Aqueous processing and solubility fractionation of Titan's surface organics

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Complex organics on Titan

- Tholins are the laboratory-derived complex organics that simulate the **nonbiological complex organic chemistry** in astrophysical contexts (Cable et al., 2012).
- When Titan tholins are hydrolyzed in water, they react to form **prebiotics** in timescales as short as days or weeks (Neish et al., 2010; S. Hörst et al., 2012; Cleaves et al., 2014).
- On Titan, complex organics are formed in the atmosphere through the photolysis of methane (Lavvas et al., 2011; Cable et al., 2012).
- These haze particles undergo gravitational settling and **coat Titan's water-ice surface**.
- Through impact events or cryovolcanism, **pools of liquid water may exist episodically at the surface** of Titan (protected by a thin ice layer) for 10^2-10^3 years (Crósta et al., 2021; Wakita et al., 2023).

What happens after hydrolysis?

- If haze particles from Titan's surface mix into liquid water, the particles would undergo **hydrolysis and fractionation**, separating the soluble (liquid) and insoluble (solid) products.
- After freezing, soluble and insoluble fractions may become separated further through differential erosion.
- The **early Earth** was likely also characterized by a similar organic haze layer, with abundant pools of liquid water. The fractionation of soluble and insoluble organics may have played an important role in which organic molecules became incorporated into early life.

Methods: Tholin Production

We produce Titan tholins in our Planetary HAZE Research (PHAZER) chamber (Fig. 1). Cold plasma in the chamber simulates high-energy particles, producing similar chemistry to the photolysis activated by solar radiation but at a rate fast enough to produce a laboratory sample in a reasonable timeframe. The atmosphere simulation experiment is run continuously for as long as 192 hours. During the experiment, the tholins that are produced stick to the walls of the chamber; after the experiement, the tholins are collected under nitrogen in a glove box (Fig. 2).

Acknowledgements

We gratefully acknowledge that this project was supported by access to the PRECISE Planetary Science Enabling Facility, grant 80NSSC25K7201.

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE2139757. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

NASA Solar System Workings Grant 80NSSC24K0888.

Thank you to the DPS Travel Grant for funding to attend this meeting.

Methods: Hydrolysis

We prepared two different types of hydrolyzed tholins that represent the two possible endmembers of an ammoniated Titan melt pool: one hydrolyzed in pure water, and one hydrolyzed in 30% aqueous ammonia (Figure 2). Once the solutions are prepared, they are placed on a nutating mixer to be mixed gently and continuously for 3 weeks. This represents the minimum time required for a single half-life of the longest reaction times found in previous studies (Neish et al., 2010).

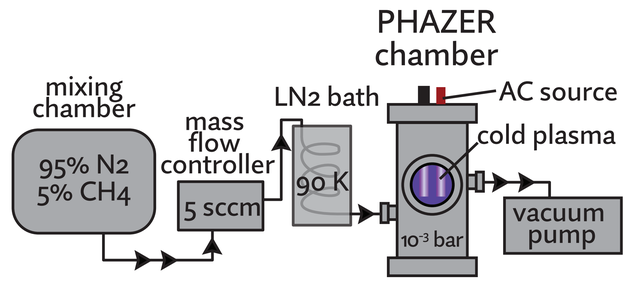

Figure 1: Schematic of Titan tholin production. A mixture of 95% N2, 5% CH4 gas flows at 5 sccm through a liquid nitrogen bath to cool it to ~90 K, then through the Planetary HAZE Research (PHAZER) chamber where it is exposed to an AC plasma discharge at 0.05 psi (He et al., 2017).

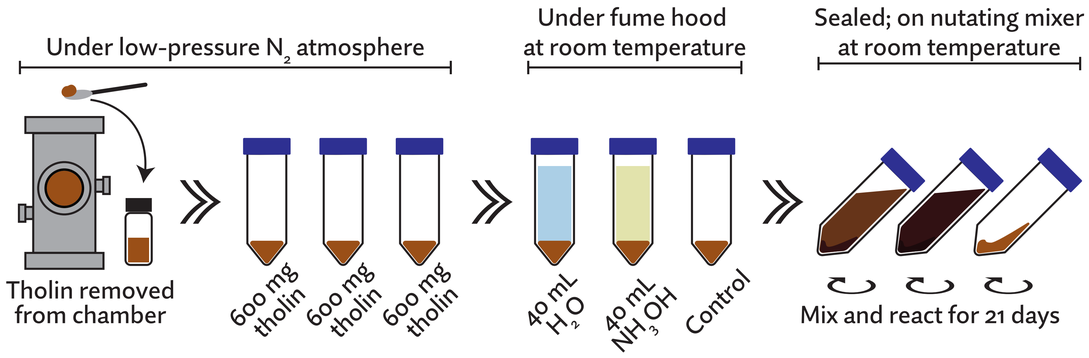

Figure 2: Schematic of hydrolysis processing. At the end of the atmospheric simulation experiment, the chamber is closed to maintain vacuum and transferred into a glove box of inert nitrogen atmosphere, which does not affect the chemistry of the tholins. Then, the tholins are scraped from the walls of the chamber and stored in glass vials. For each hydrolysis preparation, 600 mg of tholins were added to centrifuge tubes, removed from the glove box to a fume hood, and then mixed with 40 mL of solvent to produce a 1.5% solution by mass. The tubes were then sealed, and allowed to mix and react for 21 days.

