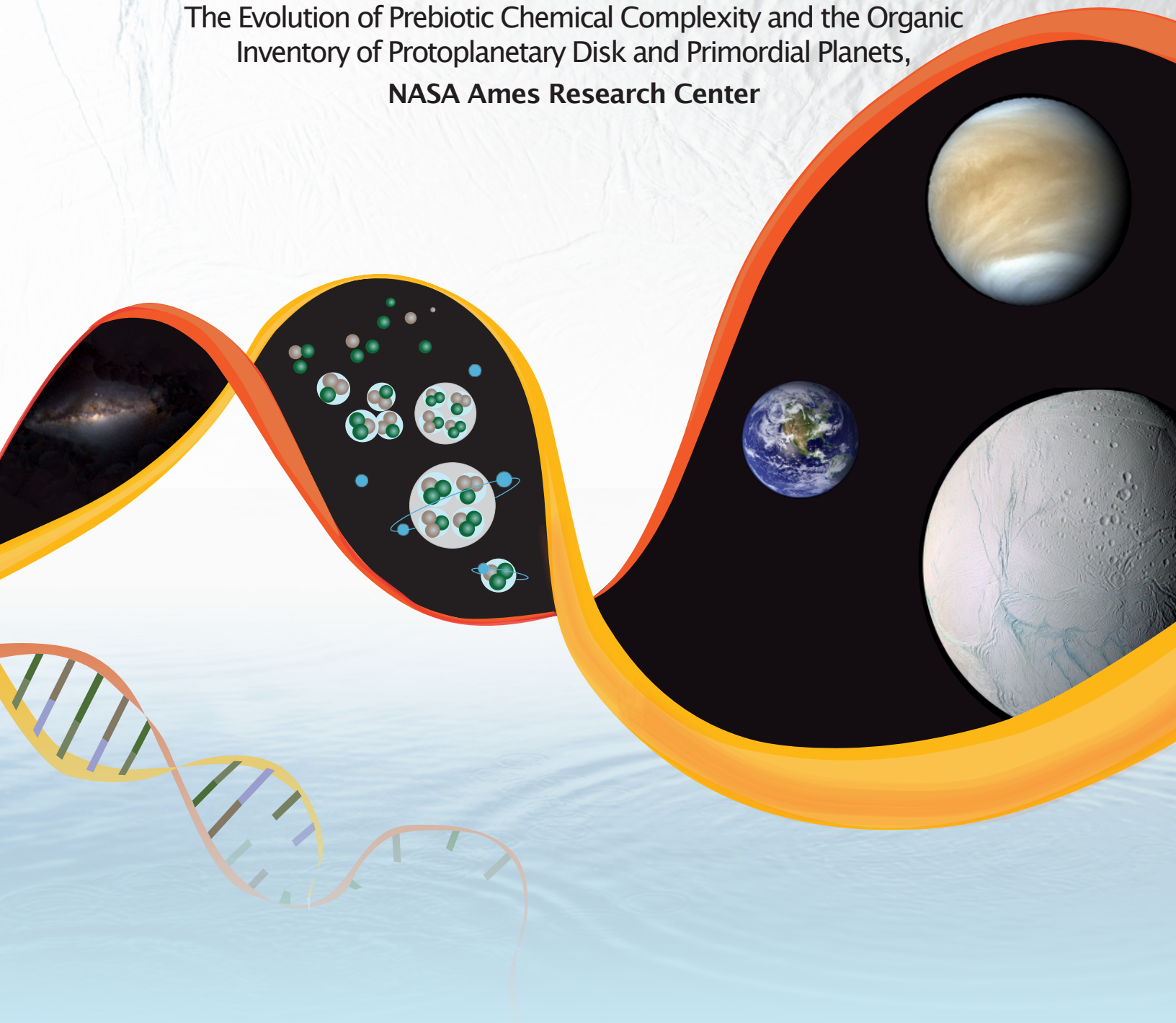
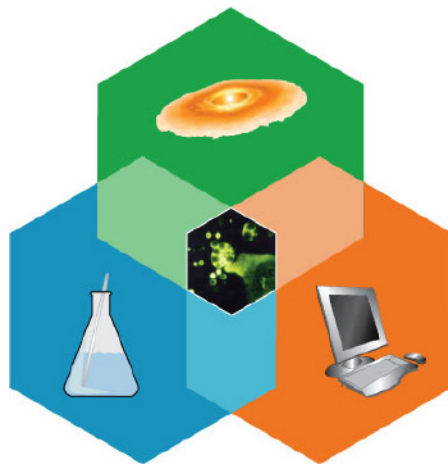




NASA Astrobiology Institute 2016 Annual Science Report Team Report:

The Evolution of Prebiotic Chemical Complexity and the Organic
Inventory of Protoplanetary Disk and Primordial Planets,
NASA Ames Research Center





The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disk and Primordial Planets

Lead Institution:
NASA Ames Research Center



Team Overview



Principal Investigator:
Scott Sandford

The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disks and Primordial Planets Team seeks a greater understanding of the chemical processes that occur at every stage in the evolution of organic chemical complexity, from quiescent regions of dense molecular clouds, through all stages of disk and planet formation, and ultimately to the materials that rain down on planets. The effort is an integrated, coherent program involving the interaction of a number of well-integrated research projects:

