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Abiotic synthesis of complex organics in the Universe

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Abstract. The late stages of stellar evolution from asymptotic giant branch stars to planetary nebulae are now known to be an active phase of molecular synthesis. Over 80 gas-phase molecules have been detected through rotational transitions in the mm/submm region. Infrared spectroscopy has also detected inorganic minerals, fullerenes, and organic solids. The synthesis of these molecules and solids take place over very low density ($<10^6$ cm^{-3}) and short ($\sim 10^3$ yr) time scales. The unidentified infrared emission (UIE) bands observed in planetary nebulae commonly attributed to polyclcyic aromatic hydrocarbon (PAH) molecules are better explained by mixed aromatic/aliphatic organic nanoparticles (MAONs). These stellar organics have structures that are similar to the complex organics found in meteorites, comets, interplanetary dust particles, and planetary satellites, suggesting that they may share a common origin. The possibility of contamination of the primordial Solar System and the early Earth by stellar organics is discussed.
The efficient synthesis of complex organics by stars suggests that abiotic organic synthesis is prevalent in the Universe. Extreme caution must be exercised in interpreting spectral signatures of organics as evidence for extraterrestrial life.

Key words. Astrobiology – Astrochemistry – Solar System – Stars: evolution – Origin of Life – Interstellar Medium

1. Introduction

The origin of organic matter has long been a mystery in science. Before the 19th century, organic matter was believed to be in the exclusive domain of living organisms and was assumed to possess a unique property of "vitality" not found in minerals and non-living substances. After a sequence of successes of laboratory synthesis of biomolecules from common inorganic molecules (urea from ammonia cyanate in 1823, alanine from acetaldehyde, ammonia, and hydrogen cyanide in 1850), it was realized that organic matter is just a group of molecules and compounds based on the elements of carbon (C), hydrogen (H), nitrogen (N), sulphur (S), phosphorus (P) and other natural chemical elements. The number of theoretically possible organic structures is very large, ranging from 10^{33} to 10^{180} (Meringer & Cleaves 2017).

The discovery of extraterrestrial organics in carbonaceous meteorites (Nagy et al. 1961) has led to the realization that organic matter is not confined to the Earth. The detection of amino acids and other biomolecules (Kvenvolden et al. 1970) suggests that complex organics can exist totally independent of life. Since carbonaceous meteorites are among the most pristine objects in the Solar System, it was recognized that organic matter was present since the beginning of the Solar System.

The commonly accepted view in the space science community is that these organic compounds were synthesized from simple gaseous molecules during the formation of the Solar System. However, recent astronomical observations have found that complex organics are being commonly synthesized in the late stages of stellar evolution. In this paper, we will review the observations of organics in the Solar System and in stars and to explore their possible connections.

2. Stellar synthesis of complex organics

Since the 1950s, astronomers have realized that with the exception of H, and some of the helium (He) and lithium (Li), all other natural chemical elements have their origin in stars. On the main sequence, H is fused into He in the stellar core. All other chemical elements are produced in post-main-sequence evolution either by direct fusion, or through neutron capture followed by β decay (Wallerstein et al. 1997). The element carbon, the most basic ingredient in organic compounds, is produced by direct fusion of three He nuclei.

For stars that have evolved off the main sequence in our Galaxy, most (>95%) will evolve through the red giant and asymptotic giant branch (AGB) to the planetary nebulae phase and end as C−O white dwarfs. AGB stars maintain their luminosity through H- and He-shell burnings and the fusion products are dredged up to the surface via envelope convection. With continuous increase in luminosity and envelope expansion, AGB stars can grow to have luminosities thousands times and sizes hundreds times larger than the current Sun. Molecules and solids begin to form in the very extended atmospheres of these stars, and radiation pressure on the condensed solids can drag the gaseous atmosphere outward to form a stellar wind (Kwok 1975). Over a time span of hundreds of thousands of years, a significant fraction of the stellar mass can be removed by these stellar winds. When the stellar wind depletes the entire stellar envelope and expose the core, a faster stellar wind develops and compresses the previously ejected materials into high-density shells. UV radiation from the exposed core then photo-ionizes and illuminates the compressed shells to bright emission-line objects called planetary nebulae (Kwok 2000).

