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Chemical Evolution in the Interstellar Medium: Feedstock of Solar Systems

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Great strides have been made in our understanding of interstellar material thanks to advances in infrared and radio astronomy and laboratory astrophysics. Ionized polycyclic aromatic hydrocarbons (PAHs), shockingly large molecules by earlier astrochemical standards, are widespread and very abundant throughout much of the cosmos. In cold molecular clouds, the birthplace of planets and stars, interstellar atoms and molecules freeze onto dust and ice particles forming mixed molecular ices dominated by simple species such as water, methanol, ammonia, and carbon monoxide. The interplay between the gas and the dust leads to a very rich chemistry in these clouds. Within these clouds, and especially in the vicinity of star and planet forming regions, these ices and PAHs are processed by ultraviolet light and cosmic rays forming hundreds of far more complex species, some of biogenic interest. Eventually, these are delivered to primordial planets by comets and meteorites. The chemical context, highlights of this field from a chemist's perspective, and the astronomer's infrared toolbox will be reviewed.

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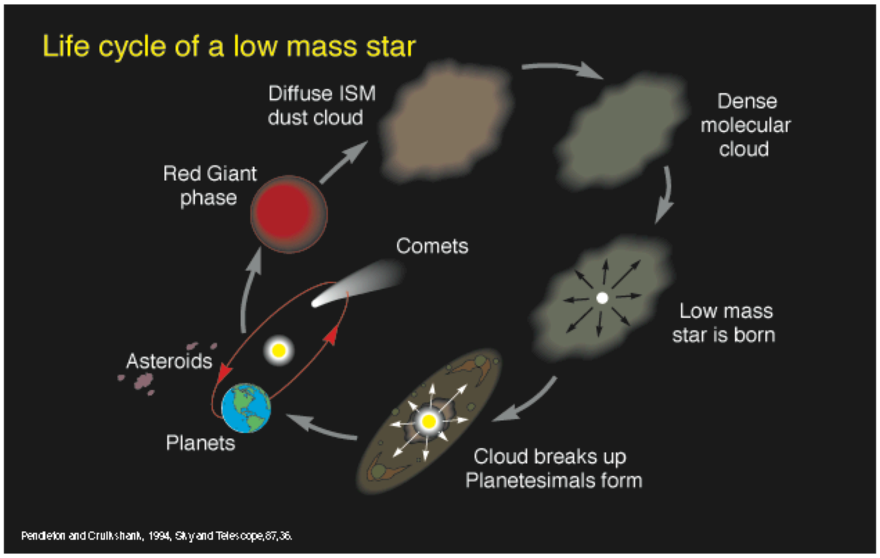
Introduction

Throughout most of the last century it was believed that the chemical compounds in space are rather simple, with chemical complexity limited by harsh radiation fields and extremely low densities. Indeed, the only interstellar species known through most of the first half of the 20th century were the highly reactive CH, CH^+, and CN (*1*). The picture of a chemically sterile universe was so ingrained that the discovery of interstellar OH in the early 1960's made headlines. This broke the spell and detections of interstellar NH_3, CO, and H_2CO followed over the next few years. The realization that deep space might harbor polyatomic molecules was so startling that the discoverers of interstellar H_2CO concluded their paper stating 'Polyatomic molecules containing at least two atoms other than H can form in the interstellar medium" (*2*).

We have come a long way from those early days of interstellar molecule detection in a very short time. Thanks to breakthrough developments in observational infrared (IR) and radio astronomy, combined with dedicated laboratory experiments, we now know that the cosmic chemical inventory is far richer than found in any chemistry department stockroom. Today the list of interstellar molecules in the gas phase numbers over 130 and includes exotic species such as the linear cyanopolyacetylene, $HC_{11}N$. Large, complex polycyclic aromatic hydrocarbons are ubiquitous throughout the modern Universe and there is mounting evidence that they were already present only a few billion years after the Big Bang. Furthermore, complex molecules, including some that are biologically interesting, are readily formed in realistic laboratory simulations of interstellar and Solar System ices. Consequently, it is entirely possible that the extraterrestrial evolution of chemical complexity may play a crucial - perhaps even a determinant - role in defining the early, chemical state of young planetary systems. Compelling evidence is mounting that a substantial fraction of the compounds incorporated into planets, their satellites, asteroids, and comets in developing planetary systems is in the form of complex organic molecules. Moreover, the relative cosmic abundances of O, C, and N underscore the fact that (ignoring the chemically inert helium) these elements are *by far* the most abundant chemically reactive elements after hydrogen, dwarfing the amounts of the next tier of elements including that of silicon. This implies that chemistry throughout the cosmos is most likely composed of these most abundant elements and therefore evinces a chemistry similar to our own.

The history of the elements heavier than Li begins with their nucleosynthesis deep within the interiors of late-type stars (*3,* and references therein). Once formed they become part of the repeating cycle shown in Plate 1. These elements are thrown off into the surrounding interstellar medium during the periods of intense mass-loss that occur during the late asymptotic giant branch, or Red Giant, phase (Plate 1). Densities are high enough in the stellar "atmosphere" to allow chemical reactions to occur and a wide array of materials are produced as these elements are ejected into the interstellar medium (ISM), the space between the stars. For carbon-rich stars



Pendleton and Cruikshank, 1994, Sky and Telescope, 87, 36.

Plate 1.The chemical elements heavier than Lithium are produced by nucleosynthesis in Red Giant stars and injected into the interstellar medium during the Red Giant phase. Once in the interstellar medium, they participate in the chemsitry at each stage of this cycle. These objects are not drawn to scale. A Red Giant can swell to sizes that engulf the inner planets of our Solar System. The diffuse ISM can be as vast as the space between the spiral arms of our Galaxy, The Milky Way, while molecular clouds measure from hundreds to hundreds of thousands of light years across. There are many star forming regions in molecular clouds, each several times the size of the Solar System. Figure reproduced with permission from (12).

this includes simple radicals and molecules (<20 atoms) such as C_2, acetylene, carbon monoxide, the polyacetylenes and cyanopolyacetylenes; large, robust molecules (tens to hundreds of atoms) such as polycyclic aromatic hydrocarbons (PAHs) and heterocyclics; and small (100-1000 Å, several thousands of atoms or more) amorphous carbon dust particles (*4* and references therein). The ejecta for oxygen-rich stars includes molecular species such as H_2O, CO, OH etc.; mineral building blocks including silicon and magnesium oxides; and silicon rich dust particles. The vast surrounding diffuse ISM (Plate 1) is generally very tenuous. In the diffuse ISM, these compounds and particles are further modified through a variety of physical and chemical processes including: UV irradiation; cosmic ray bombardment; very low density gas-phase chemistry; some accretion and reaction upon grain surfaces; and destruction by shock waves generated by supernova explosions. While refractory dust particles and large molecular species such as PAHs are relatively immune to photodestruction in the diffuse

ISM, the simpler polyatomic molecules cannot withstand the harsh interstellar UV-radiation field and quickly dissociate.

However, the existence of interstellar matter is not limited to these tenuous, transparent regions. Much material is concentrated in large, relatively opaque, interstellar molecular clouds (Plate 1) (*5-7*). In contrast with the diffuse interstellar medium which is characterized by very low hydrogen number densities (~1-10 H atoms cm^{-3}), the number densities in molecular clouds are much higher (>10^4 H atoms cm^{-3}). Astronomers often express measurements in terms of hydrogen because, as illustrated in Figure 1, it is the most abundant of the cosmic elements. Hydrogen is some three to four orders of magnitude more abundant than C, N, and O, and has a number density that is roughly twelve orders of magnitude greater than that of the submicron sized dust particles. Although interstellar molecular cloud number densities correspond to the best vacuum achievable on Earth, and the optical path across any laboratory chamber at this pressure would be quite transparent, the background starlight that fills the diffuse ISM is strongly attenuated by dust particles in these "dense" clouds. This is because the clouds are hundreds to hundreds-of-thousands of light years across and, although their number densities are low, they are so large that the dust particles block out the starlight from the surrounding diffuse ISM.

This screening out of the UV-rich diffuse ISM radiation field permits simple, fragile molecules to form and flourish within these clouds through a rich network of gas phase reactions. Although a wide variety of these simple molecular species have been identified in the gas phase by extensive radio and infrared observations (*8*, and references therein) of their rotational and vibrational transitions, these represent only one aspect of the chemical inventory of these regions. At the low temperatures which characterize these dark molecular clouds (≈ 10 - 50 K), the majority of molecular species are expected to be frozen out upon the surfaces of cold, refractory grains (*9*). Thus, the molecular inventory of cold, dark interstellar clouds must be shaped by a *combination* of ion-molecule reactions in the gas phase and gas-grain surface reactions (*6, 10*). Moreover, the attenuated diffuse interstellar UV which penetrates dense clouds, as well as UV from internal sources and penetrating cosmic ray particles are sufficient to drive *in-situ*, solid-state reactions within the icy dust grain mantles leading to a variety of even more complex species (*11*). The chemistry in these dense, interstellar molecular clouds involves a complex interplay of these three processes.

It is within cold, dark molecular clouds such as this that new stars and planetary systems are born (Plate 1). Once part of a molecular cloud becomes unstable under its own gravitational field, it will begin to collapse, forming a protostar. As this collapse proceeds, the angular momentum possessed by the infalling material draws it into a disk. Planetary systems are thought to coalesce from the remnants of this protostellar accretion disk after the young star springs to life (the "Solar Nebula"). Thus, the raw material from which planetary

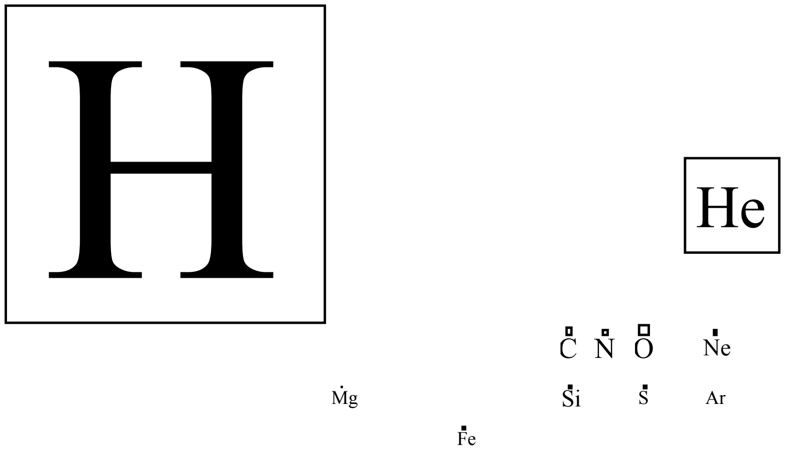


Figure 1. Astronomer's periodic table of the elements. The areas of the boxes illustrate the relative cosmic abundances of the most plentiful elements. Figure courtesy of Professor Ben McCall.

systems form contains the elements in the same diverse states of molecular complexity found in the parent molecular cloud. Naturally, this material may also be modified to some extent by chemistry taking place during the collapse as well as in the accretion shock. Chemical processes at work during this epoch include equilibrium gas-phase reactions in the warmer regions of the nebula and non-equilibrium processes in colder regions and on coalescing planetessimals. Ultimately, the compounds present, whether produced or modified in the nebula or accepted unchanged from the ISM, are incorporated into the condensed matter that became the planets, satellites, asteroids, and comets. Once a terrestrial planet is sufficiently cool to retain volatile materials, cometary and meteoritic materials continuously pepper it with copious quantities of this complex chemical inventory. Eventually, the star exhausts its nuclear fuel, swells into a Red Giant swallowing many of its planets and moons, and its ejecta join the cycle. Thorough reviews of interstellar and solar nebula processes are given in references 5, 6, and 7.