- Modeling and observations of protoplanetary disks
- Modeling and observations of exoplanets
- Laboratory studies of gas-grain chemistry
- Laboratory studies of ice photolysis
- Computational quantum chemistry

These projects interact closely with each other so that each benefits from advances made in the others and helps guide future work. For example, the modeling of the chemistry that takes place in protostellar disks benefits from inputs provided by spectral, physical, and chemical properties of molecules determined by the laboratory and computational projects, but also provides guidance for key areas of future computational and laboratory work. Similarly, the computational studies can be used to help interpret laboratory results and extend them to additional materials or environments, while the lab results can provide confirmation of computational reaction paths.

2016 Executive Summary

During 2016 our Team made significant progress on all aspects of our combined research. Some highlights are described briefly below. More details can be found in our individual project reports.

Disk Modeling - We have developed global protoplanetary disk evolution models that incorporate the formation of planetesimals in a 1+1D viscous evolution framework that combines the effects of photoevaporation, dust evolution, turbulence, and planetesimal formation by the streaming instability. This work shows that, as the gas is removed, regions with an over-density of dust grains are created that lead to the formation of planetesimals on relatively short timescales, i.e., planetesimal formation in the outer disk is a natural outcome of disk evolution. We have also begun incorporating gas-grain chemistry into the disk-modeling network to study transport of ices within disks.

Exoplanets - Our Team is at the leading edge of extrasolar planet discovery, and we are core participants in the long-running Lick-Carnegie Exoplanet Survey. Over the past year we assembled and published a compendium of 60,949 precision radial velocities for 1,624 nearby sun-like stars and red dwarfs. This data, all taken with the Keck-I Telescope over a period of more than 20 years, supports the detection of hundreds of exoplanets, including 60 new candidate worlds. Our planet detection efforts also extend to our own Solar System. Strong dynamical evidence points to the potential existence of "Planet Nine", a ~10 Earth-mass world on an eccentric ~17,000-year orbit. Our work pinpoints the as-yet unseen object at a distance of 950 AU, with a sky position near RA=3 hours, Dec=0 degrees, and apparent brightness $V \sim 23$.

Laboratory Studies - Significant progress has been made in several areas of our laboratory research. An apparatus for studying gas-grain chemistry has been developed and constructed. We have also completed a preliminary study of the abiotic production of sugars and sugar derivatives during the photolysis of simple ice mixtures. We have also completed studies that have demonstrated that all of the nucleobases used by modern life, as well as a host of related compounds, can also be produced by ice photolysis (Fig. 1).

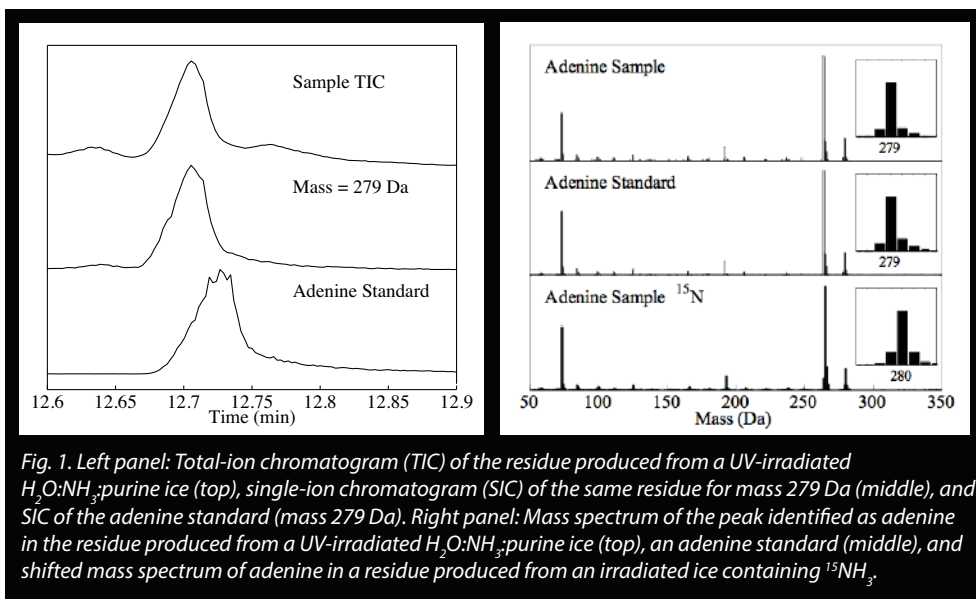


Fig. 1. Left panel: Total-ion chromatogram (TIC) of the residue produced from a UV-irradiated $H_2O:NH_3$:purine ice (top), single-ion chromatogram (SIC) of the same residue for mass 279 Da (middle), and SIC of the adenine standard (mass 279 Da). Right panel: Mass spectrum of the peak identified as adenine in the residue produced from a UV-irradiated $H_2O:NH_3$:purine ice (top), an adenine standard (middle), and shifted mass spectrum of adenine in a residue produced from an irradiated ice containing $^{15}NH_3$.