Millimeter-wave and infrared spectroscopic observations have detected a wide range of molecules and minerals in the stellar winds of AGB stars. Molecules detected include inorganics (e.g., CO, SiO, SiS, NH_3, AlCl, etc.), organics (C_2H_2, CH_4, H_2CO, CH_3CN, etc.), radicals (CN, C_2H, C_3, HCO^+, etc.), chains (e.g., HCN, HC_3N, HC_5N, etc.), and rings (C_3H_2), and solids detected include silicates, silicon carbide, and other refractory oxides (Kwok 2004).

The most interesting aspect of circumstellar chemistry is the discovery of a family of unidentified infrared emission (UIE) bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm in the planetary nebula NGC 7027 (Russell et al. 1977). An example of the UIE bands observed in planetary nebulae is shown in Figure 1. The UIE bands are strong and are broader than atomic emission lines commonly seen in planetary nebulae. Spectral decompositions of the UIE spectra seen in planetary nebulae and proto-planetary nebulae (objects in transition between the AGB and planetary nebulae phases) reveal broad emission plateau features around 8, 12 and 17 μm. The UIE bands are usually associated with a strong underlying continuum of color temperature ~100 K observable from 1 μm to 1 mm. This strong continuum, lying above the $b - f$ and $f - f$ gas continuum in the infrared region, is likely to arise from thermal emission from micron-size solid particles.

Soon after their discovery, the UIE bands were suggested to be due to organic aromatic compounds (Knacke 1977; Duley & Williams 1981). At that time, organics in space was considered too fantastic and radical an idea to be taken seriously, and this suggestion was largely ignored. It was only after the detection of a wide range of interstellar molecules in the 1980s that the hypothesis polycyclic aromatic hydrocarbons (PAH) molecules, the simplest aromatic compounds, were proposed as the carrier of the UIE bands (Allamandola et al.

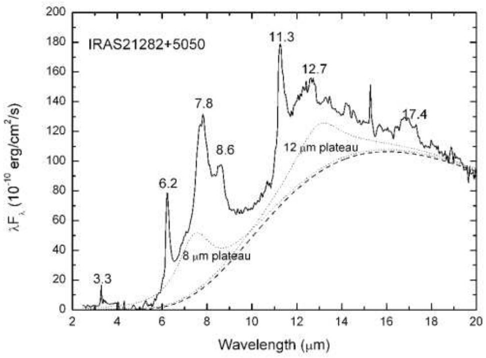

Fig. 1. UIE bands in the young planetary nebula IRAS 21282+5050. The wavelengths of some of the UIE bands are marked. The dotted lines represents fits to the broad emission plateau features around 8 and 12 μm and the dashed line represents an approximation to the underlying continuum emission.

1989; Puget & Léger 1989). The PAH hypothesis has since been widely accepted in the astronomical community and the UIE bands are commonly referred to as PAH bands in the astronomical literature.

In spite of its popularity, the PAH hypothesis suffers from a number problems, some of which were recognized as early as 30 years ago (Donn et al. 1989; Papoular et al. 1989):

i) PAH molecules have well-defined sharp features but the UIE features are broad;
ii) PAH molecules are primarily excited by UV, with little absorption in the visible, but UIE features are seen in protoplanetary nebulae and reflection nebulae, objects with very little UV background radiation. The shapes and peak wavelengths of UIE bands are largely independent of temperature of the exciting stars (Uchida et al. 2000);
iii) the strong PAH gas-phase electronic bands in the UV are not seen in interstellar extinction curves to very low upper limits (Clayton et al. 2003; Salama et al. 2011; Gredel et al. 2011);
iv) no specific PAH molecule has been detected in spite of the fact that the vibrational and rotational frequencies of PAH molecules are well known;
v) there are great difficulties in reconciling the band positions or relative intensities of laboratory PAH molecular spectra with astronomical UIE spectra (Schlemmer et al. 1994; Cook et al. 1996, 1998; Wagner et al. 2000);
vi) the UIE bands sit on a strong continuum which cannot be produced by molecules;
vii) the large number of free parameters used in the PAH model to fit the astronomical UIE spectra suggests that such fittings are not very meaningful (Zhang & Kwok 2015).

