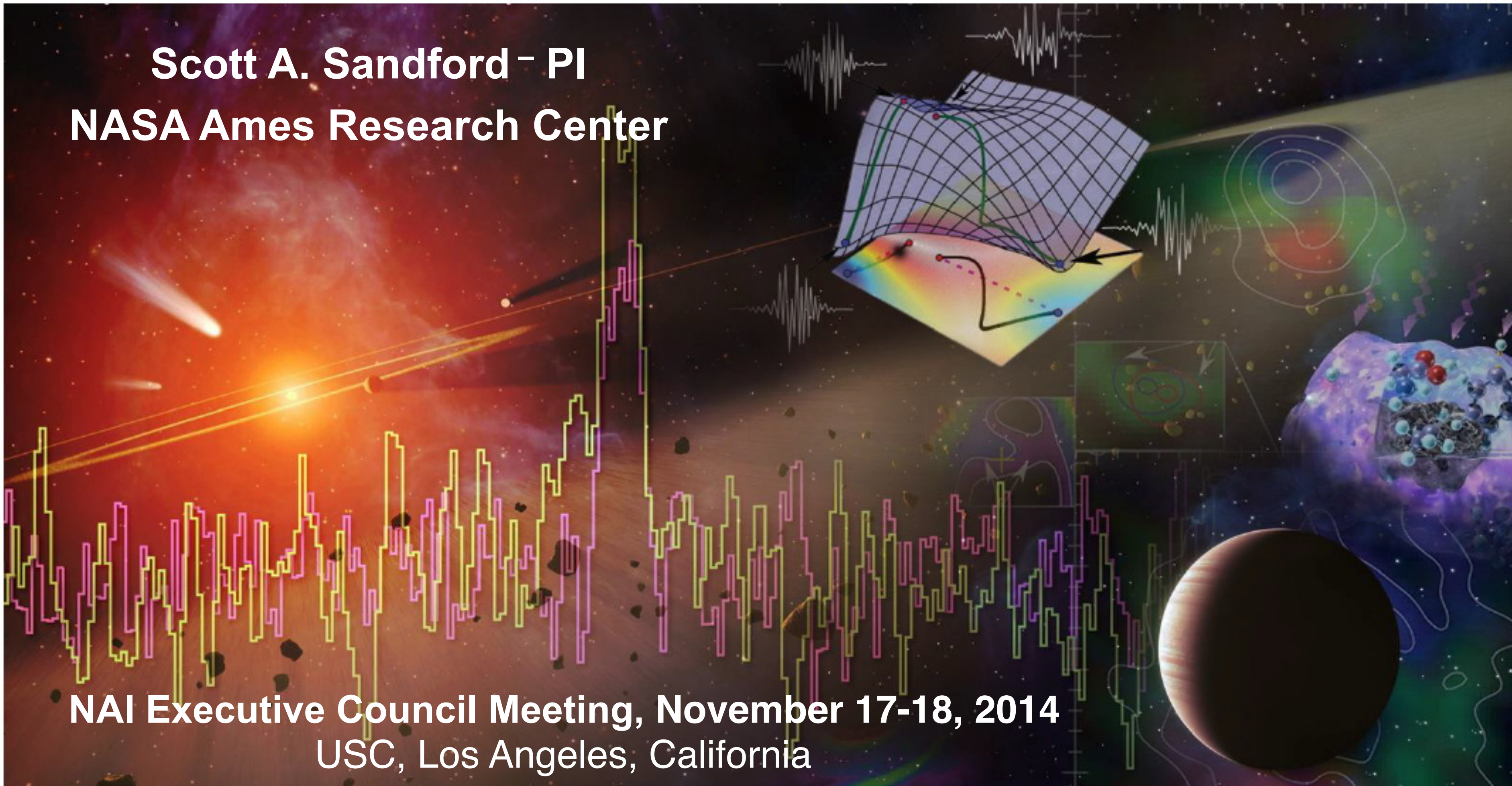
The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disks and Primordial Planets