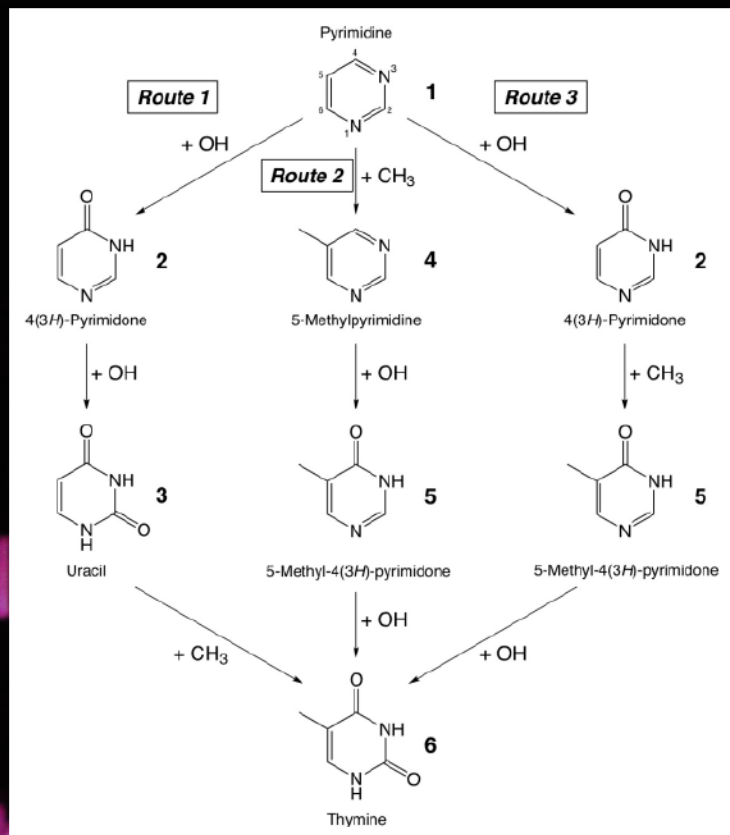


Fig. 2. Diagram illustrating the three reaction pathways from pyrimidine 1 to uracil 3 and thymine 6 we studied using quantum chemical computations.

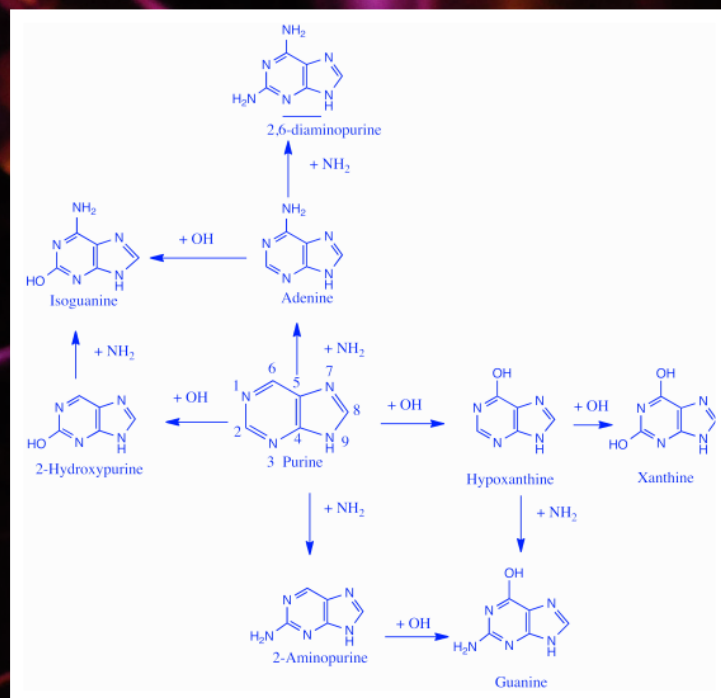


Fig. 3. Reaction scheme indicating the amino and hydroxyl group substitutions on the purine molecule and pathways to the nucleobases adenine and guanine studied with quantum chemical computations.

Computational Quantum Chemistry - In conjunction with the laboratory studies of nucleobase production, we investigated the formation of nucleobases in irradiated astrophysical ices containing pyrimidine and purine using computational quantum chemistry. This work demonstrated that the formation of nucleobases is energetically and kinetically favorable given the presence of one or several water molecules, i.e., it can occur in the solid state, but not in the gas phase (Fig. 2 and 3). This work also explains why some nucleobases (uracil) are made efficiently, while others (thymine) are not. In another study, electronic structure calculations were performed on $C_4H_3^+$, $C_6H_3^+$ and $C_6H_5^+$. $C_6H_5^+$ was found to be very stable and may be a good nucleation center for the growth of larger polycyclic aromatic hydrocarbons (PAHs), one of the most abundant families of molecules in space. We also continued our work with the Dutch Astrochemistry Network (DAN) on the computation of infrared emission from PAHs.