The chemistry of dense, dark molecular clouds prior to planet formation is the topic of this paper. Dr. Ziurys has discussed the inventory and measurement of gas phase interstellar molecules associated with dense molecular clouds in the chapter, "Identifying Molecules in Space" (*8*). Here, the focus is on the chemistry in and on the ices and the interaction of these ices with species in the gas. Since these ices represent the largest repository of interstellar molecules in dense clouds, they tie up a large fraction of the chemical inventory in molecular clouds. As this Chapter is intended for use as a guide book for the undergraduate chemistry student, many of the details presented here utilize material from the younger days of the field to present the foundational ideas. Current references are also included in each area for those interested in following specific topics further.

Infrared Spectroscopy of Molecular Clouds

Interstellar Ice

Before getting into the chemistry, it is important to understand how we determine what is out there and probe the chemistry that occurs thousands of light years away. It is easy to grasp how one can point a telescope at a visible star and, passing the captured ultraviolet and visible light through a spectrometer, identify some of the species comprising the star and the intervening diffuse ISM. This is how the elemental cosmic abundances illustrated in Figure 1 were initially determined. However, molecular clouds are dark. Probing the composition and chemistry within these clouds has come about thanks to fundamental advances in two areas, astrospectroscopy at infrared (IR) and longer wavelengths (Radio) and dedicated laboratory experimentation. Molecular clouds are not "dark" at these longer wavelengths. Experimentalists use modern laboratory tools to measure the IR and radio spectra of interstellar analog materials under simulated, realistic interstellar conditions and these laboratory spectra are used to interpret the astrospectra of molecular clouds.

Radio astronomy measures molecules in the gas phase. Transitions between the rotational states of most molecules that possess a permanent dipole moment absorb or emit electromagnetic radiation at wavelengths spanning the radio range. These observations and implied chemistry are reviewed in reference 8. Since molecules condensed on cold dust grains cannot rotate, they do not possess a rotational spectrum and are undetectable by observations at radio wavelengths. Infrared astronomy, which probes molecules in both the gas and solid phases, provides the rest of the story. The vibrations between atoms and subgroups that comprise a given molecule vibrate at specific, characteristic frequencies. Those vibrations that involve a change in dipole moment absorb or emit electromagnetic radiation at these bond-specific frequencies. Since these transitions fall in the mid-infrared region, chemists routinely use IR spectroscopy to characterize the chemical make-up of materials.

Plate 2 illustrates the dramatic difference between the visible and infrared image of the sky looking towards Orion. The infrared radiation that dominates the IR image of the constellation (colored red in the figure) comes from the blackbody radiation of the interstellar dust particles comprising what is known as the Orion Molecular Cloud which lies behind the stars we see. The IR hot spots (colored yellow) are associated with regions where intense UV radiation is striking the cloud.

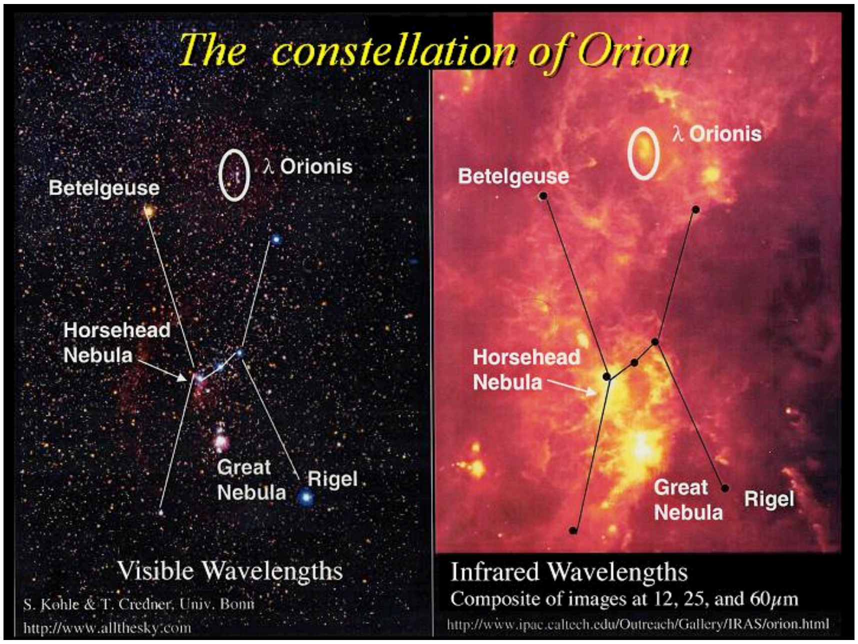


Plate 2. Visible and infrared images of the sky toward the Orion Constellation. Left: Visible Image. The white lines indicate the main stars of the well-known constellation. Right: The Infrared Astronomical Satellite IR image of the same region of the sky. The interconnected dark circles indicate the positions of the now invisible constellation stars. The reddish glow is from the dust in this enormous cloud which is many thousands of light years across. The yellow areas correspond to emission from the warmest dust, generally regions illuminated by light from nearby stars. Clouds such as these are the birthplace of stars and planets and are home to complex interstellar molecules. In this case the cloud is behind the stars that make up the constellation. Otherwise this would appear as a dark patch in the night sky. Figure courtesy of Dr. Andrew Mattioda

Once a dense cloud is formed, thanks to the attenuation of the general interstellar radiation field, gas-phase and gas-grain chemistry leads to the production and sustaining of more complex species in the gas than possible in the diffuse ISM. At the same time, since the dust in a dense molecular cloud is so cold (~20K), any polyatomic molecule striking a dust grain should condense (*9*), and one might expect grain composition to reflect gas composition. However, the simplest and most abundant gas-phase *polyatomic* molecules known from radio observations are orders of magnitude lower in abundance than their frozen counterparts (*13*). Thus, direct accretion of interstellar gas-phase species plays a very minor role in determining interstellar ice composition since the ice grains are chemical factories in their own right, generally harboring far greater amounts of material than the gas.

Interstellar ice compositions are revealed through their IR spectra. As illustrated in Plate 3, a star, fortuitously situated in or behind a molecular cloud, can provide a reasonably featureless, continuous mid-IR background spectrum much as a glow-bar does in a conventional laboratory spectrometer. As this radiation passes through the cold cloud, the intervening molecules in the gas and dust *absorb* at their characteristic vibrational frequencies. Since the diffuse ISM between the outer "edge" of the cloud and the Earth is far less dense, and the majority of interstellar polyatomic molecules are frozen on the grains, the IR absorption spectrum of objects obscured by molecular cloud material is mainly that of the dust in the dense molecular cloud. Since the ice features dominate these spectra, interstellar ice composition can be analyzed by directly comparing the astronomical data with the spectra of ices prepared in a laboratory which duplicate the salient interstellar conditions. This can be accomplished using a cryogenic sample chamber in which thin layers of mixed molecular ices are deposited on a cold (10 - 20 K), IR transparent sample window maintained under vacuum. Sample ice thickness is comparable to that of all the interstellar grain mantles along the line of sight. The infrared spectrum of the ice is then measured and compared directly with astronomical spectra. In a typical experiment, the spectrum of the sample would be measured before and after several periods of exposure to UV radiation and thermal cycles. A more detailed discussion of this approach is given in reference 14.

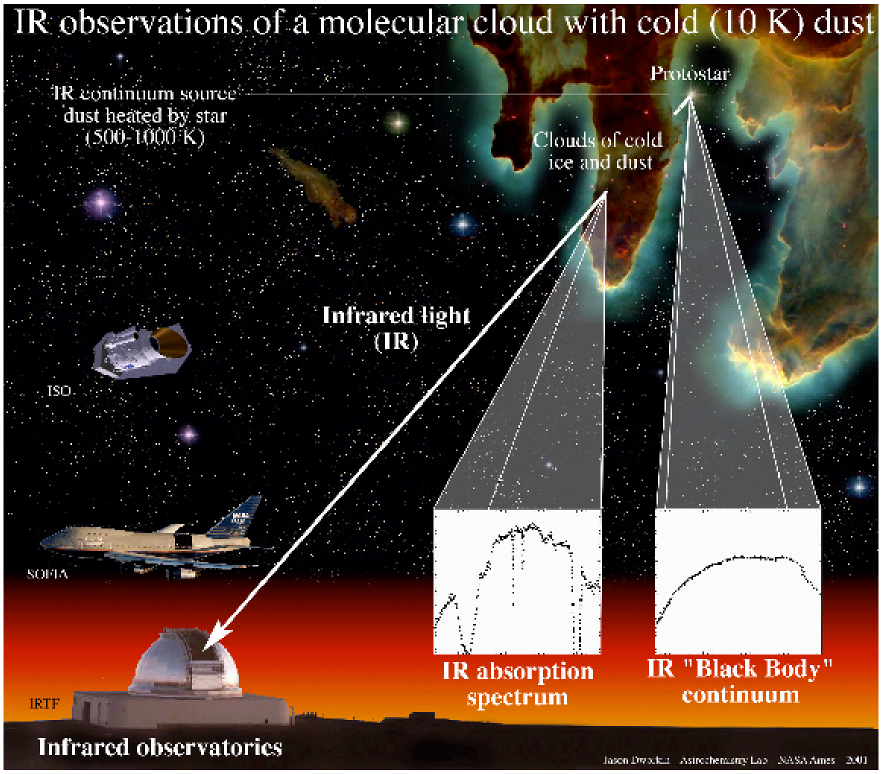


Plate 3. An illustration of how one measures the IR absoption spectra of interstellar clouds. A background star (protostar) serves as the IR source, the cloud is the sample, and the telescope gathers the light and sends it to a monochromator or spectrometer. The advent of airborne IR telescopes in the 70's and orbiting telescopes in the 80's made it possible to avoid IR absoptions by atmospheric H_2O*,* CO_2*, and so on, opening a new window into the Cosmos. Figure courtesy of Dr. Jason Dworkin.*