Scott A. Sandford – PI
NASA Ames Research Center

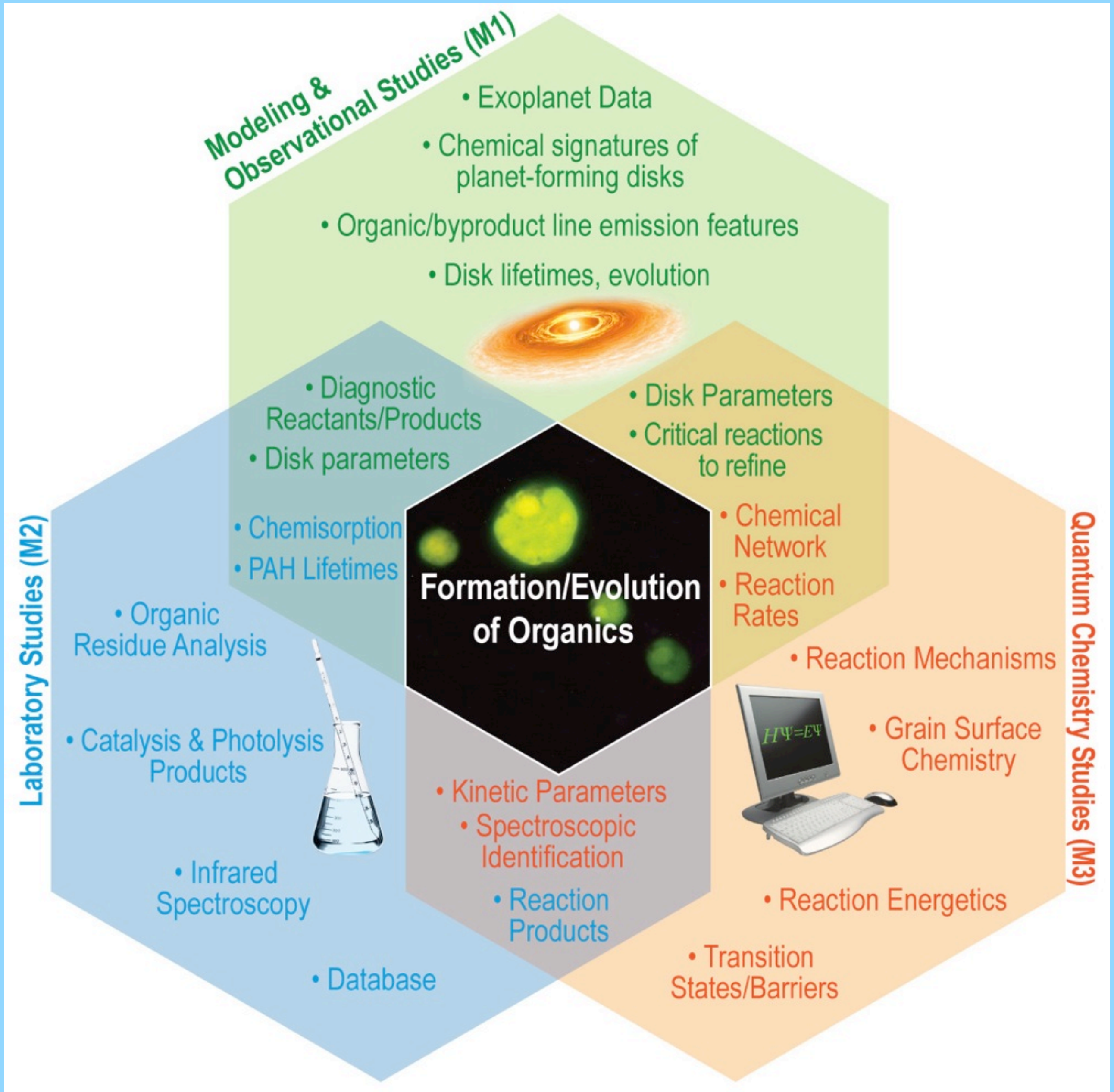
NAI Executive Council Meeting, November 17-18, 2014
USC, Los Angeles, California

Team Members

Team members come from a diversity of institutions:

- **NASA Ames Research Center**
  - Scott Sandford – PI and Laboratory Module
  - Louis Allamandola – Laboratory Module
  - Andy Mattioda – Laboratory Module
  - Timothy Lee – Quantum Chemistry Module
  - Partha Bera – Quantum Chemistry Module
  - 1.5 postdocs (TBD) and 3 summer interns from Langston University
- **SETI - Uma Gorti – Disk Modeling Module**
  - 1 NPP postdoc
- **UC Santa Cruz** – Gregory Laughlin – Exoplanet Observations
  - 1 graduate student
- **UC Berkeley** – Martin Head-Gordon – Quantum Chemistry Module
  - 1 graduate student
- **Universiteit Leiden** – Xander Tielens – Collaborator with the Dutch Astrochemistry Network

Three Tasks Focused on the Formation and Evolution of Organics in Astrophysical Settings



Task 1 - Disk Modeling Studies and Exoplanet Observations

We will use exoplanet and protoplanetary observations and disk thermochemical and dynamical models to study the formation and evolution of organics in disks in:

(i) the anhydrous inner terrestrial planet forming regions (high densities, irradiation due to UV and X-ray photons, mostly dry dust grain surfaces), and

(ii) the outer hydrous regions where H_2O ice-dominated grains in shielded cold regions lead to different surface chemistry and disk chemical evolution.