Team Members

Partha Bera
 Uma Gorti
 Martin Head-Gordon
 Gregory Laughlin
 Timothy Lee
 Andrew Mattioda
 Michel Nuevo
 Xander Tielens
 Gustavo Cruz-Diaz
 Christopher Materese
 Tamar Stein

Project Reports

Planetesimal Formation and Transport of Ices in Protoplanetary Disks

We developed global protoplanetary disk evolution models that incorporate the formation of planetesimals in a 1+1D viscous evolution framework. We combined the effects of photoevaporation, dust evolution, turbulence, and planetesimal formation by the streaming instability to study how dust forms planetesimals in an evolving disk. As the gas is removed by photoevaporation, dust is retained in the disk since flow gas densities are too low to entrain dust. A steady increase in the amount of dust relative to gas triggers the streaming instability due to the back-reaction of the dust with the gas. Regions with an over-density of dust grains are created and lead to the formation of planetesimals on relatively short timescales. Our models produce ~76-153 Earth masses of planetesimals. Thus, planetesimal formation in the outer disk is found to be a natural outcome of disk evolution.

We have begun incorporating gas grain chemistry into the disk modeling network to study transport of ices. To that end, a gas-grain chemical network was added to augment our current gas-phase and photo-reaction chemistry in disk models. Dust grains continually collide and fragment or coagulate (depending on local conditions in the disk) throughout the disk as it evolves, leading to their size redistribution. Molecules preferentially freeze on small grains, which have greater total cross-sectional area. Ices moreover change the local fragmentation threshold for destructive collisions compared to bare grains, as ices are more “sticky” and facilitate coagulation. We have constructed simple semi-analytical formulations to include the effects of gas-grain chemistry and freeze-out to study the distribution of CO and H₂O ice as the disk evolves. Parameter studies involving a few species at a time are being conducted to gain a better understanding of ice chemistry in disks.

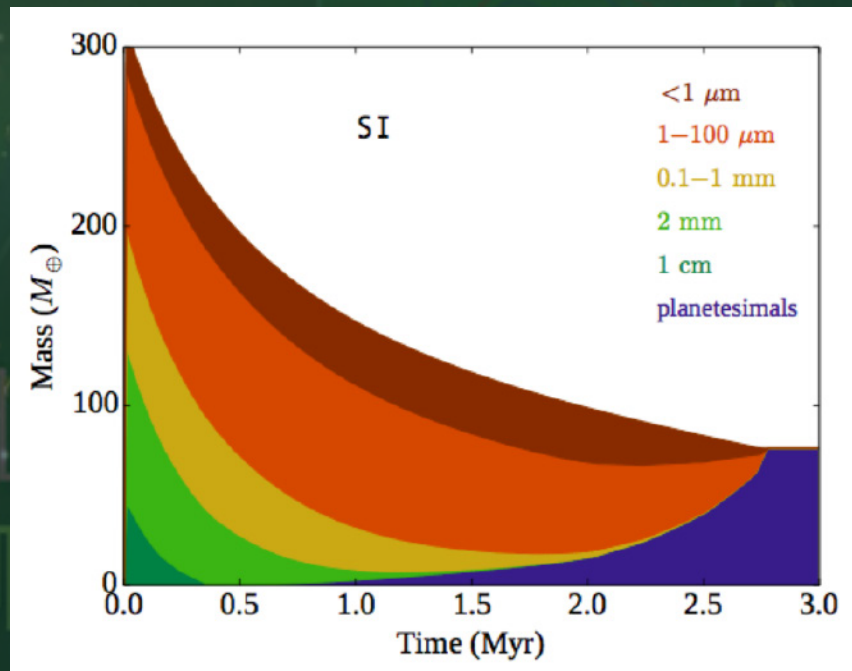


Fig. 4. The total mass in solids in different size ranges (color-coded) evolves with time as the disk disperses, and is shown in the figure above. The streaming instability can efficiently convert dust (<1 cm) into planetesimals (in blue), and in the model here, about 76 Earth masses of dust is converted during the disk lifetime of about 3 million years.

Exoplanet Studies

We have continued our radial velocity surveys to detect and characterize extrasolar planets. The highlight of the past year's effort has been the publication of the full catalog of high-precision velocities obtained over the past two decades with the Keck Telescope (Butler, Vogt, Laughlin et al. 2017). This compendium of 60,949 precision Doppler measurements is accompanied by detailed spectral indices, tabulated host star properties for 1,624 nearby sun-like stars and red dwarfs, and a catalog of sixty new candidate exoplanets, including a low-mass world orbiting Lalande 21185, the fourth nearest main-sequence stellar system to the Sun.

We have also focused research on worlds much closer to home. The past year has seen a flurry of activity associated with Planet Nine, a proposed Solar System planet with a period of order 17,000 years. If it exists, this world provides a novel and unexpected chance to advance the scientific goals of our NAI consortium.