In order to save the PAH hypothesis, a number of modifications have been proposed, including the incorporation of different ionization states and large sizes to increase the absorption cross sections in the visible, introduction of dehydrogenation, superhydrogenation and minor aliphatic side groups to explain the aliphatic features, and the use of a large mixture of different PAH molecules to explain the lack of detection of individual PAH molecules. Since known PAH molecules have problems reproducing the wavelengths of the UIE bands, a large mixture of diverse PAH molecules of different sizes and structures (compact, linear, branched) is needed to fit the observed astronomical spectra. Hetro atoms such as N and O are also introduced to explain the 6.2 and 11.3 μm bands. These modifications have moved so far away from the chemical definition of PAH that the use of this term as carrier of the UIE bands is no longer appropriate.

If the UIE bands are not due to PAH molecules, then what kinds of carriers may be responsible? It turns out that just two elements H and C can form a variety of amorphous carbonaceous solids. Figure 2 shows a schematic of such compounds. At the top corner is diamond, a pure C substance with sp^3 hybridization. On the lower left corner is graphite, a pure C substance with sp^2 hybridization. With different H to C ratios and a mixture of sp^2/sp^3 hybridization states, a variety of amorphous hydrocarbons can be found inside this triangle. The PAH molecules with pure sp^2 hybridization (the bottom edge of the triangle) represent only a small fraction of all possible structures.

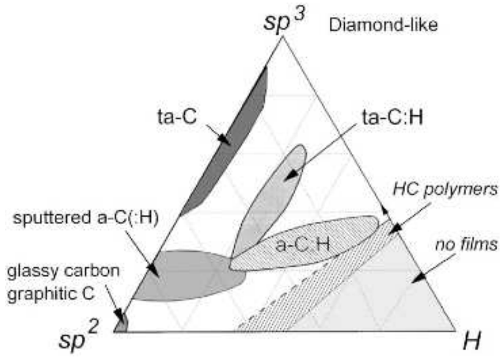

Fig. 2. Phase diagram of amorphous carbon based on pure C and H compounds. The lower right corner of the triangle represents pure H, lower left corner pure graphite-like (sp^2) materials (C rings on a plane with no H), and the upper corner pure diamond (sp^3, C arranged in tetrahedral forms). Areas inside the triangle represent various H/C ratios and sp^2/sp^3 mixed hybridization states. Figure adapted from Robertson (2002).

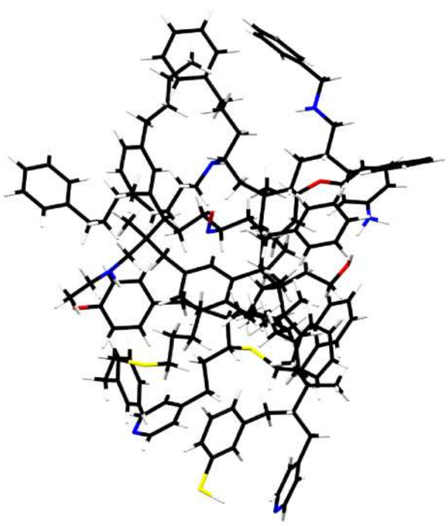

Fig. 3. An example of partial structure of MAON. This structure ($C_{169}H_{225}N_7O_4S_3$) is characterized by a highly disorganized arrangement of small units of aromatic rings linked by aliphatic chains. Other impurities such as O (in red), N (in blue), and S (in yellow) are commonly present. This structure contains 169 C atoms and a typical particle may consist of multiple structures similar to this one. (Figure created by Seyedabdolreza Sadjadi.)

By subjecting different mixtures of gas-phase hydrocarbon molecules to a variety forms of energy input (electric discharge, microwave irradiation, laser pyrolysis, flame combustion) and collecting the products on cooled substrates, a variety of artificial hydrocarbons can be produced. These compounds show spectral similarities to the UIE bands observed in planetary nebulae (Herlin et al. 1998). Specifically, these amorphous compounds show broad features on even broader plateaus characteristics of observed astronomical UIE spectra.

It is certain that the carriers of UIE bands are not pure aromatic substances. An aliphatic component is evident in the presence of the 3.4 and 6.9 μm bands (Hrivnak et al. 2007) and the broad emission plateaus around 8 and 12 μm, which represent superpositions of in-plane and out-of-plane bending modes of aliphatic groups (Kwok et al. 2001). We propose that the UIE bands can be better explained by a class of mixed aromatic/aliphatic organic nanoparticles (MAON) (Kwok & Zhang 2011; Kwok & Zhang 2013). The basic structure of MAON is illustrated in Figure 3. It contains small units of aromatic rings linked by aliphatic chains and contains impurities such as O, N, and S. A typical nanoparticle may contain multiple of similar structures shown in Figure 3.