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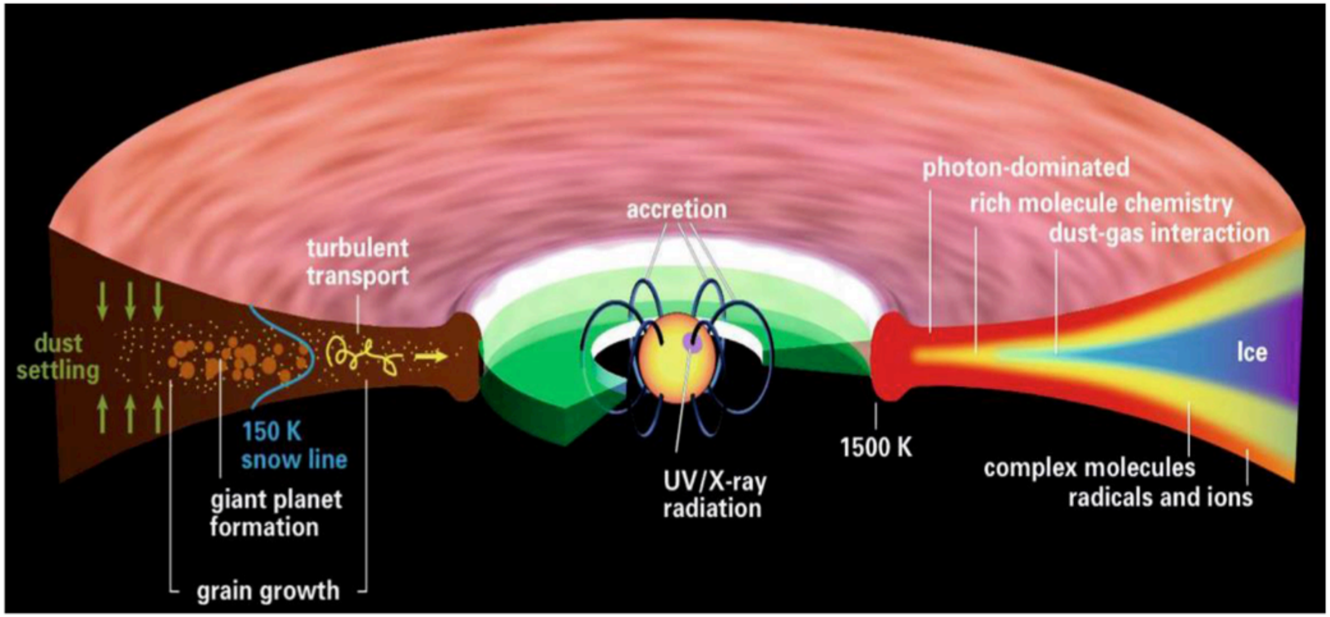


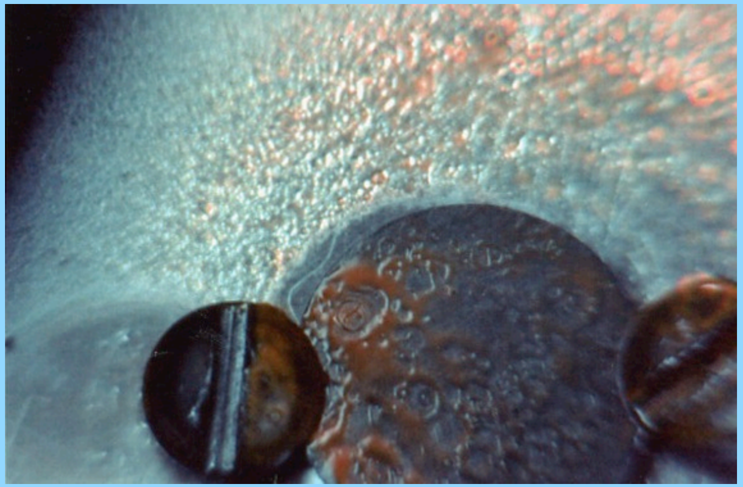
Fig. E4. A schematic of a protoplanetary disk, showing the three spatially distinct chemical regions on the right and depicting the process of planet formation on the left[233].

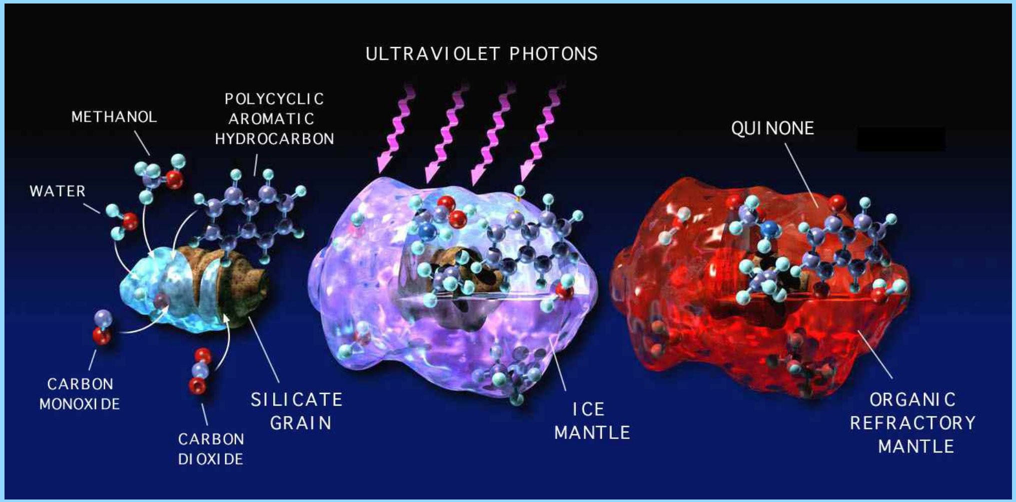
Disk Modeling Studies and Exoplanet Observations

- Dynamic modeling will be used with chemical network models (from laboratory results and quantum chemical computations) to track the abundances of species as they form, alter, and are transported in the disk as it evolves.
- Modeling of disk conditions will predict expected line emission signatures for comparison with observations.
- This research will help elucidate how the time-dependent composition of protostellar disks is reflected in the population of planets that emerges as the end product of disk evolution and how these relate to initial conditions.