In order to aid its detection, and to assess its likely properties, we constructed atmospheric models that predict its reflection and emission spectra in the optical and the infrared. We found that it should have a very pure H-He atmosphere in which methane and other volatiles are fully condensed into deep-layer cloud. It should thus have a high albedo (and a light-blue overall appearance) characterized by Rayleigh scattering. (Fortney, Marley, Laughlin et al. 2016). Through a Monte-Carlo survey, we established that if it exists, Planet Nine is very likely ($P \sim 98\%$) in low-order mean-motion resonances with the most distant Kuiper Belt Objects, including Sedna and 2012 VP 113. A large-scale supercomputer-based optimization then allowed us to pin down its likely sky position (see accompanying Figure and Millholland and Laughlin 2016).

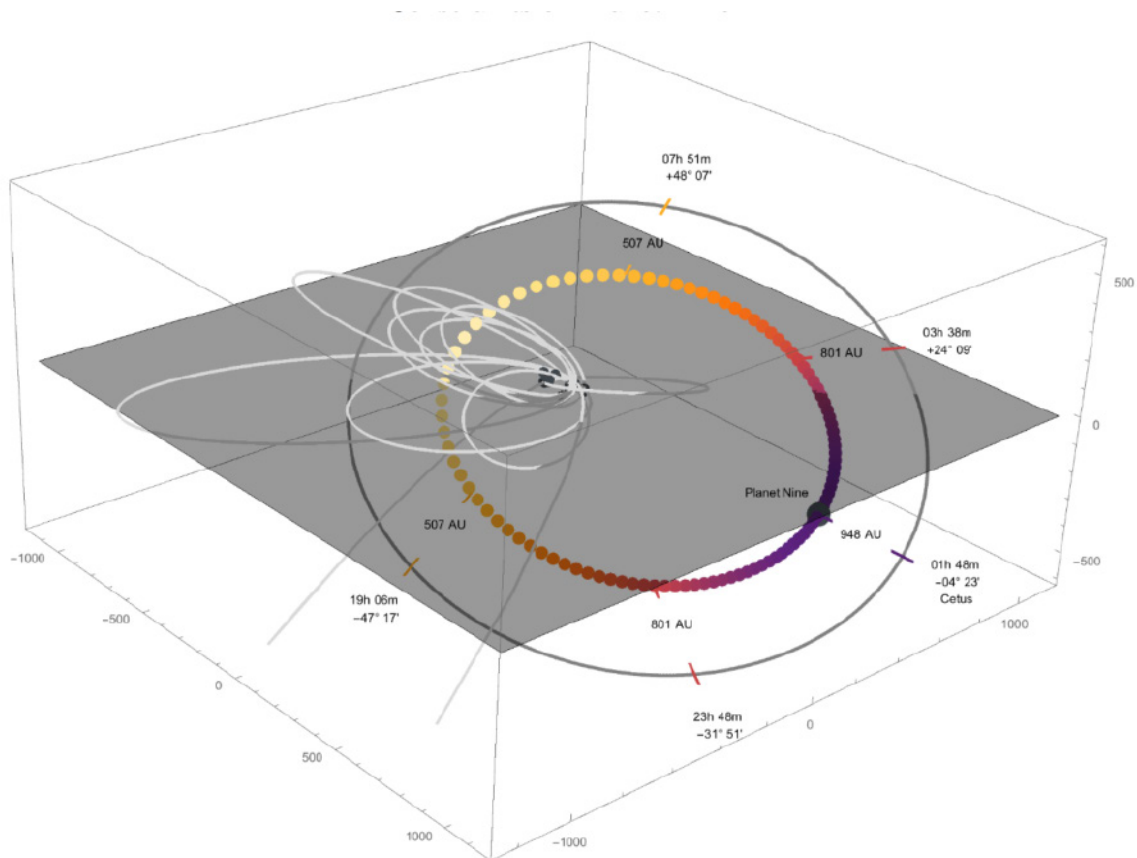


Fig. 5. Planet Nine orbit and likely current location. A 3D manipulable version of this figure is available at https://smillholland.github.io/P9_Orbit/

Laboratory Studies of Gas-Grain Chemistry

During 2016, Team members Drs. Mattioda and Cruz-Díaz modified a Harrick Praying Mantis Diffuse Reflectance apparatus and corresponding low temperature cell to accommodate a flowing hydrogen discharge lamp (see Fig. 6 and 7). This was accomplished through the design and fabrication of a high vacuum adapter for which a new technology report is being submitted to NASA.

The high vacuum adapter is equipped with two gas inlet ports, permitting the deposition of multiple gas (H_2O , etc.) and organic (PAH, etc.) samples onto a mineral surface for the creation of astrobiologically interesting ice and mineral mixtures. The apparatus will allow us to study the adsorption/desorption processes of Polycyclic Aromatic Hydrocarbons (PAHs) and ice mixtures onto mineral grain surfaces. We will also be able to determine any catalytic properties the grains may exhibit when irradiated via high energy UV photons (primarily Lyman alpha). This year we have measured the infrared reflectance spectra of the hematite, magnetite, silicon dioxide, graphite as well as iron (II) and iron (III) oxides. We have also performed initial studies of benzene adsorption onto several mineral surfaces.