In order to understand the vibrational spectral properties of MAON, we have undertaken quantum chemistry calculations of complex organics. We start from PAH molecules with simple aliphatic side groups (Sadjadi et al. 2015a) and proceed to interpret the vibrational nature of the 3.3/3.4, 6.2, and 11.3 μm UIE bands (Sadjadi et al. 2015b; Hsia et al. 2016; Sadjadi et al. 2017). Many of the spectral bands are due to coupled vibrational modes and their origin is not trivial (Sadjadi et al. 2016).

3. Chemical sequence of stellar organic synthesis

The sequential observations of simple molecules in early AGB stars to complex

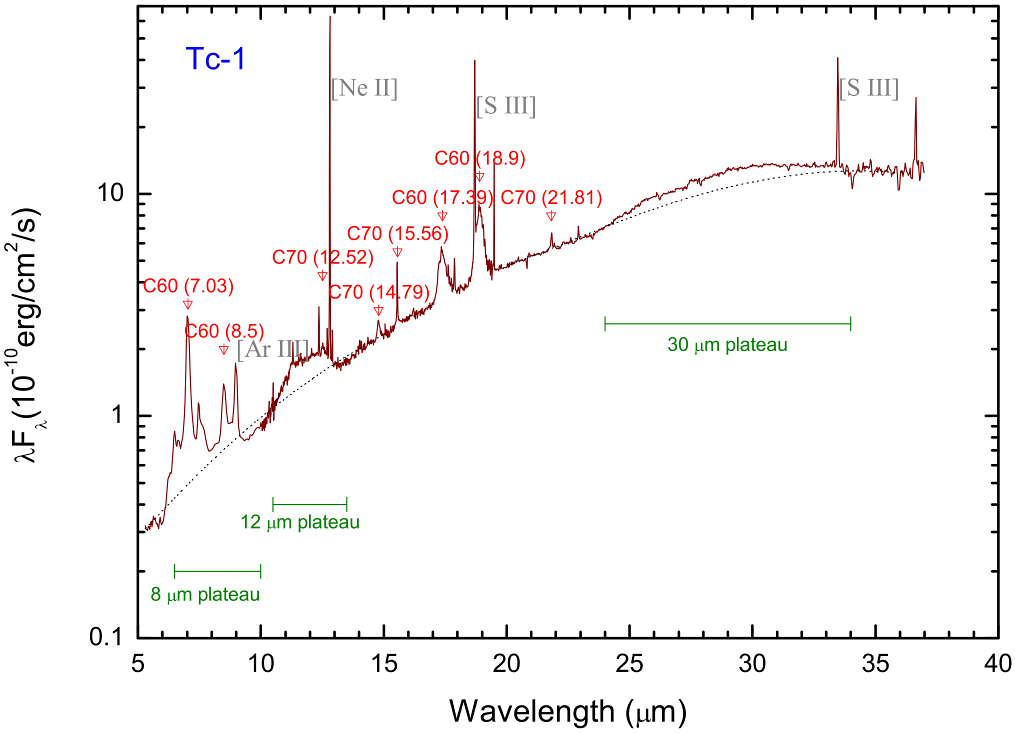

Fig. 4. *Spitzer* IRS spectrum of planetary nebula Tc-1 shows C_{60} and C_{70} emission bands (in red) as well as broad emission plateau features at 8, 12, and 30 μm (in green). The narrow lines are atomic lines (in grey). No UIE bands are seen in this object.

organics in planetary nebulae suggest that the synthesis of organic dust is not a breakdown of biological compounds but a bottom-up synthesis from simple molecules. The formation of the linear molecule acetylene in highly evolved AGB stars (Volk et al. 2000) is the first step for the formation of benzene (Cernicharo et al. 2001), the simplest aromatic molecule, in proto-planetary nebulae. The emergence of aromatic and aliphatic bands in the transition from AGB to planetary nebulae suggests that small rings group into larger aromatic islands, attached with aliphatic side groups. Since circumstellar chemical synthesis must occur over times scales much shorter than the dynamical time scale of expansion and evolution time scales of the central star, organic synthesis can occur very rapidly ($\sim 10^3$ yr) under very low density ($<10^6$ cm^{-3}) conditions.