Figure 2 shows a collage of comparisons between the composite spectrum of W33A, a protostar deeply embedded within a molecular cloud, with the laboratory spectra of interstellar ice analogs (*15-19*). This spectrum of W33 is a combination of spectra measured at different telescopes. With the exception of the strong absorption near 10 µm for which the Si-O stretch from the silicate dust particles overwhelms the overlapping ice features (*20*), most of the absorptions in the spectrum of W33A are readily assigned to ice components. Excellent matches between the interstellar absorption features with laboratory spectra of the type shown in Figure 2 represent the basis of our knowledge of the

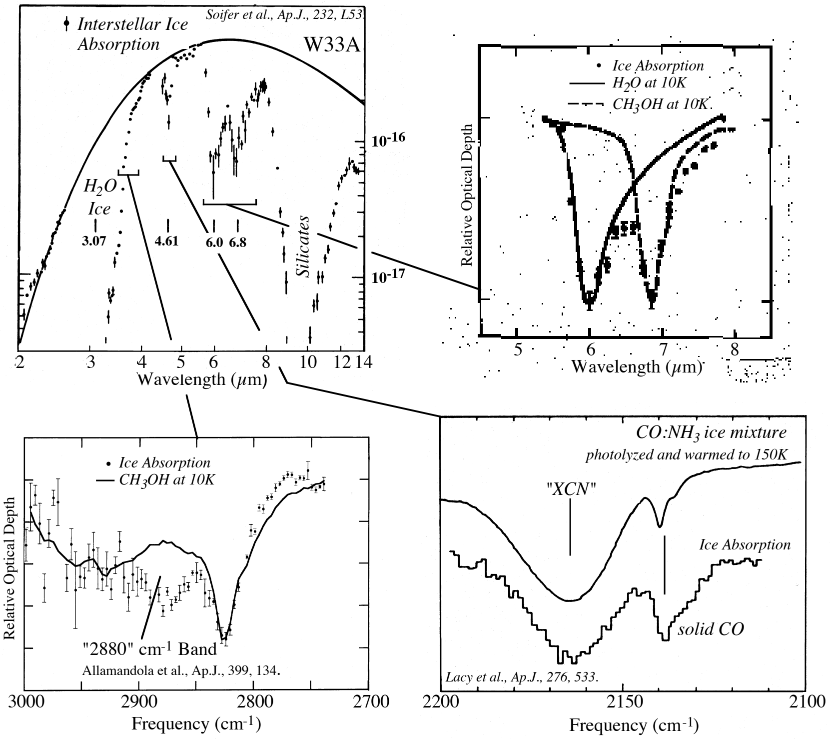


Figure 2. Comparisons of laboratory analog spectra with spectra from the object W33A, a protostar deeply embedded in a dense molecular cloud. Upper left: The dots trace out the interstellar spectrum and the solid line corresponds to the quasi-blackbody emission spectrum thought to be produced by the protostar. The strong absorption near 10 μm is due to the silicate grains and the excess absorption labeled "2880 cm^{-1} Band" visible in the lower left-hand panel is thought to arise from interstellar microdiamonds in the cloud. All the remaining absorptions are produced by interstellar ices. These features are highlighted and compared to laboratory spectra on expanded scales in the surrounding frames. Lower left: The solid line is due to methanol in a laboratory ice. Lower right: The upper smooth line corresponds to a laboratory analog comprised of CO (sharp band) and OCN$^-$ (XCN, broad band). Upper right: The solid and dashed lines correspond to spectra of H_2O and CH_3OH respectively. These data are presented and discussed in references 15-19.

composition of interstellar ice particles. Until quite recently, much more was known of interstellar ice grain composition - submicron sized particles hundreds of light years away - than of cometary ices in our own Solar System. This is still the case for most other icy objects in the Solar System!

Over the past decade, deeper insight into the nature of interstellar ice and dust has been achieved through analysis of data from the European Space Agency's (ESA) Infrared Space Observatory (ISO) and NASA's Spitzer Space Telescope. These missions have enabled measurement of the complete mid-IR spectrum with one instrument, eliminating the need to piece together bits from different telescopes taken at different locations, under different atmospheric conditions and with different spectral parameters (Figure 3). The IR spectra obtained with these telescopes are pushing this field beyond analysis of the strongest spectral features, revealing important subtleties in the spectra that probe details of interstellar chemistry, grain evolution, and cloud development (*6,7,21-23*). Table I compares the dominant interstellar ice constituents with the inferred components from several comets and gives their average abundance with respect to H_2O. Detailed reviews of this topic can be found elsewhere (*6,7*).

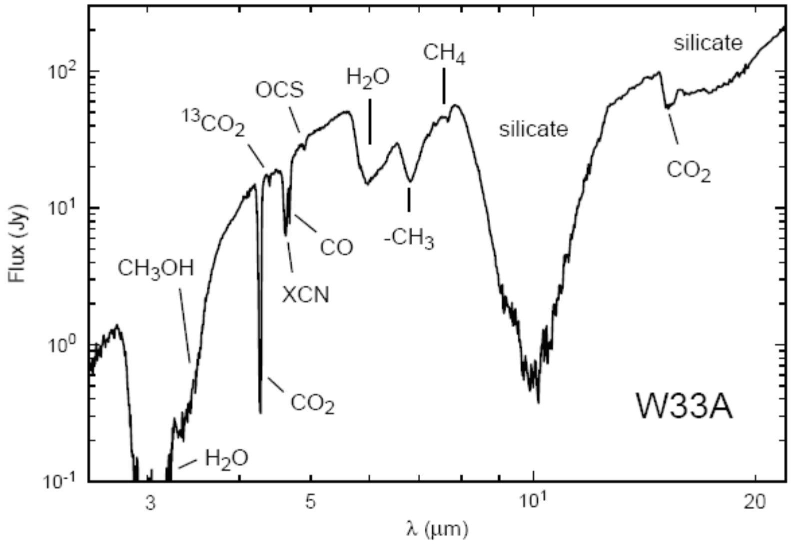


Figure 3. The complete mid-IR spectrum toward W33. The bands have all been identified as described here. This spectrum, measured with ISO, shows the full power of mid-IR astrospectroscopy (6, 21).

Table I. The main interstellar ice components (relative to H_2O) compared to that inferred for several comets. Cometary references: Halley (*24*), Hyakutake and Hale-Bopp (*25*). See Table 2 in Reference 6 for details.

Molecule	Interstellar Ice	Comet Parent Molecules		
	Abundance	Halley	Hyakutake	Hale-Bopp
H_2O	100	100	100	100
CO(polar ice)	1-10			
CO(non-polar ice)	10-40	17	6-30	20
CH_3OH	<4-30	1.25	2	2
CO_2	1-10	3.5	<7	6
OCN^- (XCN)	1-10	---	---	---
NH_3	5-10	1.5	0.5	0.7
CH_4	~1	<0.8	0.7	0.6
H_2CO	1-4	3.8	0.2-1	1
OCS or CO_3	few	0.2	0.1	0.3

Interstellar Polycyclic Aromatic Hydrocarbons

Since this chapter is intended for chemists and the goal is to focus on interstellar chemistry, it would be seriously remiss to omit discussion of the discovery that polycyclic aromatic hydrocarbons (PAHs), large, complex, chicken-wire structured, organic molecules, are ubiquitious and abundant throughout the cosmos (*26, 27*). This realization, also driven home by IR astrospectroscopy and dedicated laboratory analog studies, has shaken the astrochemist's view of the universe to its foundation. In a nutshell, an infrared *emission* spectrum is observed from a wide variety of galactic and extragalactic objects that is produced by vibrationally excited (hot) PAHs. The picture that has emerged is one in which the PAHs and nitrogen heterocycles (PANHs), which were formed during the Red Giant mass loss phase, survive the rigors of interstellar space because of their inherent chemical stability and participate in *every* stage of the cycle shown in Plate 1. The distribution of PAH emission from a spiral galaxy similar to our own is shown in Plate 4. The interstellar PAH IR emission features, shown in red in Plate 5, are obvious in many spectra of the cosmos. They are even implicated in the spectra of objects that appeared only a few billion years after the Big Bang. A thorough presentation of the cosmic PAH model, incorporating a chemist's perspective, is given in reference (*28*), and a recent review of the observations can be found in reference (*29*). The presence of such complex organic species, apparently widespread and abundant throughout the Universe, has come as quite a surprise, and the implications of this realization are yet to be understood.

Plate 4. Spitzer Space Telescope IR image of M 81. The red color traces the strong PAH emission band between about 7 and 9 µm shown in Plate 5.