Dr. Ana Ferreira de Barros (Professor and Researcher at the Federal Center for Technological Education – CEFET/RJ), Rio de Janeiro, Brazil, started a 1-year Visiting Researcher position in which she'll be working with Dr. Mattioda on the photochemistry of PAHs in water ices. This research exchange is in alignment with the agreements between NASA and the Brazilian Space Agency (AEB) to enhance collaborations between the agencies. Dr. Barros has completed the infrared measurements on the photochemistry of the PAH Coronene ($\text{C}_{24}\text{H}_{12}$) under various PAH:Water ice ratios and has started the investigation of the photochemistry of the PAH Ovalene ($\text{C}_{34}\text{H}_{12}$) in water ice. The larger sizes of these PAHs are astrophysically relevant to the PAHs found in interstellar environments.

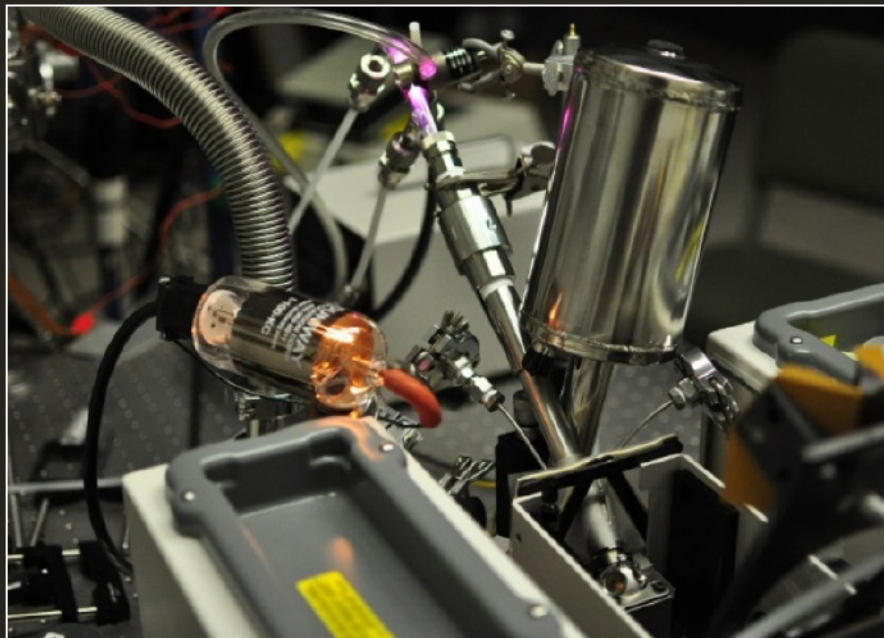


Fig. 6. Harrick Praying Mantis low-temperature setup with the flowing hydrogen lamp adapter. Note the two gas inlet ports on the adapter, which permit the introduction of astrobiologically relevant gases.

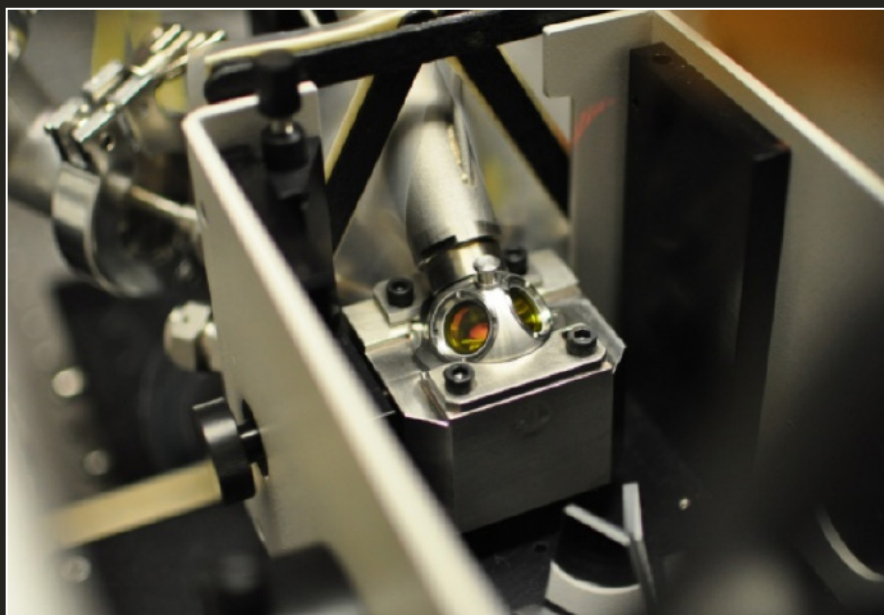


Fig. 7. Close-up of the low temperature Harrick Praying Mantis cell. The enclosed area allows the sample to be heated and cooled under vacuum, as well as for the introduction of gas mixtures onto the solid sample. The photolysis of the sample with UV photons can be monitored in real time via in-situ infrared spectroscopy.

Laboratory Studies of Ice Photochemistry and the Production of Sugar Derivatives and Nucleobases

During the past year, we studied the formation of (i) sugars and their derivatives, in particular those seen in meteorites, and (ii) purine-based compounds, in particular the purine-based nucleobases, during the UV irradiation of low-temperature ices under astrophysical conditions.

