Simulating prebiotic terrestrial waters to investigate influence of UV on organics at depth

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Terrestrial prebiotic ponds

For shallow ponds to be contenders for the venue of the emergence of life, they would have had to provide sufficient protection from ultraviolet (UV) radiation to allow for the preservation of organic molecules.

Shallow ponds of a variety of compositions are proposed for early Earth and Mars, many of which may have provided ample shielding effects by attenuating UV light via absorption by (in)organic ions (Ranjan et al. 2022).

In this work we present an experimental setup designed to simulate an irradiated water column, to investigate the preservation/degradation of organic molecules (Picture 1) and by proxy the attenuation of UV radiation in ponds of diverse compositions.

We report on a pilot study wherein glycine was exposed to ultrapure water, carbonate-rich and ferrocyanide pond simulants (Table 1) and irradiated for several days.

UV irradiation of glycine in ultrapure water, carbonate-rich and ferrocyanide pond simulants

Due the lack of ozone layer, the Hadean Earth was exposed to harsh UV irradiation. Could ionic 'sunscreen molecules' act as a shield against UV radiation by absorbing and consequently diminishing its impact?

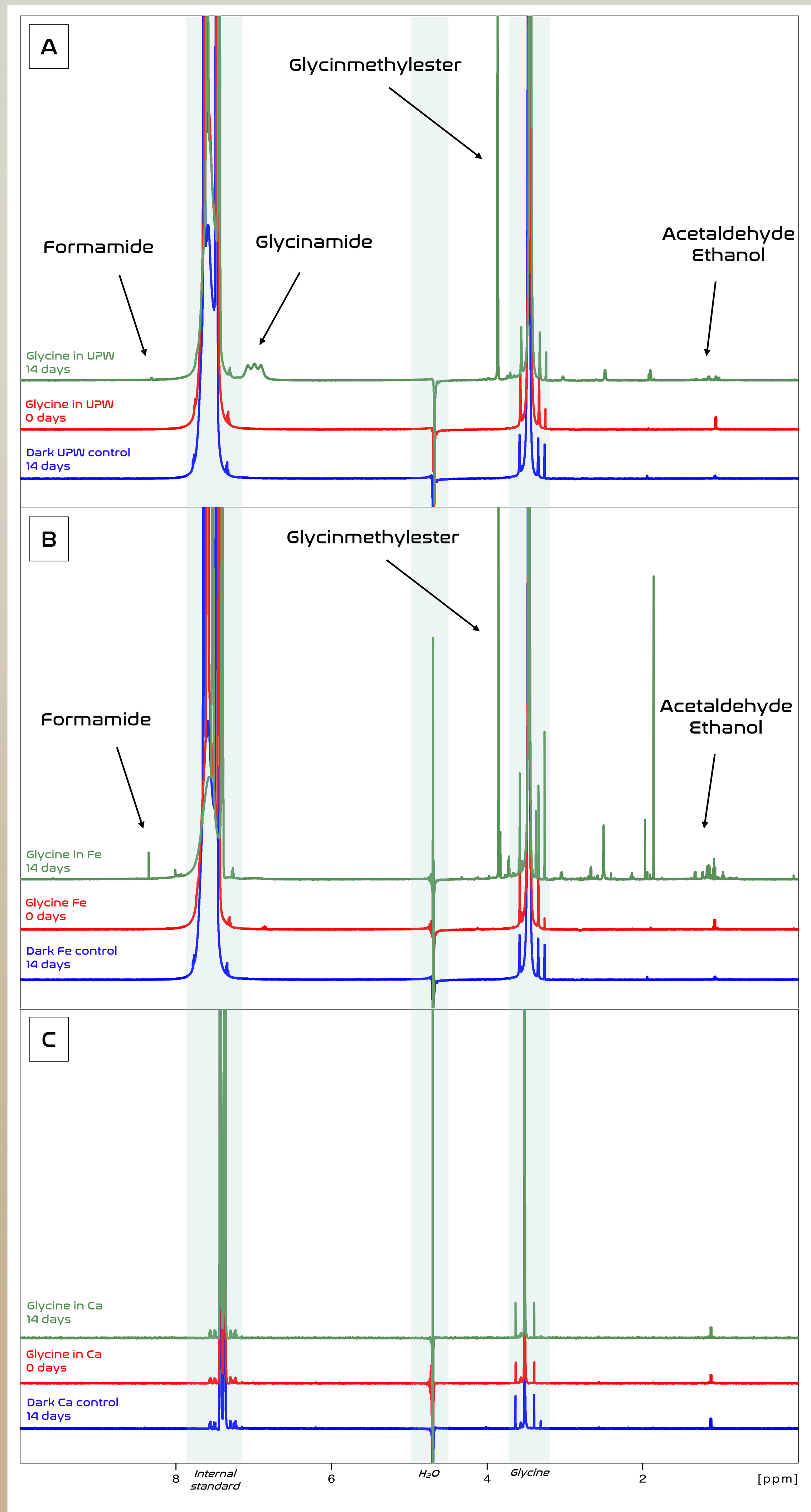

Table. 1: Chemical ionic compositions of the ferrocyanide and carbonate-rich pond simulants developed in this work.

Ferrocyanide Pond

Component	Concentration
$K_4Fe(CN)_6$	0.1 mM
NaBr	0.15 μM
KBr	0.15 mM
NaCl	0.2 mM
KI	600 nM
$NaNO_3$	10 μM
Na_2SO_3	100 μM
$NaHSO_3$	200 μM
Na_2SO_4	0.021 mM
$NaHCO_3$	1mM
Na_2CO_3	100 nM
$MgCl_2$	0.19 mM
$CaCO_3$	0.23 mM

Carbonate-rich Pond

Component	Concentration
NaCl	3 M
Na_2HPO_4	0.1 M
KBr	10 mM
Na_2SO_4	0.1 M
Na_2SO_3	0.4 mM
$NaHSO_3$	0.2 mM
$NaHCO_3$	0.1 M
Na_2CO_3	7 mM
$NaNO_3$	1 mM
KI	0.6 mM
H_3BO_3	1 M
$CaCO_3$	10 mM
$CaCl_2$	10 mM
Na_2SiO_3	22 mM
NaSH	0.08 nM