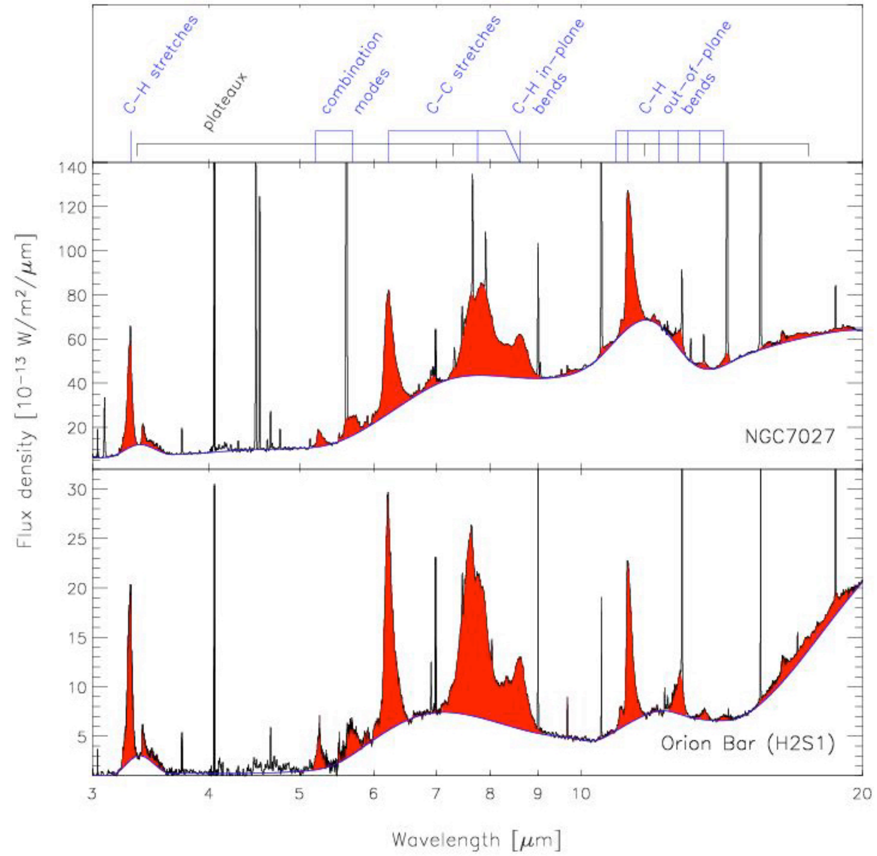


Plate 5. Two examples of the IR emission spectra from interstellar PAHs. The upper spectrum is of PAHs that were "freshly" ejected from a Red Giant. The lower spectrum is from the Great Nebula in the Orion molecular cloud (Figure 3, bottom, center,both panels) where it is exposed to the intense UV field from hot, young stars. The red features are all attributed to PAHs. The fundamental vibrations which produce the features are summarized across the top of the figure. The underlying broad structure is thought to arise from overlapping individual bands from PAHs and larger species. The variations between spectra reveal differences in the PAHs present in each object, reflecting the unique chemical history and conditions within the PAH emission region. Plate courtesy of Dr. Els Peeters, see reference (29). Examples of PAH structures are shown in Figure 8.

Chemical Evolution within Dense, Dark, Molecular Clouds

The picture of mixed molecular interstellar ice described up to this point is supported by direct spectroscopic evidence (e.g. Figures 2, 3). The identities, relative amounts and absolute abundances of the ice species listed in Table I are sound (see references 6 and 7 and references therein for detailed discussions). However, this is not the entire story. Indeed, from a chemist's perspective, this is only the beginning of the story. As mentioned above, throughout the cloud's lifetime, processes such as accretion of gas phase species, simultaneous reactions on the surfaces involving atoms, ions, and radicals, as well as energetic processing within the body of the ice by ultraviolet photons and cosmic rays all combine to determine the ice mantle composition (*5-7*). Theoreticians are continuously developing and improving models that attempt to describe this chemistry, account for the species observed, and predict their abundances (*30-32*). However, due to the range of the very different chemical processes posited, our poor understanding of the chemical processes involved, and the very limited amount of experimental kinetic data taken at the relevant temperatures and pressures, a detailed description of the chemistry is well beyond current capabilities. Consider the following; since hydrogen is 3 to 4 of orders of magnitude more abundant than the next most abundant reactive elements such as C, N, and O, overall grain surface chemistry is strongly moderated by the H/H_2 ratio in the gas. In regions where this ratio is large, H atom addition (hydrogenation) dominates and species such as CH_4, NH_3 and H_2O are expected to be prominent (*33*). If the H/H_2 ratio is substantially less than one, however, reactive heavy atoms such as O and N are free to interact with one another forming molecules such as CO, CO_2, O_2 and N_2. Thus, two qualitatively different types of ice mantle may be expected from grain surface reactions; one dominated by hydrogen-rich, polar molecules, capable of hydrogen-bonding and the other dominated by hydrogen-poor, non-polar (or only slightly polar), highly unsaturated molecules. The different types of chemistry that polar and non-polar ice mantles promote are as different as the processes that can occur in oil versus those that can occur in water. Add to this the interplay between condensation of larger interstellar species from the gas phase, UV and cosmic ray bombardment, thermal cycling, etc. and the computational challenge is clear.

Interstellar Ice Photochemical Evolution

Experimentalists in several laboratories around the world have focused on the photochemical evolution of ice grain mantle analogs to shed some light on the chemistry that occurs when the ices in dense molecular clouds are irradiated by UV photons and cosmic rays, breaking and rearranging chemical bonds within the ice to form new species (*14, 34-36*). This chemistry is illustrated in Plate 6. Although the abundance of these new species is only a few percent, energetic processing is critically important since it can create remarkably complex molecules and chemical groups that cannot be made via gas phase and gas-grain reactions at the low temperatures and pressures characteristic of dense clouds. This is because the protection and ready availability of reaction partners in the solid phase favors chemical complexity and diversity while the energetics, radiation fields, and low densities of the gas phase favor simplicity.

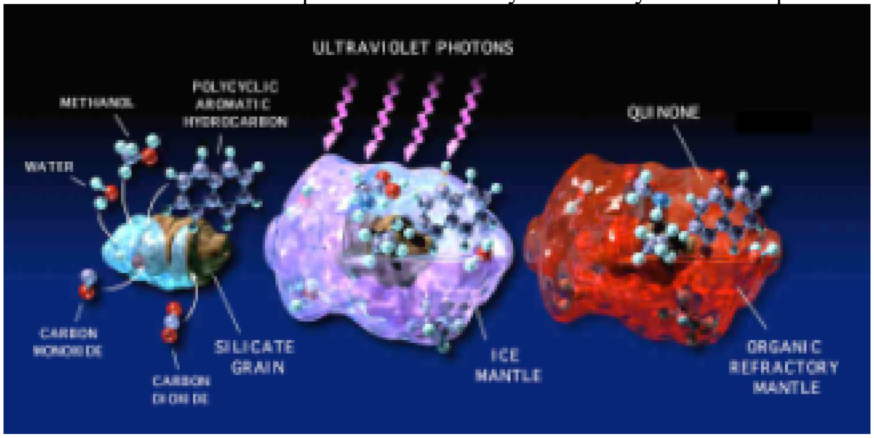


Plate 6. The Greenberg model of interstellar ice mantle formation and chemical evolution. The mantle grows by condensation of gas phase species onto the cold dust grains. Simultaneously, surface reactions between these species, ultraviolet radiation and cosmic ray bombardment drive a complex chemistry. These ice-mantled grains are thought to be micron sized at most. Figure reproduced from (37).

The interstellar/precometary ice composition along the lines-of-sight to regions such as W33 where stars are developing is of particular relevance since these are places where new planets are also forming. The material *immediately* surrounding these star forming regions dominates the absorption spectrum because the volume concentration of gas and dust is many orders of magnitude greater here than it is along the rest of the line of sight. These are the regions in which the OCN^- (formerly XCN), CO_2, and CH_3OH bands are present. The evidence has been building for some time now that these species are tracers of grain reactions and *in-situ* energetic processing. The presence of methanol in these ices is of pivotal importance since it drives a rich interstellar ice photochemistry (*14, 38-40*) and plays an important role in gas phase chemistry (*41*). Furthermore, methanol has profound effects on the physical behavior of H_2O-rich ices (*42*). Since CH_3OH is often an abundant ice component in comets (Table I, cf. references 43 and 44), it may impact their structural, chemical, and vaporization behavior as well.

Figure 4 shows the spectral evolution of an interstellar ice analog comprised of H_2O:CH_3OH:CO:NH_3:C_3H_6 (100:50:10:10:10) as a function of UV photolysis. Except for the C_3H_6, this analog mixture reflects the major interstellar ice components associated with protostellar environments. The

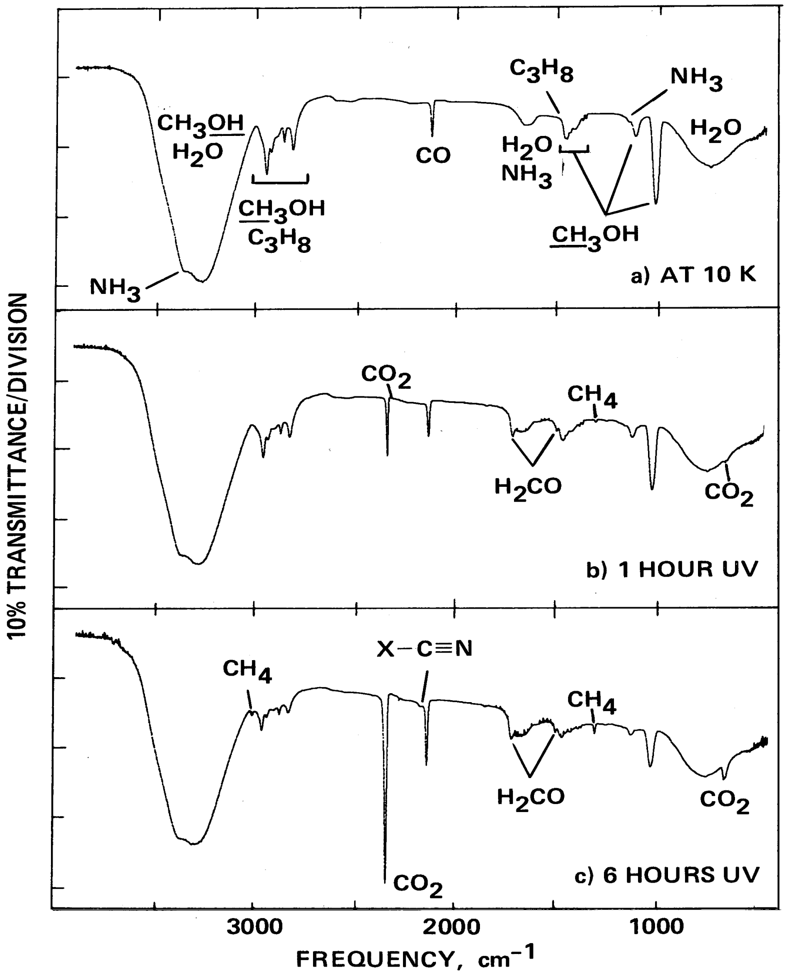


Figure 4. The photochemical evolution of an H_2O:CH_3OH:NH_3:CO:C_3H_8 (100:50:10:10:10) interstellar ice analog as traced by infrared spectra measured at 10 K. The spectra were taken before (a) and after 1 hour (b) and 6 hours (c) of UV irradiation. Note the ready formation of CO_2, H_2CO, CH_4, and XCN (now known to be OCN^-) at the expense of CH_3OH. Figure adapted from reference 14

exposure to UV results in the destruction of several species (particularly methanol) and the creation of others. The simplest and most abundant include the radical HCO, as well as the molecules H_2CO, CH_4, CO, and CO_2. As shown in Table I, almost all of these new species have been identified in interstellar ices and there is indirect evidence for HCO. The detection of these ice components in dense molecular clouds does not necessarily imply radiation processing is responsible for their production since many of these molecules can also be formed by gas-phase or gas-grain chemistry. So, at present, all we can say is that observations are consistent with energetic processing. To reiterate, the strongest evidence that energetic processing is important, at least in some locations within dense clouds, is provided by the OCN^- feature (XCN in Figures 2 and 3) and perhaps by CH_3OH and the ubiquity of CO_2. While CO_2 is readily produced by UV photolysis, it can also be formed by reactions between CO and O on the ice surface (*45*). The OCN^- feature cannot be explained by any of the more abundant species predicted by gas-phase and gas-grain chemical models, but is readily made by the radiative processing of laboratory ices containing C, N and O. Excellent, detailed descriptions of the UV-induced chemical evolution of interstellar ice analogs can be found in the literature (*14, 38, 46, 47*). The role of methanol in the ice photochemistry discussed here is very critical to the kinds of compounds produced.

