THE FORMATION OF NUCLEOBASES FROM THE IRRADIATION OF PURINE IN ASTROPHYSICAL ICES AND COMPARISONS WITH METEORITES. S. A. Sandford1, C. K. Materese1,2, and M. Nuevo1,2, 1NASA Ames Research Center (Scott.A.Sandford@nasa.gov), 2Bay Area Environmental Research Institute.

Introduction: N-heterocycles have been identified in meteorites and their extraterrestrial origins are suggested by isotopic ratio measurements [1]. Although small N-heterocycles have not been detected in the interstellar medium (ISM), recent experiments in our lab have shown that the irradiation of the aromatic molecules like benzene (C6H6) and naphthalene (C10H8) in mixed molecular ices leads to the formation of O- and N-heterocyclic molecules [2]. Among the class of N-heterocyclics are the nucleobases, which are of astrobiological interest because they are the information bearing units of DNA and RNA. Nucleobases have been detected in meteorites [3–5], with isotopic signatures that are also consistent with an extraterrestrial origin [1]. Three of the biologically relevant nucleobases (uracil, cytosine, and guanine) have a pyrimidine core structure while the remaining two (adenine and guanine) possess a purine core. Previous experiments in our lab have demonstrated that all of the biological nucleobases (and numerous other molecules) with a pyrimidine core structure can be produced by irradiating pyrimidine in mixed molecular ices of several compositions [6–8].

In this work, we study the formation of purine-based molecules, including the nucleobases adenine, and guanine, from the ultraviolet (UV) irradiation of purine inices consisting mixtures of H2O and NH3 at low temperature. The experiments are designed to simulate the astrophysical conditions under which these species may be formed in dense molecular clouds, protoplanetary disks, or on the surfaces of icy bodies in planetary systems.

Experimental: Gas mixtures were prepared in bulbs attached to a glass line. The relative proportions of each component were established using partial pressures. An evacuated sample tube containing pure purine was prepared separately, attached to the vacuum chamber, and wrapped with heat tape and a thermocouple to monitor temperature. The bulbs containing gas mixtures were deposited on an aluminum foil attached to a cold finger (< 20 K) along with purine from the heated sample tube. The combined ices formed from the gases and purine were simultaneously irradiated with an H2-discharge lamp emitting UV photons (Lyman α at 121.6 nm and a continuum at ∼160 nm). After irradiation, samples are warmed to room temperature, and refractory residues are recovered for derivatization and analysis using gas chromatography coupled with mass spectroscopy.

Results: The UV irradiation of our experimental ice mixtures results in the formation of refractory residues containing functionalized purines. This included the nucleobases adenine (Figure 1) and possibly guanine, in addition to hypoxanthine, isoguanine, several aminopurines, and 2,6-diaminopurine. While adenine is one of the most abundant photoproducts of these UV-irradiation experiments, guanine appears to be produced with very low to undetectable levels of abundance. One possible explanation of this may just be that guanine production is far less favorable than alternative structural isomers. However, guanine has a propensity form strong hydrogen bonds with itself and other molecules, which greatly reduces its solubility in most solvents and thereby makes it more difficult to derivatize and detect in the GC-MS. In this case, guanine may be being produced but not be amenable to detection by GC-MS. This same chemical behavior would have represented a significant difficulty in the inclusion of guanine into early RNA and DNA, and it has been suggested that the compound hypoxanthine may have preceded guanine in this capacity [9]. In this regards, it is interesting to note that hypoxanthine is abundant in the organic products found in our experiments.