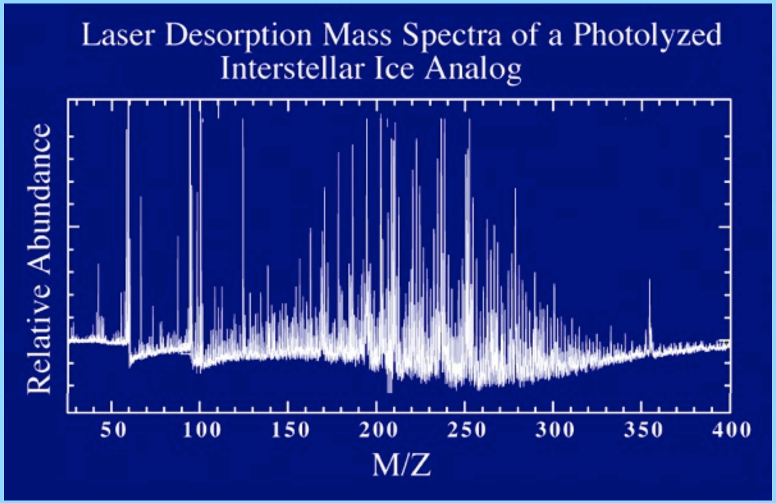
Task 2 - Laboratory Studies - Simulation of Astrochemical Environments

We have studied the chemistry that happens in astrophysical environments in the Astrochemistry Laboratory at NASA-Ames for many years using experimental setups that provide Low Pressures (near vacuum), Low Temperatures (T < 50 K), and High Radiation Levels (particles and photons)



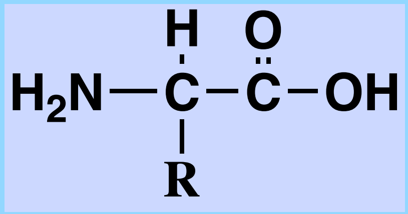


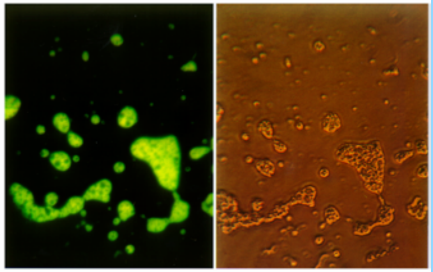
Bernstein, Sandford, Allamandola , Sci. Am. 7,1999, p26



Every peak in this mass spectrum is at least one new molecule

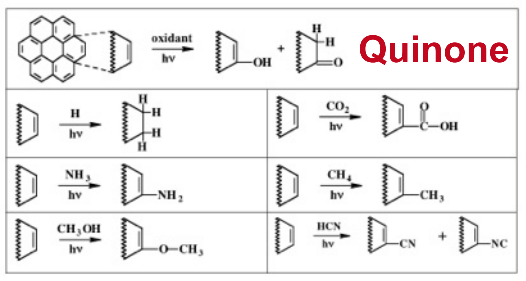
Many new organic species created in these simulations are of astrobiological interest

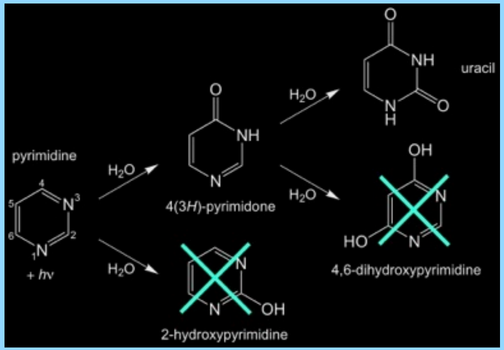




Using a variety of analytical techniques we have shown that these residues contain a number of molecules of biological interest, including:

- **Amino Acids** (building blocks of proteins)
  [Bernstein et al. (2002). *Nature* 416, 401-403]
- **Amphiphiles** (building blocks of membranes)
  [Dworkin et al. (2001). *PNAS* 98, 815-819.]
- **Quinones** (oxidized PAHs with many functions)
  [Bernstein et al. (1999). *Science* 283, 1135-1138]
- **Nucleobases** (building blocks of DNA and RNA)
  [Nuevo et al., Astrobiology, 9, 683 (2009);
  Materese et al. (2013). Astrobiology, 13, 948;
  Nuevo et al. (2014). ApJ, 793, 125]





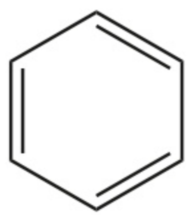
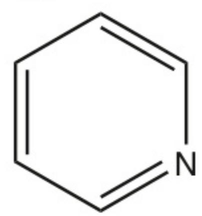
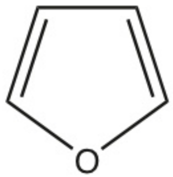
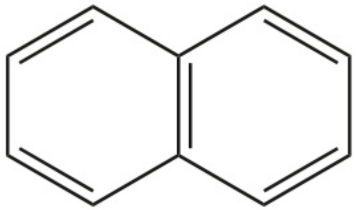
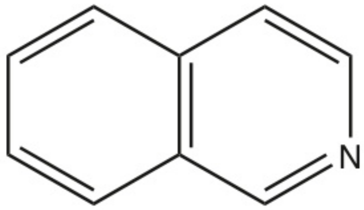
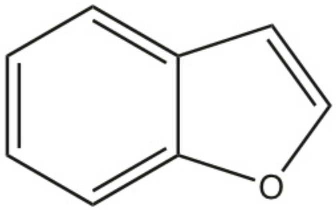
Laboratory Studies of Photolysis and Surface Chemistry