Methods: Separation of soluble and insoluble fractions

After three weeks, the solid insoluble fraction and the liquid soluble fraction are separated: first with a centrifuge, and then the liquid fraction is siphoned off, filtered, and stored. The solid fraction is then washed under its original solvent, dried, and collected (Fig. 3).

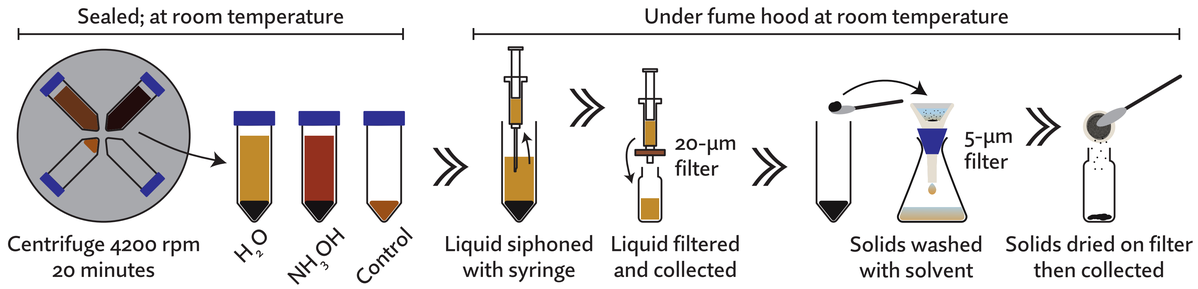

Figure 3: Schematic of soluble and insoluble separation. The solutions are centrifuged at 4200 rpm for 20 minutes. The solid, insoluble fraction is pulled to the tip of the tube, while the liquid, soluble fraction floats above. Next, under a fume hood, the soluble fraction is siphoned off using a plastic luer lock syringe fitted with a needle tip. The solution is then pushed through a 20-µm filter tip into a glass vial, which is then sealed. The remaining solid fraction in the tube must be washed by the solvent to remove the remaining liquid surrounding the particles. An aliquot of the unwashed insoluble fraction is scooped onto a 3-micron cellulose filter in a Hirsch vacuum filtration funnel. The original solvent is added to the funnel and removes the soluble fraction through the filter; this process is repeated until the solvent runs clear. The insoluble particles are allowed to dry onto the filter. Once fully dry, the particles are gently scraped into a glass vial, which is then sealed.

Analytical Methods

We use both qualitative and quantitative analysis of Gas Chromatography Mass Spectroscopy (GCMS) and Liquid Chromatography Mass Spectrometry (LCMS) to detect prebiotic molecules, such as amino acids and nucleobases, and to determine their relative concentration. We compare detections across the soluble (liquid) fraction, insoluble (solid) fraction, and pristine tholin, and across solvents (pure water vs. aqueous ammonia).

Initial Results

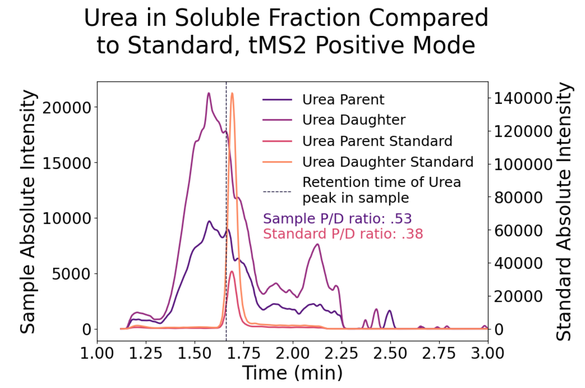

Figure 4: LCMS targeted MS/MS (tMS2) chromatogram showing counts of ions with the same mass-to-charge ratio in positive mode of the parent and daughter products of urea. The two solid darker color lines show the peaks detected in the soluble sample. The two solid lighter color lines show the peaks detected in the standard. The dashed line shows the retention time at which the parent-to-daughter ratio was calculated for the sample. The peak is shifted slightly to the left (at 1.66 min) from the standard peak (at 1.69 min).

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