Simultaneous deposition and UV irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice mixtures was found to produce complex sugars and sugar derivatives with up to 6 carbon atoms, including ribose (the sugar of RNA; Fig. 8), glucose, and some of their isomers. Contamination of our samples was ruled out using two methods: (i) the analysis of residues produced from ices whose methanol was isotopically labeled with ^{13}C , and (ii) the use of a chiral derivatization agent to separate enantiomers. We also conducted experiments in which $\text{H}_2\text{O}:\text{CO}_2$ and $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}_2$ ices were used to see how they matched the high abundance of sugar acids in meteorites. Preliminary results show a slight increase in the abundances of sugar acids in these residues.

Nucleobases can be subdivided into two major categories: the pyrimidines (uracil, cytosine, and thymine) and the purines (adenine and guanine). We earlier demonstrated that UV irradiation of ices containing pyrimidine leads to the production of uracil, cytosine, thymine, and other pyrimidine derivatives. During the past year we studied similar ices containing purine and demonstrated the formation of adenine and guanine, as well as other functionalized purines including hypoxanthine, isoguanine, several aminopurines, and 2,6-diaminopurine. The relative abundance of photoproducts appears to be controlled by three factors in decreasing order of importance: 1) the number of functional group additions required to form the product; 2) the type of functional group added; and 3) the position where the addition takes place. Collectively, our results on pyrimidine and purine demonstrate that all the biological nucleobases can form under the same astrophysical conditions.

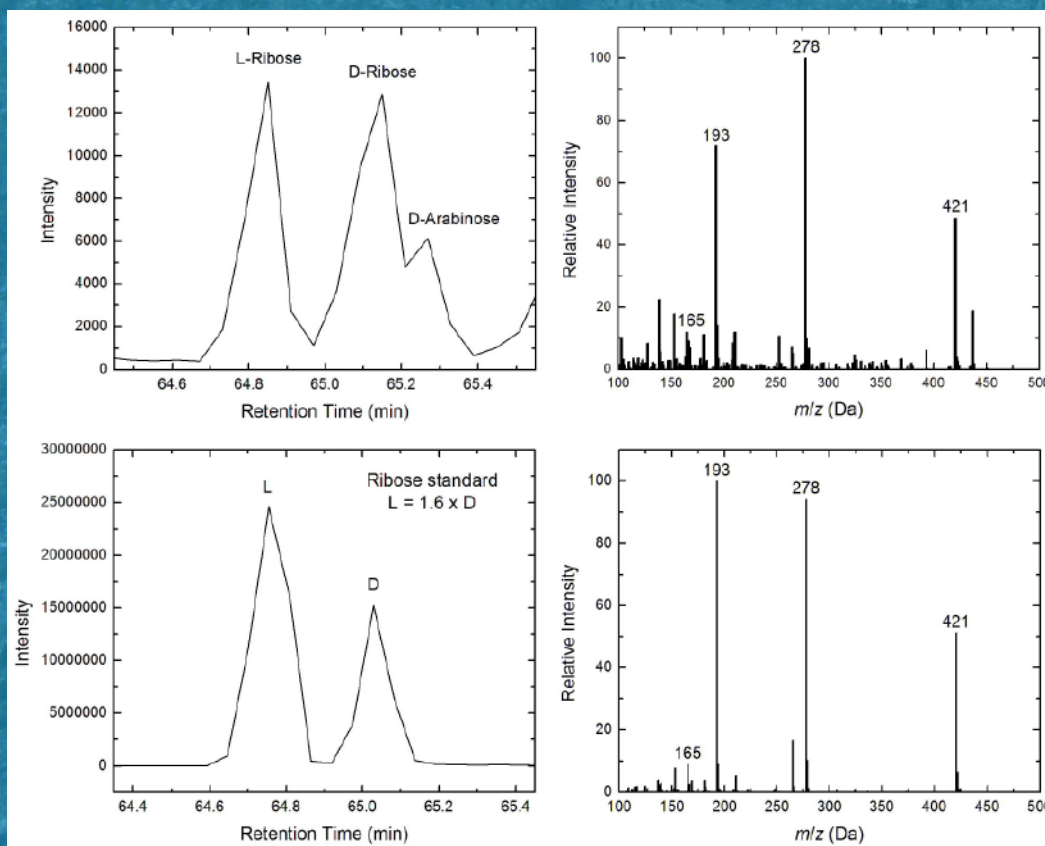


Fig. 8. Identification of racemic ribose in a residue produced from the UV irradiation of an $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (2:1) ice mixture at 12 K for 18 hours. The top plots show the GC-MS chromatogram of the residue in the retention time range of where ribose elutes (left), and the mass spectrum of the first peak (right). The bottom plots show the same plots of a DL-ribose standard where L is 1.6 times more abundant than D. This confirms the identification of ribose in the residue, present in racemic amounts. The peak overlapping with D-ribose in the chromatogram of the residue (top left) corresponds to D-arabinose, an isomer of ribose.