For the remainder of this paper we focus on the photochemical processing of the H_2O-rich, polar ices associated with the environments of high mass protostars. The ice chemistry so far considered involves the photoproduction of the most abundant, simple species in the solid state at 10 K. However, the full scope of the chemistry is much more complex. Upon warm-up to about 200 K under vacuum one observes that the parent compounds and most volatile ice constituents sublime, leaving a residual mixture of less volatile species on the substrate. Of the staggering array of compounds produced from even the simplest starting ice containing H_2O, CH_3OH, NH_3, and CO, only a few have been identified. These are presented in Figure 5. In keeping with their expected low concentration and abundance, clear-cut IR spectroscopic evidence for these types of compounds in interstellar ices is presently lacking, although some of the weak spectral structure detected in the 2000-1250 cm^{-1} region by the ISO and Spitzer space telescopes is consistent with their presence. Additionally, spectral screening by the much more abundant, simpler ice species will likely represent an important, long-term obstacle. Higher quality astronomical spectra than those currently available will be needed to probe the species present at this level of concentration. Even then, identifications will likely be limited to chemical classes. As an aside, the abundance of many interstellar gas phase species, including NH_3, H_2CO, and CH_3OH, is observed to increase in these warmer regions due to their sublimation from ice grain mantles.

The residue that remains after evaporation of the volatiles when the irradiated ice is warmed to room temperature under vacuum is also of interest since it is quite plausible that this type of material is closely related to that preserved in comets, meteorites and interplanetary dust particles (IDPs), and it is believed that these sources deliver between 12 and 30 *tons* of organic material to Earth monthly. During the period of great bombardment some 4

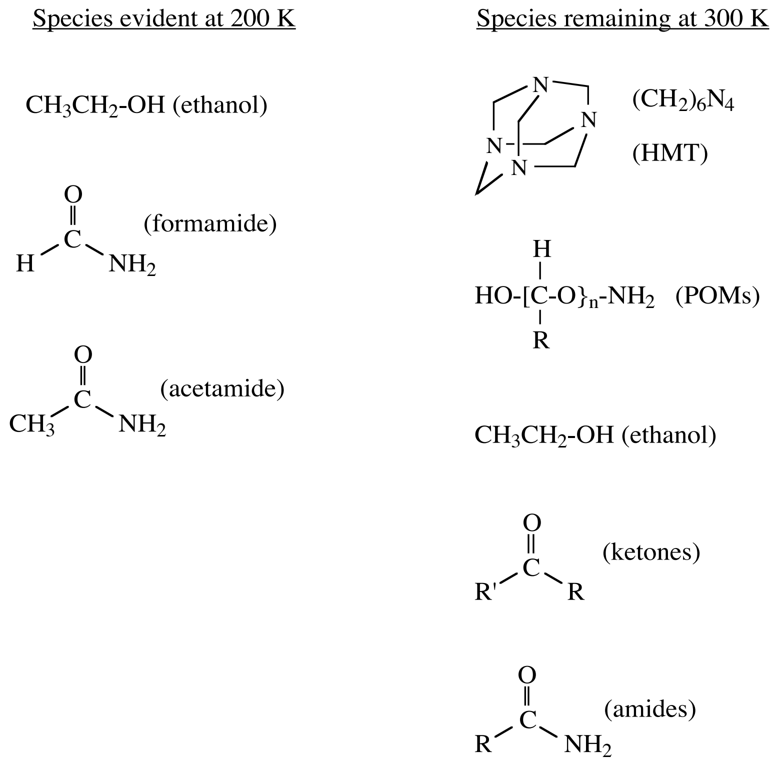


Figure 5. Identified compounds produced by the 10 K UV photolysis and subsequent warm-up of the realistic interstellar ice analogs H_2O:CH_3OH:NH_3:CO (100:50:10:10) and (100:50:1:1). Figure courtesy of Dr. Max Bernstein.

billion years ago, the amount of extraterrestrial organic material brought to the early Earth was many orders of magnitude greater. Thus, this type of material could have played an important role in steering the early chemistry on the primordial Earth.

Now, let's consider more closely the molecules which are produced upon photolysis of *realistic* interstellar ice analogs. The word realistic is used to indicate that the laboratory ice composition reflects the interstellar polar ice composition shown in Table I. The standard ice we study has a starting composition of H_2O:CH_3OH:NH_3:CO (100:50:1:1) or H_2O:CH_3OH:NH_3:CO (100:50:5:5). As evident from Table I, these have slightly higher methanol concentrations (H_2O/CH_3OH ~2/1) than the maximum observed (H_2O/CH_3OH ~3/1). There is good reason for this experimental choice. Even with the higher methanol concentrations, to produce sufficient material for one analytical run requires between two to three months of constant sample preparation. Thus, using a single apparatus for sample preparation it is typically possible to do only four to five experiments *per year*. Reducing the yield would shift this from a very difficult project to one that is impossible given our current analytic capabilities. On the other hand, as the spectra of more molecular clouds become available, higher methanol concentrations are being detected.

Lastly, a comment is in order regarding the other abundant interstellar ice components CO_2, OCN^- (XCN), CH_4, and H_2CO listed in Table I. We are not concerned with their absence in the starting mixture because, as explained above (e.g. Figure 4) they are readily produced upon photolysis at concentrations consistent with the observations. As these are produced at the expense of methanol (*14*), lowering that species concentration, *all the major interstellar ice ingredients known toward massive protostellar environments are represented in this experiment and at roughly the correct concentrations*.

Complex Organic Production in Ices without PAHs

While many of these new species sublime when the irradiated ice is warmed from 200K to room temperature under vacuum, a thick oily residue of non-volatile material remains. Among many other things, this residue is rich in the cage molecule hexamethylenetetramine (HMT, $C_6H_{12}N_4$) (*38*). This contrasts with the organic residues produced by irradiating mixed molecular ices which do not contain methanol (e.g. refs. *14, 38, 39*) and those produced in thermally promoted polymerization-type reactions in non-irradiated realistic ice mixtures (*48*). In those experiments HMT is only a minor product in a residue dominated by a mixture of polyoxymethylene (POM) related species. Remarkably, POMs already start to form in these ices at temperatures as low as 40 K, temperatures at which most chemists would consider reaction between stable species impossible. Further, POM-like species have been suggested as an important organic component detected in the coma of Comet Halley (*49*). The synthesis of HMT by photolysis implies the presence of several other interesting intermediates in these ices as well. For example, there are a variety of secondary carbon and nitrogen containing species which are readily formed by HMT hydrolysis, thermalization, or photolysis, all processes which can occur during an interstellar ice grain, comet, or asteroid's lifetime. The HMT production pathway proposed in reference 38 involves the intermediate methylimine (CH_2N). Armed with this information, radioastronomers searched for and found methylimine to be widespread throughout the gas in many molecular clouds providing additional evidence for a connection between gas and grain chemistry (*50*). Beyond HMT and POMs, the non-volatile residue of photolyzed, methanol containing ices comprises lower concentrations of a bewildering array of organic compounds.

Due to the extreme complexity and analytical challenge posed by deeper analysis, and encouraged by recent interest in the application of these results to early earth biochemistry, effort has been redirected from solely establishing the chemical inventory of species produced in these interstellar/precometary ice analogs to searching for the presence of specific biogenically important species. This effort has involved High Performance Liquid Chromatography (HPLC) and laser desorption-laser ionization mass spectroscopy (L^2MS). Access to the latter technique has been made possible through a collaboration with Prof. R. Zare and his colleagues at Stanford University (*51*). While neither technique can provide an unequivocal identification directly, they are both particularly suited to microanalysis and give very valuable insight into the chemical properties of the compounds that make up the residue.

Figure 6 shows the HPLC chromatogram of one of the residues compared to the chromatogram of a soluble extract from the primitive meteorite Murchison. There are two conclusions to be drawn from this figure. First, since each peak represents a different compound, or more likely a different family of compounds, both the laboratory residue and meteoritic extract are complex chemical mixtures. Second, the similarity in peak distributions between the two samples indicates that the kinds of chemicals present in each sample are similar. This similarity raises the interesting question, "Do the families of compounds in carbonaceous meteorites have an interstellar ice/cometary heritage?"