We will concentrate on investigating specific reactions centered on the life cycle of carbon-based molecules, particularly aromatics:

Example 1: The Formation of Aromatic Heterocycles from PAHs

Our recent work shows that photolysis of PAHs (one of the most abundant form of organics in the cosmos) in mixed molecular ices results in the production of aromatic heterocycles

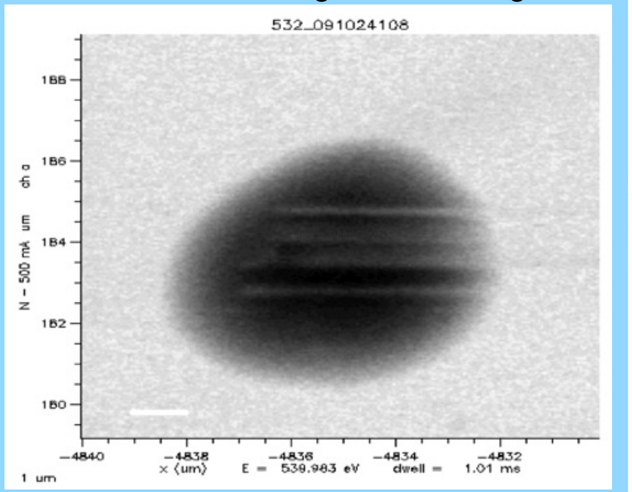
This has important implications for a number of molecular species of molecules of astrobiological significance, including the nucleobases (more about this later)

Aromatic hydrocarbon	*N-Heterocyclic aromatic hydrocarbon*	*O-Heterocyclic aromatic hydrocarbon*
		
		

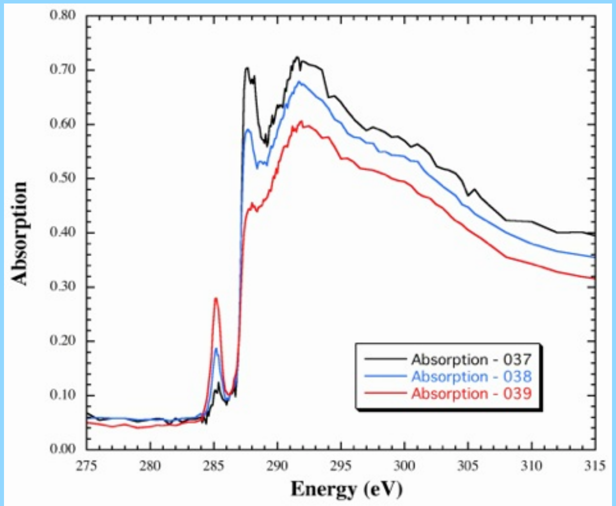
Example 2: Radiation Processing of Organic Residues

- We have embarked on a program in which we are carrying out high energy irradiation of our residues during C-, N-, and O-XANES analyses
- These studies offer a new means of comparing extraterrestrial materials with the materials made in our laboratory simulations
- X-ray exposure of ice photolysis residues produces changes in their nature, principally the conversion of carbonyl carbon into aromatic carbon, with possible loss of oxygen
- Such a process may play a key role in the production of Insoluble Organic Material (IOM), the primary form of carbonaceous material in primitive meteorites

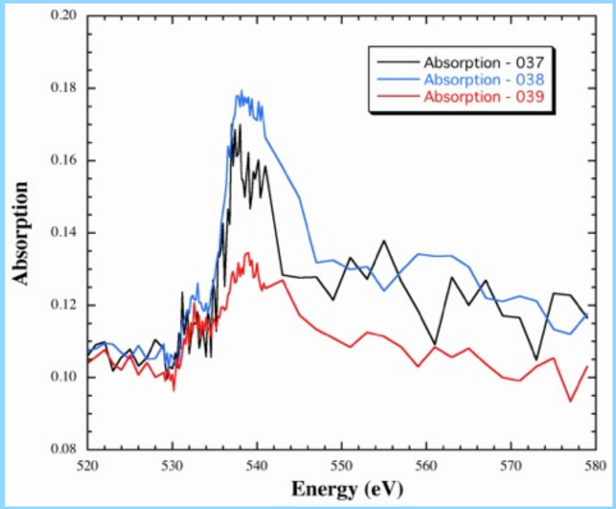
Residue showing beam damage



C-XANES edge showing aromatic growth



O-XANES edge showing loss of O



Task 3 - Quantum Chemistry Studies

- Ideally suited to explore complicated, multistep reaction mechanisms and processes