Although fullerene (C_{60}) is not an organic molecule, its detection in planetary nebulae (Cami et al. 2010) suggests that its synthesis may be related to the synthesis of UIE carriers. The spectra of fullerene sources show emission plateau features similar to those seen in UIE sources (Figure 4). It is possible that fullerenes are breakup products of complex organics (García-Hernández et al. 2012).

4. Abundance of organics in the diffuse interstellar medium

The global abundance of organic matter in the Universe can be estimated from either the total integrated flux emitted by organic grains in galaxies, or by absorption by interstellar organics against bright background sources. The UIE bands are commonly observed in active galaxies, and total flux emitted in the UIE bands can be as high as 20% of the total energy output from these galaxies (Smith et al. 2007). The derivation for the abundance of the organic carrier is dependent on the excitation model and its value can be uncertain. Nevertheless, the fact that such a large fraction of energy output comes from the UIE bands suggests that the amount of organics in these galaxies must be very high. The situation is better for absorption studies as the only parameter is the oscillator strength of the vibrational band. From the strength of the 3.4 μm aliphatic C–H stretching band observed in absorption against the infrared background of the Galactic Center, it is estimated at least 15% of the C in the diffuse interstellar medium is in the form of aliphatic carbon (Dartois 2011).

5. Organics in the Solar System

Complex organics are now commonly found in meteorites, comets, asteroids, interplanetary dust particles, and planetary satellites. Over 14,000 organic compounds with millions of diverse isomeric structures have been found in the soluble component of carbonaceous chondrites (Schmitt-Kopplin et al. 2010). Many more amino acids have been identified in meteorites than those that are used in our terrestrial biochemistry (Pizzarello & Shock 2017). Unusual nucleobases beyond the 5 used in terrestrial biochemistry are also found (Callahan et al. 2011). The large fraction (70–90%) of organic carbon in carbonaceous chondrites is in the form of a complex, insoluble, macromolecular material often referred to as insoluble organic matter (IOM, Cronin et al. 1987).

Macromolecular compounds similar to IOM are detected in cometary dust by *Stardust* (Cody et al. 2011) and *ROSETTA* (Fray et al. 2016). Infrared spectra of particles collected from Comet 81P/Wild 2 by the *Stardust* spacecraft show the 3.3 μm aromatic C–H stretch and 3.4 μm aliphatic C–H stretch, suggesting cometary dust contains both aromatic and aliphatic materials (Keller et al. 2006). The similarity between cometary dust and terrestrial kerogen (Figure 5) suggests that cometary dust has a disorganized structure (Sandford et al. 2006).

The 3.4 μm aliphatic C–H stretch was detected by the *Dawn* spacecraft in the Ernutet Crater of the dwarf planet Ceres (De Sanctis et al. 2017). Laboratory analysis of interplanetary dust particles collected in the Earth's stratosphere show the 3.4 μm aliphatic feature in their infrared spectra (Flynn et al. 2003). Images of Pluto obtained from the recent *New Horizons* mission show a range of colored surface regions, suggesting the presence of complex organics embedded in water ice on the surface. Titan's atmosphere is filled with organic haze. Radar imaging observations from *Cassini* have found hundreds of lakes and seas filled with liquid methane (Le Gall et al. 2016). Tholins, a refractory organic material containing N, is often suggested to be the material covering surfaces of Titan and asteroids (Cruikshank et al. 1998).

Although sometimes cited as signatures of life in popular accounts, the organic matter found in drill samples from Mars' Gale crater (Eigenbrode et al. 2018) and in ice grains in the plumes of Enceladus and Saturn's E ring (Postberg et al. 2018) can be traced to complex macromolecular organics with structure similar to that of MAON. They are almost certainly of abiotic origin.

6. Enrichment of the early solar system by stellar organics

Isotopic analysis has identified pre-solar grains in meteorites. Grains of diamonds, silicon carbide, corundum, and spinel originating from AGB stars have been found to have traversed the interstellar medium and embedded in primordial solar nebula (Zinner 1998). Macromolecular solids like MAON are extremely sturdy in structure and can easily survive the UV background and shock conditions in the interstellar medium. Since organic grains are commonly produced by ordinary stars in their late stages of evolution, the early Solar System was likely to have been enriched by stellar organic ejecta.