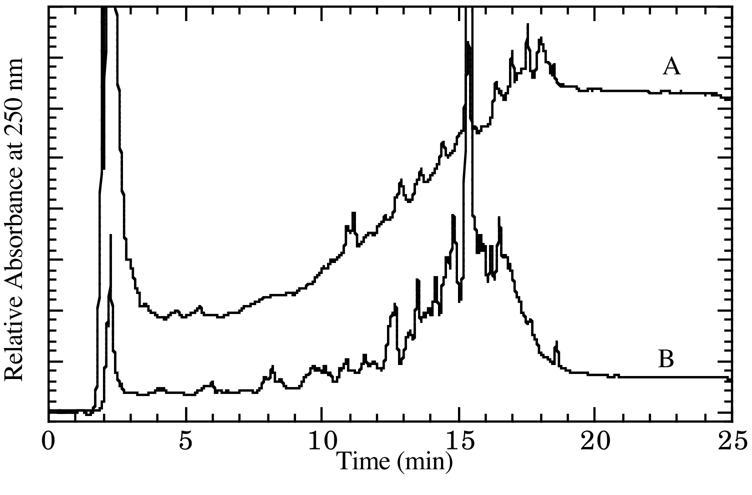


Figure 6. The high performance liquid chromatogram (HPLC) of (A) the room temperature residue produced by UV photolysis of an $H_2O:CH_3OH:NH_3:CO$ (100:50:1:1) ice (profile magnified 10x) and (B) mixed acid and base extracts of Murchison meteorite. Figure courtesy of Dr. Jason Dworkin. See (40)

Figure 7 shows the L^2MS of the residue from a photolyzed $H_2O:CH_3OH:NH_3:CO$ (100:50:1:1) ice. Mass spectra such as this provide us with further critical insight into the nature of the residue, showing that there are hundreds of compounds produced. Further, this shows that they are far more complex than the starting materials. The new materials produced are responsible for the envelope spanning the mass range from about 100 m/z to 350 m/z. (m/z is equivalent to an atomic mass unit). Given that none of the simple starting materials of $H_2O:CH_3OH:NH_3:CO$ has a mass greater than 32, nor do they contain a single CC bond, the complexity and extent of the photoproducts is staggering. Many of these compounds have molecular masses up to *ten times* larger than that of any of the starting materials. When this mass spectrum is compared with those of two interplanetary dust particles (IDPs) there is an intriguing similarity between the mass envelope of the interstellar ice analog residue shown in Figure 7 and the mass envelopes in the IDP spectra (*52*). As with the HPLC results above, this resemblance between the laboratory ice residue and the extraterrestrial organics brought to Earth - this time in IDPs - again raises the question, "Do the compounds in IDPs have an interstellar ice/cometary heritage?" Since many IDPs are thought to originate in comets, the connection with interstellar cloud chemistry gets tighter.

Greenberg et al. (*53*) reported a fascinating study of residues produced by the photolysis of the somewhat different mixed molecular ices $H_2O:CH_3OH:NH_3:CO$ (100:20:20:100) and $H_2O:CH_4:NH_3:CO$ (100:40:40:40). These residues were placed in small sample chambers on the EURECA satellite and exposed to solar radiation through a UV-visible transparent MgF window. The residues were returned to Earth after a four month exposure. Subsequent analysis of these residues using the L^2MS technique showed a pattern reminiscent of the one presented in Figure 7, but now with mass peaks corresponding to the PAHs coronene, benzoperylene, pyrene, and phananthrene particularly strong.

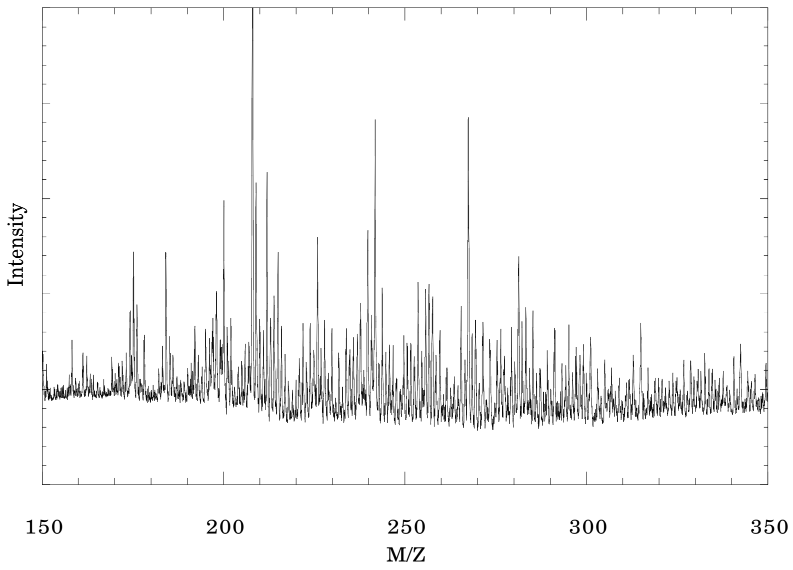


Figure 7. The laser desorption (L^2MS) mass spectrum of an interstellar ice analog residue produced by the photolysis of a H_2O:CH_3OH:NH_3:CO (100:50:1:1) ice. The complexity of the interstellar ice analog residue is clearly evident (52). See also reference (53).

Complex Organic Production in Ices with PAHs

As mentioned above, as a class, PAHs are among the most abundant interstellar polyatomic molecules known in the gas and are widespread throughout the interstellar medium. As with all other polyatomic gas phase species in dense clouds, they should freeze out onto the grains and become part of the mixed molecular ice. Indeed, weak, broad absorption bands are evident in dense cloud spectra that are consistent with PAHs frozen in the ice mantles. However, the strong absorption bands of the main ice species screen out the weaker PAH features. The photochemical behavior of PAHs in H_2O ices has also been investigated in order to lay the foundation for a study of PAH photochemistry in realistic, multicomponent interstellar ice analogs.

While the UV photolysis of PAHs in interstellar ices likely modifies only a fraction of the interstellar PAH population, this change is significant in terms of interstellar chemistry and interesting from the prebiotic chemistry perspective. Upon photolysis in pure H_2O ice at 10 K, simple PAHs are not destroyed. Almost immediately upon irradiation, 70 to 80 % of the PAHs are readily ionized to the positively charged (cation) form (*54*). Remarkably, these PAH cations are not reactive in these ices at all until they are warmed above 100 K (*55*). Even above 100 K, the PAH cation reacts slowly with other species in the H_2O ice, ultimately producing the types of species shown in Figure 8 and discussed below (*56*). Some of these PAH ion charged ices are gently colored, raising the speculation that perhaps organic ion containing ices are responsible for some of the coloring of many icy objects in the Solar System, such as Saturn's icy moons and rings and the icy moons of Jupiter.

After warm-up to room temperature, we find that the PAHs in the residue have been partially oxidized and/or reduced (hydrogenated), forming structures as shown in Figure 8 (*57*). If deuterium is present in the ice, deuterated aromatics are also produced (*58, 59*). These alterations have significantly different effects on the chemical nature of the parent. Hydrogen atom addition transforms some of the edge rings into cyclic aliphatic hydrocarbons, thereby creating molecules with both aromatic and aliphatic character and decreasing the overall degree of aromaticity. Oxygenation produces ketones or aldehydes, changes which open up an entire range of possible chemical reactions that were not available to the parent PAH. Aromatic ketones are of particular interest since they are present in meteorites and closely related compounds are widely used in current living systems for electron transport across cell membranes. In view of PAH photochemistry in pure H_2O ice, it seems plausible that aromatic structures decorated with alkyl, amino, hydroxyl, cyano, carboxyl, and other interesting functional groups may be produced when mixed-molecular ices containing PAHs are photolyzed and warmed. Laboratory experiments have demonstrated that the aromatic structures decorated with alkyl, amino, hydroxyl, cyano, carboxyl, and other functional groups seen in meteorites are consistent with a pre-solar ice chemistry driven by UV photons and cosmic rays (*60, 61*).

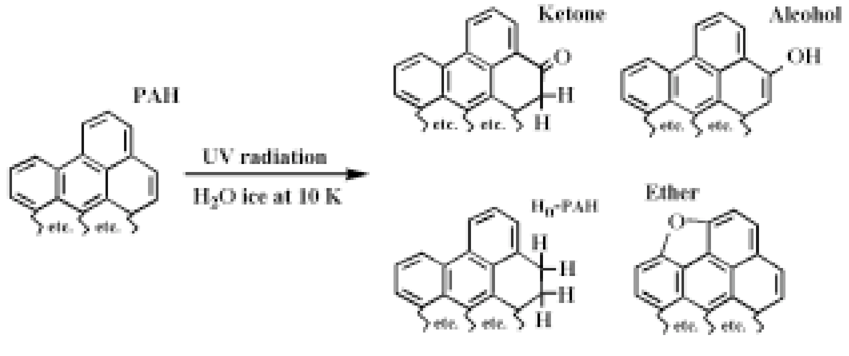


Figure 8. The types of PAH structures found in the residue that remains after PAHs are UV radiated in water ice at 10 K and the sample is warmed to room temperature under vacuum (57).

Recently, we have also investigated the chemistry of polycyclic aromatic nitrogen heterocycles (PANHs) in interstellar ice analogs (*62*). PANHs are structurally similar molecules to PAHs, with one or more nitrogen atoms substituted for carbon in the molecular skeleton. These compounds are also believed to be present in the ISM (*63*) and should be present in interstellar ices. Experiments in which PANHs are photolyzed in water ice form species that are similar to those formed when PAHs are photolyzed in interstellar ice analogs. These too are found in the Murchison meteorite (*64*).

Interstellar PAHs, Ices, and Chemistry on the Early Earth

To better understand the role these interstellar/precometary residues might have played in the chemistry on the early Earth, we have also investigated both their bulk or collective chemical properties and searched for specific molecules such as amino acids. Examples of both will be given here.

We have focused on collective chemical properties in collaboration with Professor D. Deamer from the University of California, Santa Cruz. While much of the residue described above dissolves rapidly when added to liquid water or methanol, water-insoluble droplets are also formed (*11, 40*). Plate 7 shows a micrograph of these non-soluble droplets in water. Many of the droplets also show intriguing internal structures. Droplet formation shows that some of the complex organic compounds produced in these interstellar ice analogs are amphiphilic, i.e. they have both a polar and non-polar component, similar in structure to the molecules which comprise soap. These are also the types of molecules that make up cell membranes, and membrane production is considered a critical step in the origin of life. These droplets can encapsulate

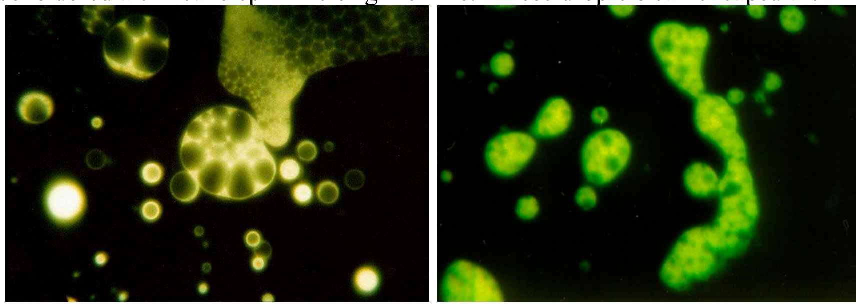


Plate 7. (A) Fluorescence micrograph of the water insoluble droplets formed from a Murchison meteorite extract (67) compared to (B) the fluorescent droplets produced from the photolysis residue of the interstellar/precometary ice analog: H_2O:CH_3OH:NH_3:CO (100:50:1:1) at 10 K (40). The similarity between these vesicles is another indication of similarity between the laboratory ice residue and extraterrestrial organics in meteorites.

hydrophilic fluorescent dyes within their interior, demonstrating that they are true vesicles (hollow droplets) with their interiors separated from the surroundings by their lipid multilayer (see Figure 5 in reference 40). Vesicle formation is thought critical to the origin of life since vesicles provide an environment in which life can evolve, isolating and protecting the process from the surrounding medium. For example, within the confines of a vesicle, pH can be moderated and held at a different value from that in the surrounding medium, and nutrients, catalysts, and other materials can be concentrated and held together. While it is uncertain where membrane formation falls in the sequence of events leading up to the origin of life, with some arguing that it must have been one of the first steps (*65*), and others that it occurred at a later stage (*66*), it is considered a very crucial step (*68*).