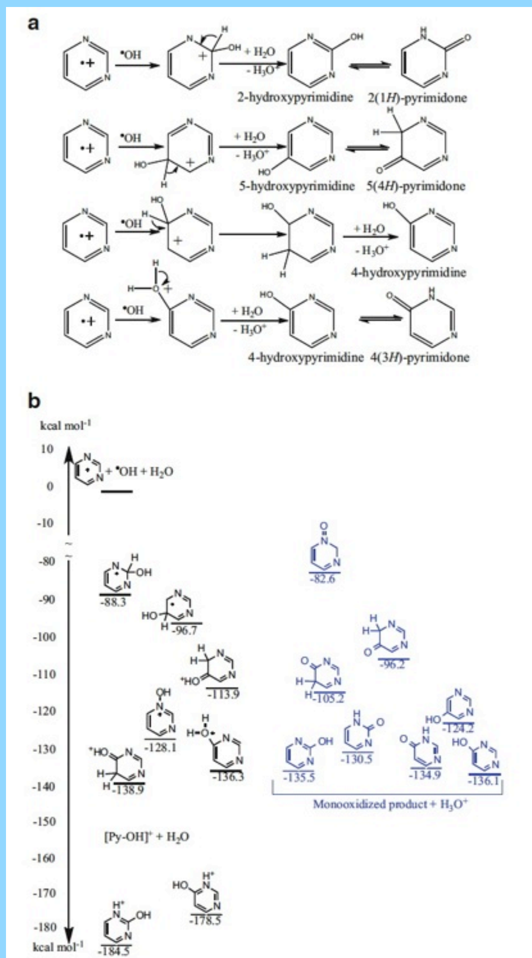
- Understanding the similarities/differences between processes in the condensed and gas phases is a main goal. This will help determine the catalytic role of ice matrices and mineral surfaces in the chemical evolution of prebiotic molecules.

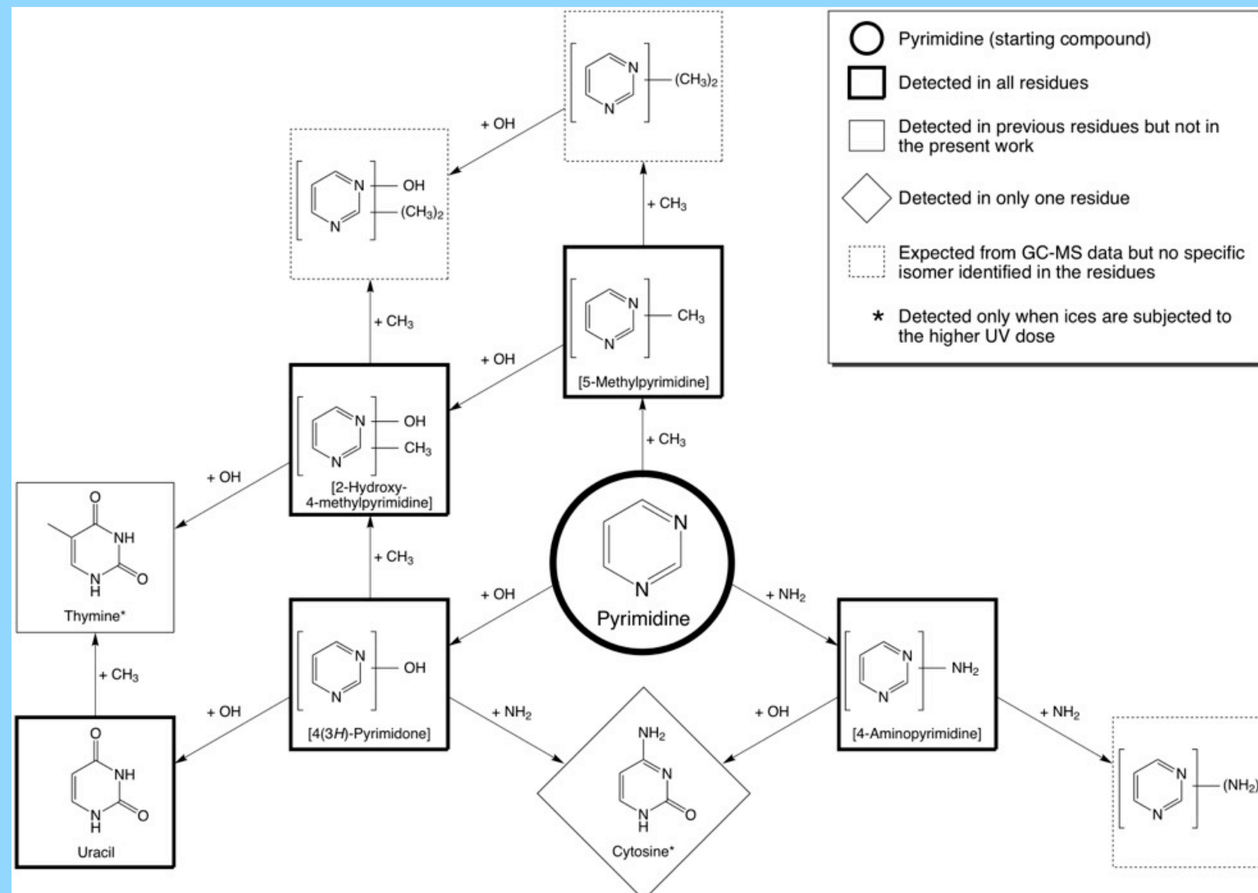
- Combining *ab initio* theoretical investigations with experiments will improve our understanding of the formation and evolution of complex organic molecules via gas-phase and gas-surface reactions, as well as reactions in pure and mixed ices.

