rastered across the surface in 3x3 maps at 400 or 800 laser pulses per point. Calibrations used ACN and a Hg lamp; data was normalized and cosmic rays were removed, and Raman spectra were analyzed with Igor Pro 8 software [6].

Results: *Carboxylic acids:* 15 indigenous CAs are detected in all AZ samples. After UV, abundances of short-chain formic (C_1) & acetic ($C_{2:0}$) acids increase by 179 ±7% (C_1) & 185 ±8% ($C_{2:0}$) compared to lab controls. Longer ($C_{3:0}$+) CAs are either unchanged or display slight decrease (<50% reduction) in abundance. This results in a net increase in total CAs of 179 ±9% for UV samples compared to lab controls (**Fig. 1**).

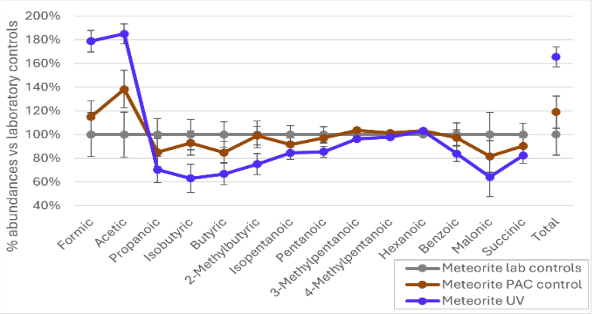

Figure 1. Relative change in abundance of 15 indigenous CAs in Aguas Zarcas after Mars-like UV. % change in abundance for each molecule for PAC control (Mars conditions, no UV) and UV (Mars conditions + UV) samples are normalized to amounts in lab controls. A net increase in total CA content is observed following UV, due to contributions from new C_1 & $C_{2:0}$, despite reduction in some longer ($C_{3:0}$+) compounds.

SiO_2 lab controls contain no CAs, while SiO_2 PAC control and UV experimental sets display an increase in C_1-$C_{2:0}$, similar to AZ. *Bulk C:* Elemental abundances for AZ are unchanged (1.6 wt.%) across sample sets, and SiO_2 increases from 0.12 wt.% (lab controls) to 0.23

wt.% (PAC controls) to 0.33 wt. % (UV). Bulk residue isotopes are unchanged, with AZ $\delta^{13}C$ values of -9‰ and SiO_2 of -28 to -29‰. *Compound-specific C isotopes:* $\delta^{13}C$ for C_1 & $C_{2:0}$ change across sample sets, with ^{13}C enrichment inversely correlated with molecule abundances: AZ lab control C_1 & $C_{2:0}$ $\delta^{13}C$ are +44‰ ±8‰ and +23‰ ±1‰, AZ PAC control are +28‰ ±5‰ and -5‰ ±3‰, AZ UV are +5‰ ±3‰ and -15‰ ±5‰. SiO_2 PAC control C_1 & $C_{2:0}$ $\delta^{13}C$ are -11‰ ±10‰ and -40‰ ±3‰, and SiO_2 UV are -18‰ ±6‰ and -35‰ ±3‰. *Raman:* D- & G-bands are detected in all AZ samples (**Fig. 2a**), with peak positions at 1431-1438 cm^{-1} and 1608-1609 cm^{-1}; peak positions and ratios of D:G peak areas, heights, and FWHM do not vary across the three sets. New peaks are observed in SiO_2 PAC control and UV samples (**Fig. 2b**), not present in lab controls, including the most prominent at 2930-2933 cm^{-1}, and minor peaks at 822-825 cm^{-1}, 1095-1099 cm^{-1}, 1457-1459 cm^{-1}, and 1627- 1641 cm^{-1}. Peak intensities are highest for UV samples compared to PAC controls.

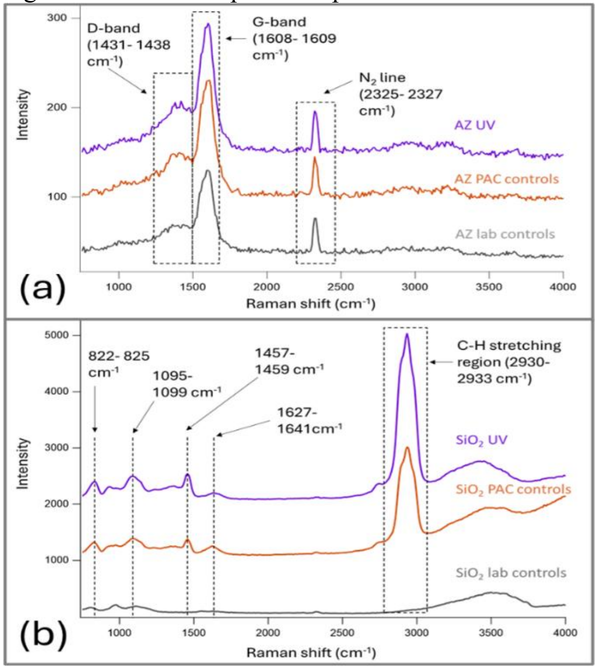

Figure 2. Raman spectra from lab control, PAC control & UV sets, offset applied (100 counts AZ, 1000 counts SiO_2). (a) AZ samples display D- & G-bands unchanged across treatment sets (plus atmos. N_2 & O_2 [under G-band] lines). (b) SiO_2 samples in UV & PAC control sets display C-H stretching & additional minor peaks.

Discussion: Our experimental results preliminarily indicate (1) UV irradiation of carbonaceous meteorites may be an abiotic synthesis mechanism producing short organic acids on Mars, (2) over 154-sol timescales, UV is unlikely to significantly destroy (<50% reduction) indigenous CAs in meteoritic mineral matrices, (3) IOM in powdered Aguas Zarcas-like CCs is unlikely to display reduction in wt. % C, changes to bulk $\delta^{13}C$ isotopes, or variance between disordered and graphitic carbon, after short-duration exposure to Mars-like UV.

Synthesis of short organic acids via photochemical conversion of meteoritic C to metastable byproducts (e.g., oxalate, acetate, mellitic acid) has been proposed on Mars [8]. Potential C sources and mechanisms in our experiments include Fenton-like reactions of meteoritic OC [8], photooxidation of IOM [5], photoreduction of meteoritic carbonates, or photoreduction of atmospheric CO_2 [9]. Our compound-specific ^{13}C analyses indicate C for new molecules is from a more depleted pool.

Previous laboratory exposure experiments have predicted rapid (hours) destruction of OC following exposure to UV on Mars, but most use organic standards [4]. UV irradiation of CCs demonstrated CH_4 is evolved from IOM, but remaining OC was not measured [5]. Molecule-mineral associations in natural samples can slow or prevent degradation through physical shielding and associations with photoprotective minerals [5,4], including Fe-oxides which are abundant in AZ [10]. Samples were <0.5 mm; photons can penetrate µm- mm [5]. Physical shielding at depth may enhance protection.

This data demonstrates that photochemical processing of exogenous material can be both a potential source and sink of OC on Mars. Results help set expectations for the UV-altered exogenous fraction of the abiotic background on Mars, which may include recalcitrant IOM and increased abundances of C_1 & $C_{2:0}$. Additionally, our combined spaceflight-like and benchtop analyses demonstrate that coupled application of *in situ* and laboratory benchtop analyses is critical for characterizing OC in planetary samples, highlighting the importance of returning Martian samples to Earth.

Future work includes targeted analyses of other soluble organics (*i.e.*, hydrocarbons, amino acids), IOM extraction + analysis, analysis of SHERLOC-like fluorescence spectroscopy, and repeated UV exposures.

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