Plate 7 also shows that the membranes trap other, photoluminescent, molecules that are produced within the ice by UV irradiation (*11, 40*). Thus, not only are vesicle forming compounds produced from the simplest and most abundant interstellar starting materials, complex organics which absorb UV are also formed. The ability to form and trap energy receptors within these structures is considered another critical step in the origin of life as it provides the means to harvest energy available outside the system.

Another class of potentially important organic molecules brought to the earth by meteorites are amino acids, the molecular building blocks of proteins and enzymes. That these amino acids in meteorites are extraterrestrial is demonstrated by their deuterium enrichments - the highest of any ever measured in a meteorite (*69*). The high abundances of deuterium suggested that these amino acids had a low temperature heritage (*70*). Consequently, it is widely held that meteoritic amino acids formed from interstellar precursors in liquid water in the asteroidal or cometary meteorite parent body within the forming solar nebula (*71*). However, since laboratory photolysis experiments of plausible presolar ice mixtures also produce amino acids (*72*), presolar ice photochemistry could also be a source of these amino acids. .

The mounting evidence in favor of a strong connection between interstellar organic materials and the carbonaceous fractions of meteorites and IDPs (and by implication comets) strengthens the case for taking interstellar PAHs and ices into account when pondering an exogenous contribution to early Earth chemistry (see Figure 9).

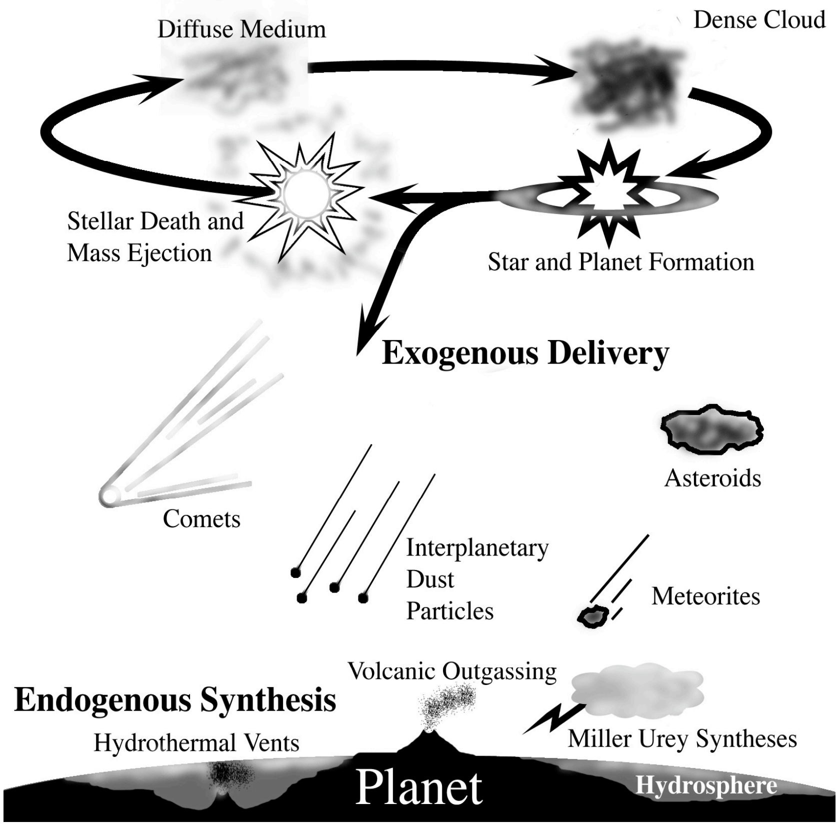


Figure 9. The cycle of stellar birth/death that leads to the production and evolution of organic compounds that can be delivered intact to and mixed with those produced on planetary surfaces (from reference 68).

Conclusion

Over the past thirty years tremendous strides have been made in our understanding of the complex chemistry in dense, dark, interstellar molecular clouds. This has come about because of fundamental advances in observational infrared astronomy and laboratory astrophysics. Thirty years ago the composition of interstellar dust was largely guessed at; the concept of ices in dense molecular clouds ignored; and the notion of large, abundant, gas phase, carbon-rich molecules widespread throughout the interstellar medium considered impossible. Astronomical infrared spectroscopy and dedicated laboratory experimentation has changed all that. Today the composition of interstellar dust is reasonably well understood. Cold dust particles are coated with mixed molecular ices in molecular clouds and the signature of carbon-rich, large polycyclic aromatic hydrocarbons (PAHs), shockingly large molecules/particles by usual interstellar chemistry standards, is widespread throughout the Universe: even at cosmological distances.

Both these ice and PAH spectral features are now being used as new probes of the interstellar medium of our Galaxy, the Milky Way and other galaxies throughout the Universe. The ices probe chemical processes in dark clouds and planet forming regions and the PAH features reveal the ionization balance as well as the energetic and chemical history of the medium. This paper has focused on the role of ices in the formation of complex molecules that are part of the raw materials from which stars, planets, satellites, and comets form.

Further, cometary observations and meteoritic and interplanetary dust particle (IDP) isotopic anomalies now indicate that some interstellar material could be delivered to planetary surfaces essentially unmodified. Taken together, these results are driving a large change in our understanding of the kinds of materials that might fall on primordial planetary systems. Today we are in the midst of a major shift in our understanding of what contributed to the 'atmospheres' of the terrestrial planets. Instead of simply assuming that a planet's prebiotic chemistry had to 'start from scratch', evidence is building that a far more chemically complex interstellar broth was present right from the start.

Interstellar ice composition depends on local conditions. In areas associated with star, planet, and comet formation, ices comprised of simple, polar species and entrapped volatiles such as H_2O, CH_3OH, CO, CO_2, and NH_3, are most important. Energetic processing of these ices produces the simple species H_2, H_2CO, CO_2, CO, CH_4, HCO as well as an extremely rich mixture of complex organic molecules. We now know that this prebiotic cocktail includes unsaturated fluorescent compounds; self-assembling, amphiphilic molecules; sugar precursors; and amino acids and we have just scratched the surface. These same lines of sight also show evidence for polycyclic aromatic hydrocarbons (PAHs), the organic molecules known from their characteristic emission to be widespread and abundant throughout the interstellar medium. Including PAHs in the irradiated ices adds PAH cations to the list of ice species, adds color, and, upon warm-up, additionally yields aromatic alcohols, quinones and ethers, species similar to those found in meteorites and having similar chemical properties to functionalized aromatic species used in living systems today. All of the above compounds are readily formed and thus likely cometary constituents at the 0.1 to few percent level. Evidence is growing that this interstellar heritage did not become erased during the Solar Nebula phase, implying that some of the interstellar chemical inventory contributed to the chemistry on primitive Earth. The ready formation of these organic species from simple starting mixtures under general interstellar conditions, the ice chemistry that ensues when these ices are mildly warmed, and the observation that the more complex refractory photoproducts form fluorescent vesicles upon exposure to liquid water underscore the possibility that interstellar and cometary ices could have played a part in the origin of life.

Acknowledgements

While I am very grateful to my many colleagues whose work is represented here, I especially wish to acknowledge the major contributions of two people, Mayo Greenberg and Douglas Hudgins. Mayo's vision and steadfast persistence opened the field of solid state laboratory astrophysics. His model of interstellar ice mantle growth and energetic processing is now central to our understanding of astrochemistry. Doug, apart from laying the very solid experimental foundation for the interstellar PAH model, contributed a professor's touch to this manuscript. The approach to many of the concepts, as well as specific topic treatments, are a direct outgrowth of our NATO Summer School chapter in Solid State Astrochemistry (13). I am also particularly grateful to NASA's Long Term Space Astrophysics, Exobiology, and Astrobiology programs for their continued support throughout this field's blossoming.

References

1. Herzberg, G.H. *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1939; p 496.
2. Snyder, L. E.; Buhl, D.; Zuckerman, B.; Palmer, P., *Phys. Rev Lett.* **1969**, 22, 6791969
3 Meyer, B.S. in *Chemical Evolution I: Chemical Change Across Space and Time*, edited by L. Zaikowski and J. Friedrich, ACS Publication, London, 2007, ppXXX
4 Lodders, K. in *Chemical Evolution I: Chemical Change Across Space and Time*, edited by L. Zaikowski and J. Friedrich, ACS Publication, London, 2007, ppXXX
5. Witt, A.N., Clayton, G.C., and Draine, B.T., *Astrophysics of Dust,* ASP Conf Ser. 309, Astronomical Society of the Pacific, San Francisco, 2004.
6. Ehrenfreund, P., and Charnley, S., B., *Ann. Rev. Astron. Astrophys*. Vol. 38, 2000, pp. 427, 483.
7. van Dishoek, E.F., *Ann. Rev. Astron. Astrophys*. Vol. 42, 2004, pp. 119, 167.
8. Ziurys, L. M. in *Chemical Evolution I: Chemical Change Across Space and Time*, edited by L. Zaikowski and J. Friedrich, ACS Publications, London, 2007, pp XXX
9. Sandford, S.A. and Allamandola L.J., *Astrophys. J.*, Vol. 417, 1993, pp. 815 and references therein.