- Rate constants determined from quantum chemistry calculations for both gas- and condensed-phase reactions will be used in the modeling studies to follow the evolution of organic compounds in the various disk environments.

Quantum Chemistry Studies

The effectiveness of a combined theoretical and experimental approach is demonstrated by our work on the formation of uracil, cytosine, and thymine from pyrimidine in ices irradiated by UV photons.

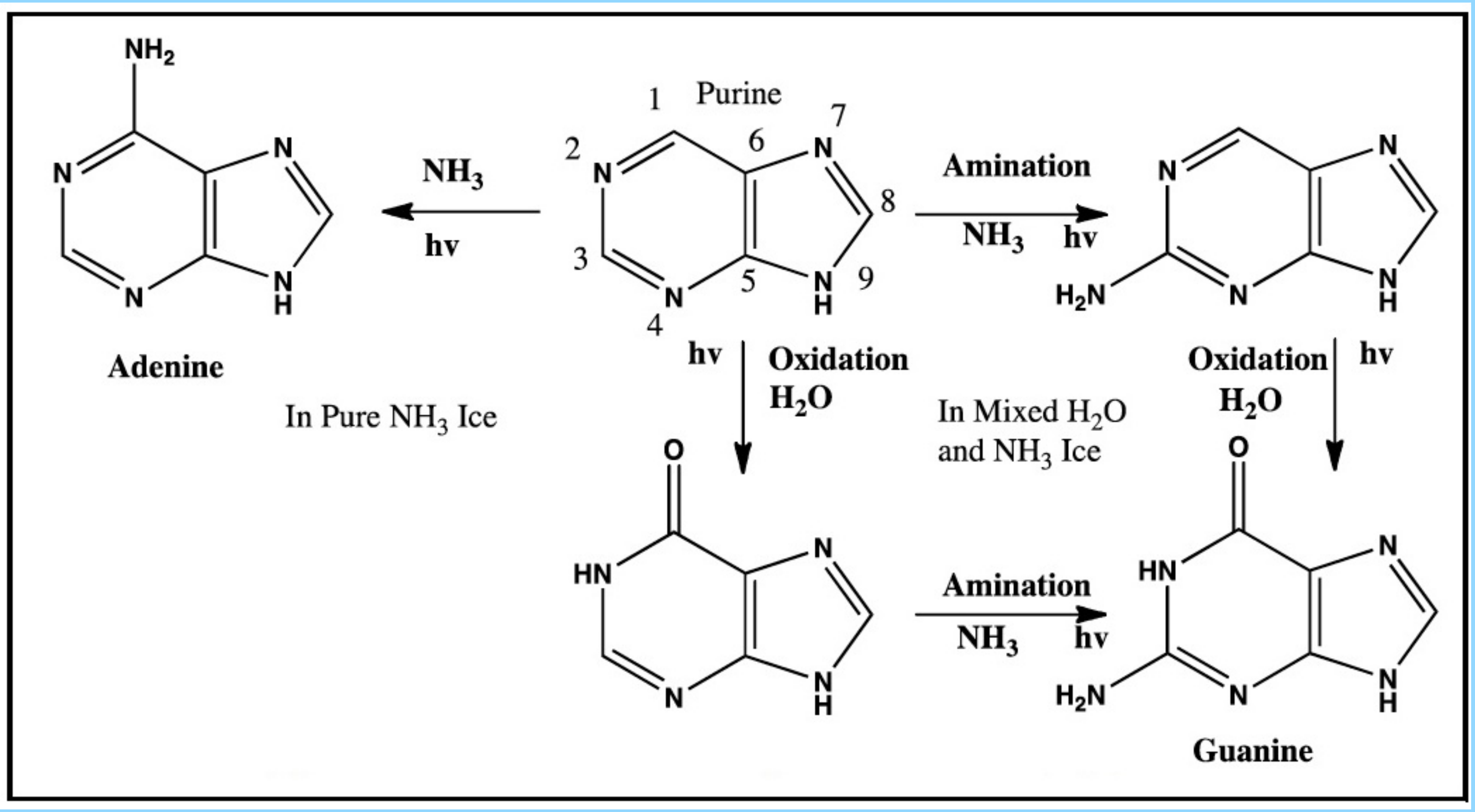




Nuevo et al., Astrobiology, 9, 683 (2009)
Bera et al., JCP, 133, 104303 (2010)
Materese et al., Astrobiology, 13, 948 (2013)
Nuevo et al., ApJ, 793, 125 (2014)

Quantum Chemistry Studies

One of our next combined tasks will be to see if similar chemical processes can produce the purine-based nucleobases