Figure 1: *1H NMR spectra of glycine solutions simulated prebiotic ponds before and after UV irradiation. Highlighted in light blue are the chemical shift of water at 4.70 ppm, the internal standard (KHP) shifts at 7.66 and 7.51 ppm, and the glycine shift at 3.5 ppm.*

(A) corresponds to glycine in ultrapure water (UPW) after 0 days and 6 days of irradiation. After 6 days, 5 regions of the spectrum show new shifts – potentially formamide (8.33 ppm), glycinamide (7.01 ppm), glycinmethylester (3.89 ppm), and acetaldehyde/ethanol (1.40-1.12 ppm).

(B) corresponds to glycine in ferrocyanide pond (Fe) after 0 days and 14 days of irradiation. After 14 days, 4 regions of the spectrum show new shifts – potentially formamide, glycinmethylester, and acetaldehyde/ethanol.

(C) corresponds to glycine in carbonate-rich pond (Ca) after 0 days and 14 days of irradiation. After 14 days of irradiation, no major UV-induced changes occur in the spectrum.

Exposure of simulated ponds to UV radiation

The UV irradiation experiments on glycine were conducted in the planetary chamber PALLAS (ten Kate & Reuver, 2016). The water column was exposed to UV irradiation up to 14 days. Samples were collected every 24 hours and analysed using Nuclear Magnetic Resonance (NMR) spectroscopy.

Picture 1: *The modular multi-compartment tower in the PALLAS chamber, positioned beneath the 450W Xenon arc lamp with range of λ=200-400 nm. The dark control capsule is shielded and not exposed to the UV beam (the right side of the image).*

Interpretations

- Ultrapure water
  - 5/5 identified degradation products
  - highest UV transparency
- Ferrocyanide pond
  - 4/5 identified degradation products
  - some shielding effect
  - catalytic reactions
- Carbonate-rich pond
  - no breakdown products
  - high salinity provides strong shielding
- Protective mechanisms at play with 'sunscreen ions'

References

Ranjan, S., Kufner, C. L., Lozano, G. G., Todd, Z. R., Haseki, A., & Sasselov, D. D. (2022). UV transmission in natural waters on prebiotic Earth. *Astrobiology, 22*(3), 242-262.

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