10. Charnley, S.B., *Advances in Space Research*, Vol 36, 2005, pp. 132, 136.
11. Allamandola, L.J., Bernstein, M.P., and Sandford, S.A., *Astronomical and Biochemical Origins and the Search for Life in the Universe*, edited by Cosmovici, C.B., Bowyer, S., and Werthimer, D., Editrice Compositori of the Italian Physical Society, Bologna, 1997, pp. 23, 48.
12. Pendleton, Y.J.; Cruikshank, D.P. *Sky and Telescope*, **1994,** *March*, 36
13. Allamandola, L.J.; Hudgins, D.M. Solid State Astrochemistry, V. Pirronello, J. Krelowski, G. Manico eds., Kluwer, Dordrecht, 2003, p251.
14. Allamandola, L.J., Sandford, S.A., and Valero, G. *Icarus*, Vol. 76, 1988, 225.
15. Willner, S.P., *Astrophysical J.* Vol. 214, 1977, 706.
16. Capps, R.W., Gillett, F.C., and Knacke, R.F. *Astrophysical J.* Vol. 226, 1978, 863.
17. Tielens, A.G.G.M., Allamandola, L.J., Bregman, J., Goebel, J., d'Hendecourt, L.B., and Witteborn, F.C. *Astrophysical J.* Vol. 287, 1984, 697.
18. Lacy, J.H., et al., *Astrophysical J.* Vol. 276, 1984, 533.
19. Allamandola L.J., Sandford S.A., Tielens A.G.G.M., and Herbst T.M. *Science*, Vol. 260, 1993, 64.
20. Bowey, J.E., Adamson, A.J., and Whittet, D.C.B. *MNRAS*, Vol. 298, 1998, 131.
21. Gibb, E.; Whittet, D.C.B.; Schutte, W.A.; Chiar, J.; Ehrenfreund, R. et al. 2000, Astrophys. J. 536, 347
22. Boogert et al., *Astrophys J. Supp. Ser,* Vol . 154, 2004, pp. 359,362
23. Dartois, E., Pontoppidan, K., Thi, W., F., and Munoz Caro, G.M., *Astron. and Astrophys,* Vol. 444, 2005, pp.L57, L60
24. Altwegg, K., Balsiger, H., and Geiss, J. *The Composition and Origin of Cometary Materials*, edited by Altwegg, K, Ehrenfreund, P., Geiss, J., and Huebner, W., Kluwer Academic Pub., Dordrecht, 1999, p.3.
25. Crovisier, J., and Bocklee-Morvan, D. (1999), *The Composition and Origin of Cometary Materials*, edited by Altwegg, K, Ehrenfreund, P., Geiss, J., and Huebner, W., Kluwer Academic Pub., Dordrecht, 1999, p.19.
26. Allamandola, L.J.; Hudgins, D.M.; and Sandford, S.A. *Astrophys. J. (Letters)* **1999**, *511*, L115.
27. Hudgins, D. M., in "Astrophysics of Dust", eds. A. N. Witt, G. C. Clayton, and B. T. Draine, **2004**, ASP Conference Series, *309*, 665.
28. Allamandola, L.J., Tielens, A.G.G.M., and Barker, J.R., Astrophys.J. Suppl. Ser. 71, 733-775 (1989).
29. Peeters, E., Allamandola, L.J., Hudgins, D. M., Hony, S., and Tielens, A.G.G.M. "Astrophysics of Dust", eds. A. N. Witt, G. C. Clayton, and B. T. Draine, ASP Conference Series, Vol. 309, 141-162 (2004).
30. Herbst, E., Chang, Q., Cuppen, H. M. 2005, "Chemistry on Interstellar Grains" Journal of Physics: Conference Series, 6, 18

31. Garrod, R. T., & Herbst, E. "Formation of Methyl Formate and Other Organic Species in the Warm-up Phaseof Hot Molecular Cores" *Astron. Astrophys*., **2006**, *457*, 927 (surface chemistry in the warm-up phase of hot cores)
32. Tielens, A.G.G.M. The Physics and Chemistry of the Interstellar Medium; Cambridge University Press; Cambridge, 2005; p 101-114 and 364-393
33. d'Hendecourt, L.B., Allamandola, L.J., and Greenberg, J.M., *Astronomy and Astrophysics*, Vol. 152, 1985, p. 130.
34. Gerakines, P.A.; Schutte, W.A.; Ehrenfreund, P. *Astron. Astrophys* **1996**, *312*, 289.
35. Gerakines, P.A.; Moore, M.H.; Hudson, R.L. *J. Geophys. Res.* **2001** *106*, 33381
36. Loeffler, M.J.; Baratta, G.A.; Palumbo, M.E.; Strazzulla, G.; Baragiola, R.A. *Astron. Astrophys*. **2005**, *435*, 587
37. Bernstein, M. P.; Sandford, S.A.; Allamandola, L.J Scientific American; 1999, July, p26
38. Bernstein, M.P., Sandford S.A., Allamandola L.J., Chang S. and Scharberg M.A., *Astrophysical J.* Vol. 454, 1995, 327.
39. Elsila, J., Allamandola, L.J., and Sandford, S.A., Astrophys. J. 479, 818-838 (1997)
40. Dworkin, J.P., Deamer, D.W., Sandford, S.A., and Allamandola, L.J., *Pub.Nat.Acad* , Vol. 98, 2001, 815.
41. Charnley, S.B., Tielens, A.G.G.M., and Millar, T.J., *Astrophysical J.* Vol. 399, 1992, L71.
42. Blake, D., Allamandola, L.J., Sandford, S.A., Hudgins, D.M., and Freund, F., *Science*, Vol. 254, 1991, 548.
43. Mumma, M.J., Stern, S.A., and Weissman, P.R., *Protostars and Planets III*, edited by Levy, E.H., Lunine, J.I., and Matthews, M.S., University of Arizona Press, Tucson, 1993, p.1177.
44. Mumma, M.J. *Astronomical and Biochemical Origins and the Search for Life in the Universe*, edited by Cosmovici, C.B., Bowyer, S., and Werthimer, D., Editrice Compositori of the Italian Physical Society, Bologna, 1997, p.121.
45. Roser, J.E.; Vidali, G.; Manico, G.; Pironello, V. Astrophys. J. 555, L61, 2001
46. Gerakines, P.A., Schutte, W.A., and Ehrenfreundt, P., *Astron. and Astrophys,* Vol. 312, 1995, 289.
47. Briggs, R., Ertem, G., Ferris, J.P., Greenberg, J.M., McCain, P.J., Mendoza-Gomez, C.X., and Schutte, W. *Orig.Life Evol.Biosphere*, Vol. 22, 1992, 287.
48. Schutte, W.A., Allamandola, L.J., and Sandford, S.A., *Icarus*, Vol. 104, 1993, p. 118.
49. Huebner, W.F., Boice, D.C., and Korth, A., *Adv.Space Res*., Vol. **9**, 1989, p. 29.

50. Dickens, J.E., Irvine, W.M., DeVries, C.H. and Ohishi, M. (1997) *Astrophysical J.* Vol. 479, 1997, p.307.
51. Clemett, S., Maechling, C., Zare, R., Swan, P., and Walker, R., *Science*, Vol. 262, 1993, 721.
52. Dworkin, J.P., Gillette, J.S., Bernstein, M.P.,Sandford, S.A., Allamandola, L. J., Elsila, J.E., McGlothlin, R.M., and Zare, R.N., *Advances in Space Research,* Vol. 33, 2004, pp. 67 -71,
53. Greenberg, J.M., et al. *Astrophys. J* **2000** *531,* L71
54. Gudipati, M. S., and Allamandola, L. J. *Astrophys. J* **2003**, *596,* L195
55. Gudipati, M. S., and Allamandola, L. J., *Astrophys. J* **2006**, *638,* 286.
56. Gudipati, M. S. *J. Phys. Chem. A* **2004**, *108*, 4412
57. Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Gillette, J.S., Clemett, S.J., and Zare, R.N. *Science*, Vol. 283, 1999, p.1135.
58. Sandford, S.A., Bernstein, M.P., Allamandola, L.J., Gilette, J.S., and Zare, R.N. *Astrophysical J.* Vol. 538, 2000, p. 691.
59. Bernstein, M.P., Dworkin, J.P., Sandford, S.A., and Allamandola, L.J., *Met.&Planet.Sci.*, Vol. 36, 2001, p. 351.
60. Bernstein, M. P., Moore, M. H., Elsila, J. E., Sandford, S. A., Allamandola, L. J. & Zare, R. N. (2003). Astrophys. J., 582, L25-L29.
61. Bernstein, M. P., Elsila, J. E., Dworkin, J. P., Sandford, S. A., Allamandola, L. J. & Zare, R. N. (2002). Astrophys. J 576, 1115-1120.]
62. Elsila, J.E.; Hammond, M. R.; Bernstein, M.P.; Sandford, S.A.; Zare, R.N. *Meteoritics & Planetary Science* **2006** **41**, 785.
63. Hudgins, D.M.; Bauschlicher, Jr. C.M.; Allamandola, L.J. *Astrophys. J.* **2005** *632*:316.
64. Stoks P. G. and Schwartz A. W. 1982.*GCA* 46:309–315)
65. Luisi, P.L. (1997), in Cosmovici, C.B., Bowyer, S., and Werthimer, D. (eds.), *Astronomical and Biochemical Origins and the Search for Life in the Universe*, Editrice Compositori of the Italian Physical Society, Bologna, p.461.
66. DeDuve, C. (1997), in Cosmovici, C.B., Bowyer, S., and Werthimer, D. (eds.), *Astronomical and Biochemical Origins and the Search for Life in the Universe*, Editrice Compositori of the Italian Physical Society, Bologna, p.391.
67. Deamer, D.W. (1985) *Nature*, **317**, 792.
68. Deamer, D., Dworkin, J.P., Sandford, S.A., Bernstein, M.P., and Allamandola, L. J. The First Cell Membranes, Astrobiology 2, 371-381, (2002)
69. Pizzarello, S. *Geochimica et Cosmochimica Acta,* **2005**, *69*, 5163.
70. Sandford, S. A., Bernstein, M. P., & Dworkin, J. P. (2001) Meteoritics and Planetary Science, 36, 1117-1133.]
71. Peltzer, E. T., Bada, J. L., Schlesinger, G. &Miller, S. L., Adv. Space. Res. 4, 69–74 (1984).]
72. Bernstein, M. P.; Dworkin, J. P.; Sandford, S. A.; Cooper, G. W.; Allamandola, L. J. *Nature* **2002**, *416*, 401.