Harvard Origins of Life Initiative:

Building Blocks, Protocells & UV-driven Evolution

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HOLI Graduate Consortium astrobiology field trip to Iceland 2019
How do polynucleotide molecules, e.g. RNA, arise?

Sutherland Lab
Powner, Gerland & Sutherland (2009)
New Prebiotic Chemistry Paradigm

- **UV Light is central**

- **Cyano-sulfidic chemistry driven by hydrated electrons:**

\[
\begin{align*}
2 \times \text{Fe(II)} & \quad 2e^{-}_{\text{aq}} \\
\text{H}_2\text{O} & + \text{SO}_3^{2-} \\
\text{SO}_4^{2-} & + 2\text{H}^+ \\
\text{Fe(III)} & \quad \text{Fe(II)} \\
\text{H}_2\text{O} & + \cdot\text{SO}_3^{-} \\
\text{SO}_4^{2-} & + 2\text{H}^+ \\
\end{align*}
\]

Powner, Gerland & Sutherland (2009)
Ritson & Sutherland (2012)
Patel, Percivalle, Ritson & Sutherland (2015)
Xu, Ritson, Ranjan, Todd, Sasselov & Sutherland (2018)
New Prebiotic Chemistry Paradigm

- **UV Light** is central
  - Specific, mid-range UV light (aka UVC from 200 – 300 nm) 6 – 4 eV
  - Flux & Wavelength dependence

- Cyano-sulfidic chemistry driven by *hydrated electrons*:

\[
2 \times \text{Fe(II)} + 2e^{-} (\text{aq.}) + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2 \times \text{Fe(III)} + \text{H}_2\text{O} + \text{SO}_3^{2-}
\]

\[
\text{Fe(II)} \quad \text{h} \quad \text{Fe(III)} \quad \text{h} \quad e^{-}_\text{aq.}
\]

\[
\text{H}_2\text{O} + \text{SO}_3^{2-} \quad \text{h} \quad \text{H}_2\text{O} + \cdot\text{SO}_3^{-} \quad \text{SO}_4^{2-} + 2\text{H}^+
\]

HCN reductive homologation simple sugars, hydroxy acid & amino acid precursors

[Fe(CN)\text{6}]^{4-} & \text{SO}_3^{2-}
Know your UV light
UVC light reaches the surface of Early Earth, including through shallow water.
The **3 Roles** of Sun’s UVC Light

1. **UV-driven synthesis:** source of energy \( (e.g., e^{-}_{aq}) \)

2. **UV-driven selection:** source of high yields & function

3. **UV-induced self-repair:** for polymers \( (e.g., \text{RNA, DNA}) \), the transition from survival to biological function (?)
Protocells in the UV Light

Szostak Lab (2014): lipid vesicles retaining RNA strands (green)
The balance between UV damage & UV self-repair

Protocells in a population enable RNA strands to “explore” sequence space.

The protocells need to “live off the land”, until becoming self-sufficient.
The canonical RNA/DNA bases are the most UV photostable isomers of the synthesis.
The reason - Non-radiative deactivation: ultrafast internal conversion via a conical intersection

Beckstead et al. (2016)
Excited states of DNA strands decay to long-living damaging states! e.g., cause for skin cancer.

Bucher (2014)
Base-staking Enables Oligomer Damage

Bucher et al. (2014)
...but Base-*pairing* remedies that!
Certain sequences self-repair better & survive longer

Kufner et al. (2020)
UV sculpts the molecular inventory?

1) By selecting only UV-stable ones
   - We can screen ~200 isomers & by-products of the cyanosulfidic prebiotic chemistry

2) By selecting oligomers with UV-induced self-repair properties
SUMMARY

1. Stellar UV light is commonly cut off at 204 nm on the surfaces of rocky planets (mainly by CO$_2$).

2. Planet surface UV fluxes in this 4 - 6 eV range are uniquely suited to enact both the synthesis & the selectivity of the nucleotides, and a few amino acids. The canonical monomers also happen to be the most UV photostable isomers.

3. The oligomers appear to be selected by their ability to self-repair UVC damage by UV excitation – a photolyase-like mechanism.
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