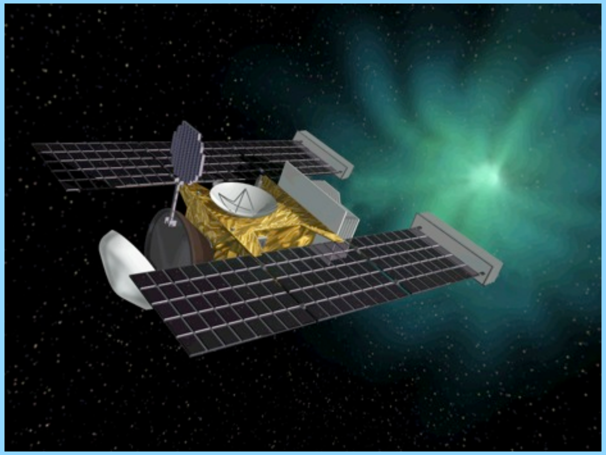
Extraterrestrial Samples and Sample Return Missions

Members of our Team, particularly the PI, have a heavy involvement in the study of extraterrestrial materials, and in past, current, and future Sample Return missions, including

- The *Stardust* comet sample return mission (past)
- The *Hayabusa* asteroid sample return mission (past)
- The *OSIRIS-REx* asteroid sample return mission (current)
- The *CORSAIR* comet surface sample return mission (concept)

These efforts give us the ability to compare computational and laboratory results against real extraterrestrial materials


Sutter's Mill meteorite


Stardust

Hayabusa


OSIRIS-REx

Conclusion

We're new, we're back, and we're chomping at the bit to get started!

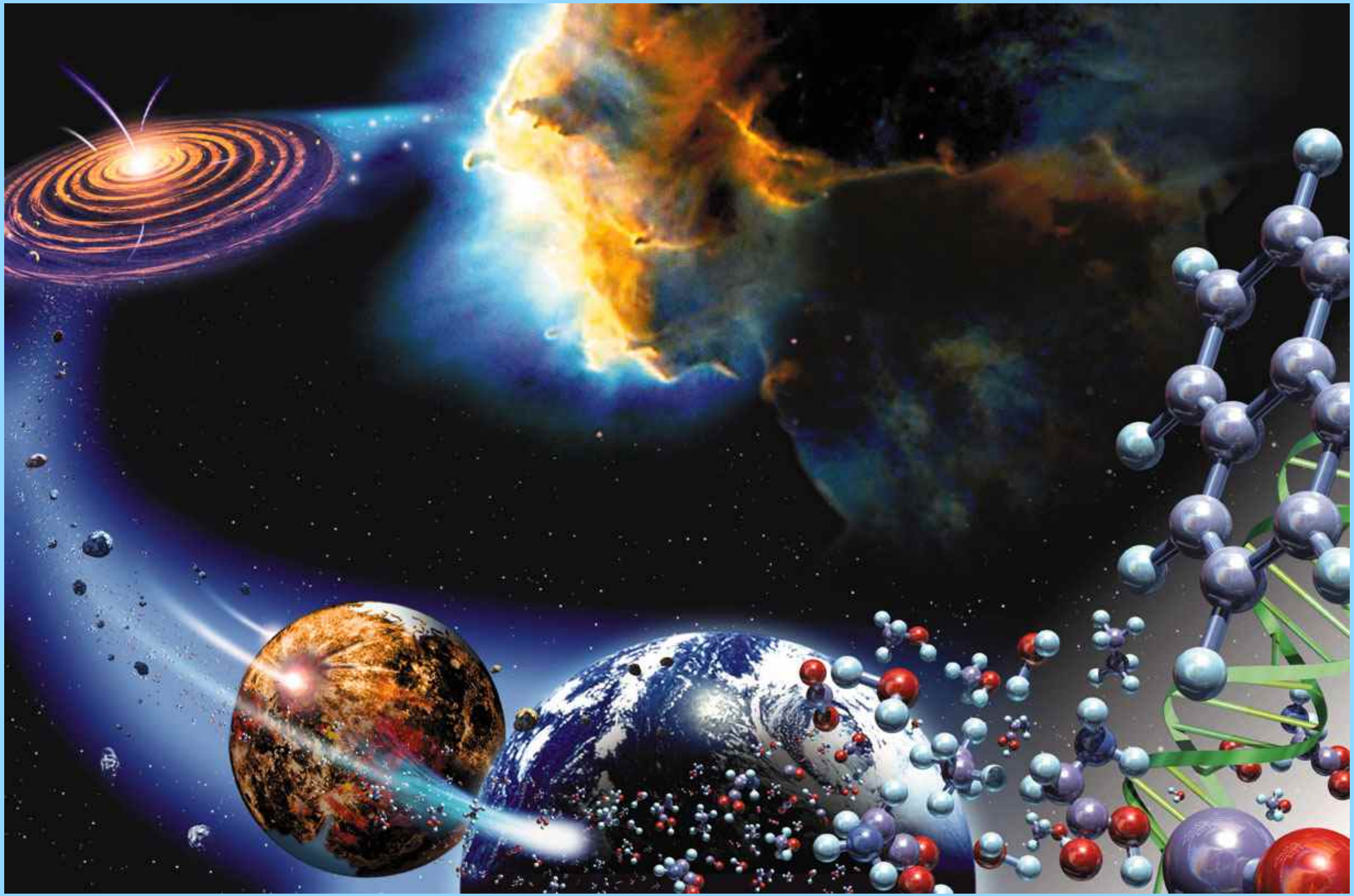


Image from Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. (1999). Life's Far-Flung Raw Materials. *Scientific American* **281**, #1, 42-49.