Although there are indications based on isotopic ratios to suggest that existence

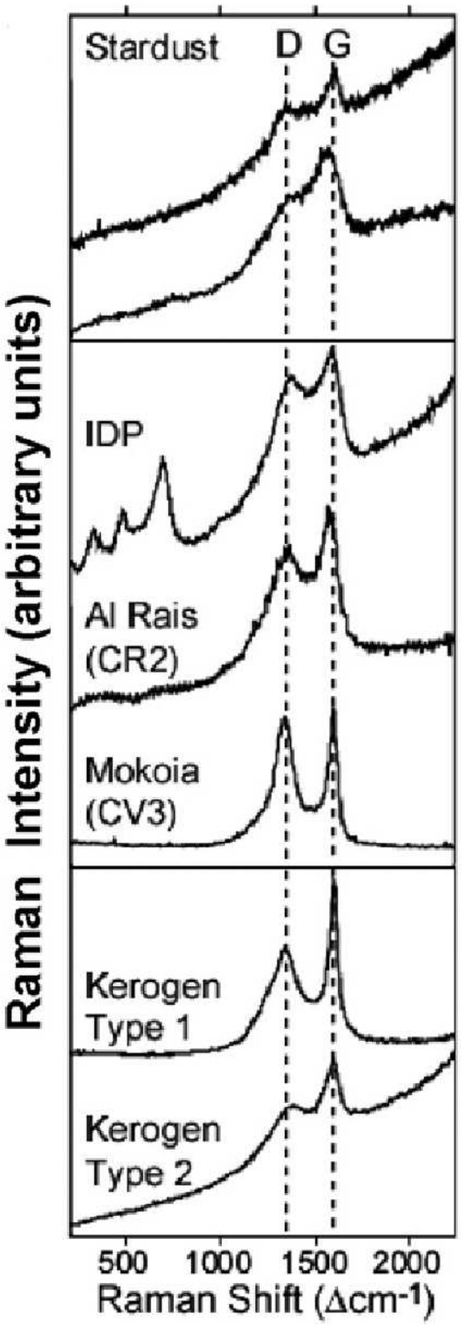

Fig. 5. Raman spectra of *Stardust* particles (top panel) compared to the spectra of interplanetary dust particles (middle panel) and spectra of terrestrial kerogen (bottom panel). Figure from Sandford et al. (2006).

of presolar organics in the Solar System (Messenger 2000; Keller et al. 2004), there is so far no direct conclusive link between Solar System and stellar organics.

7. Primordial organics in the early Earth

The main reservoir of organics on Earth is in the form of kerogen, a macromolecular compound found in sedimentary rocks. Kerogen was formed from living organisms under heat and pressure over the last several hundred million years (Vandenbroucke & Largeau 2007). In comparison, the amount of abiotic hydrocarbons on Earth is very small (Sherwood Lollar et al. 2002). The terrestrial planets (including the Earth) were formed as the result of aggregation of planetesimals. If the constituents of asteroids are indicative of the chemical contents of planetesimals, it is possible that the early Earth may have incorporated some of the primordial organics during its formation. Macromolecular compounds similar to MAON could have survived the aggregation process and remained deep inside the Earth (Kwok 2017). With time and under suitable temperature and pressure conditions, organic products could be released from these macromolecular compounds and formed the prebiotic materials that led to the origin of life (Yabuta et al. 2007).

8. Conclusions

While almost the entire organic inventory on Earth is biological in origin, there is no evidence that any of the extraterrestrial organics can be traced to living organisms. On the contrary, organic matter of abiotic origin is widely present in the Universe, from objects in the Solar System, to stars, interstellar clouds, the diffuse interstellar medium, and external galaxies (Kwok 2011). Direct observations of synthesis of complex organics over thousand-year time scales are observed in the late stages of stellar evolution. The rapid synthesis of organics by evolved stars and their ejection into the interstellar medium suggests that complex organics can spread widely across the Milky Way Galaxy. Some of these stellar organics may have contaminated our primordial Solar System. If some of these stellar macromolecular organics were embedded into the interior of the Early Earth, it would have interesting implications on the supply of fossil fuels and the origin of life on Earth.

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