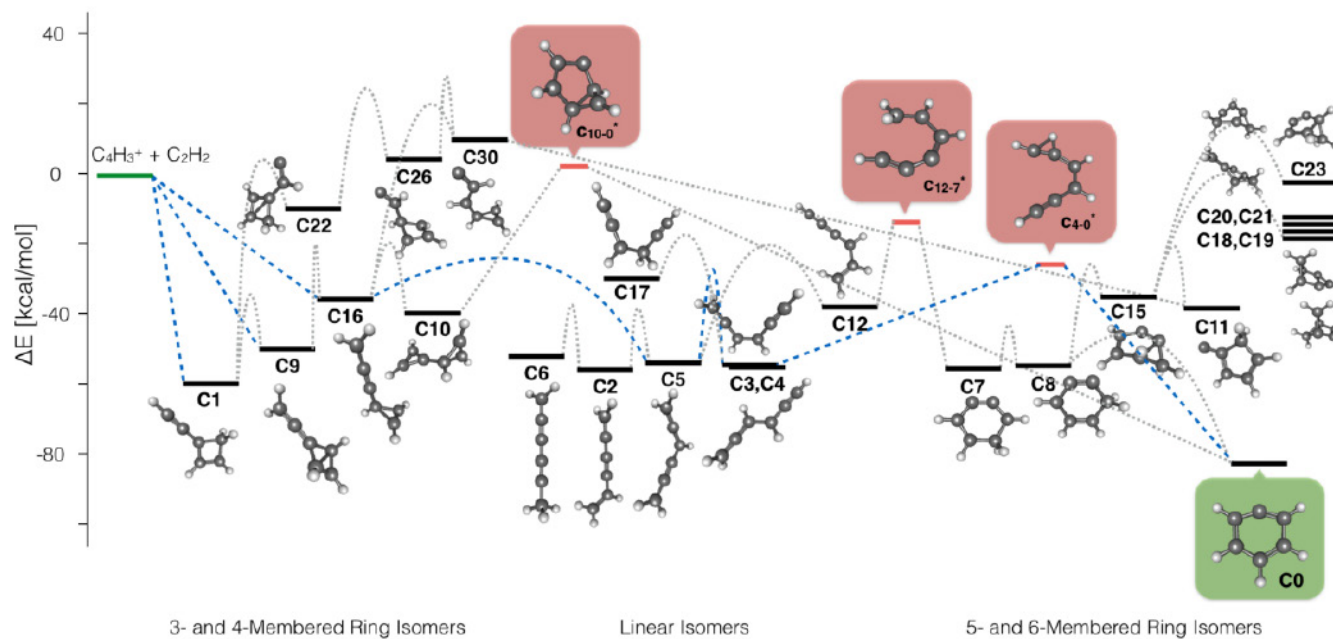


Fig. 9. Significant minima and transition states on the $C_6H_5^+$ potential energy surface. The transition states for the ring-closure reaction are reported in red, while other transition states are reported as curved pathways.

Computational Quantum Chemistry

We investigated the formation of nucleobases in irradiated astrophysical ices containing pyrimidine and purine. Quantum chemistry computations indicate thymine can be produced by reactions between pyrimidine, and hydroxyl and methyl radicals with only limited efficiency due to the difficulty of methylation, and only in the presence of a water matrix. Work estimating the efficiency of production of the purine-based nucleobases adenine and guanine in gas-phase only and condensed-phase environments revealed that the formation of nucleobases is energetically and kinetically favorable provided the presence of one or several water molecules.

Electronic structure calculations were performed on $C_4H_3^+$, $C_6H_3^+$ and $C_6H_5^+$ (Fig. 9). On the basis of the calculated minima and transition states and their relative energies, the likely pathways to $C_4H_3^+$ and $C_6H_3^+$ likely arise from unimolecular decomposition of hot $C_4H_4^+$ and $C_6H_4^+$ by H atom elimination. In contrast, $C_6H_5^+$ was found to be very stable to fragmentation and elimination pathways, and may be a good nucleation center for the growth of larger polycyclic aromatic hydrocarbons in interstellar conditions. *Ab initio* quantum chemical methods were used to

characterize the structures, relative energies, and spectroscopic and physical properties of the low-energy isomers of the aziriny cation, which could be present in the interstellar medium.

Our collaboration with the Dutch astrochemistry groups continued with two publications on the anharmonic vibrational spectra of five non-linear PAH molecules. Computed anharmonic spectra of the full set of vibrational frequencies were shown to be in good agreement with new high-resolution spectra in the C-H stretch region and with lower-resolution spectra that spanned the entire vibrational manifold.

We collaborated with colleagues at Georgia Southern University to publish predicted rovibrational spectrum and spectroscopic constants of proton bound molecular complexes for possible assignment in high-resolution astronomical observations and on the nature of bidirectionally expanded closed-shell PAH and PANH anions.



Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disks and Primordial Planets: 2016 Publications

Bandyopadhyay, B., Stein, T., Fang, Y., Kostko, O., White, A., Head-Gordon, M., and Ahmed, M. (2016). Probing Ionic Complexes of Ethylene and Acetylene with Vacuum Ultraviolet Radiation. *Journal of Physical Chemistry A*, 120, 5053-5064. DOI: 10.1021/acs.jpca.6b00107

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