



Planetary Nebulae as Sources of Chemical Enrichment of the Galaxy

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During the late asymptotic giant branch (AGB) phase of stellar evolution, the element carbon is created through the triple- α nuclear reaction. This is followed by the synthesis of other heavy elements via neutron capture in the core and the dredge-up of these elements to the surface by convection. Simple molecules and solid-state minerals begin to form in the upper photosphere. These molecules and solids are ejected into the interstellar medium by a strong stellar wind. During the subsequent post-AGB evolution, complex organics with aromatic and aliphatic structures are synthesized in the circumstellar envelope. Planetary nebulae, formed by swept-up circumstellar material, are found to show strong spectral signatures of ions, atoms, molecules, and inorganic and organic solids. These ejected materials of planetary nebulae serve as primordial ingredients of formation of new stars and planetary systems. Stellar synthesized organic solids may survive their journeys through the interstellar medium and evidence for remnants of such organics can be found in our own Solar System. In this paper, we summarize the recent observations of circumstellar synthesis of molecules and solids and discuss the implications of these ejected circumstellar materials on the chemical enrichment of the Galaxy and planetary systems.

Keywords: planetary nebulae, asymptotic giant branch stars, chemical enrichment, organic synthesis, solar system

INTRODUCTION

Planetary nebulae were first identified as extended objects in the sky and were grouped together with stellar clusters, galaxies, diffuse nebulae, and supernova remnants in Charles Messier's 1784 catalogue of nebulous objects. After the development of astronomical spectroscopy in the 19th century, planetary nebulae were recognized to be different from other nebulous objects in that they show strong atomic emission lines in their spectra. The presence of a hot star in the center of planetary nebula suggests that the nebula is illuminated by radiation from the central star (Hubble 1922). Ultraviolet radiation from the central star photoionizes the surrounding gaseous nebulae, and the recombination between electrons and hydrogen (H) and helium (He) led to the strong emission lines observed (Zanstra, 1827; Menzel 1926). Other strong emission lines in the nebulae are from collisionally excited lines of heavy elements. Together, these lines are responsible for the visible brightness of planetary nebulae.

Planetary nebulae are different from other emission nebulae (e.g., the Orion nebula) in that they show some degree of symmetry in their nebular morphology. The nebulae are the ejecta of the envelopes of their central stars, which are in the process of evolving from the red giant branch to the white dwarf stage of stellar evolution (Shklovsky 1956). The central stars of planetary nebulae are powered by H-shell burning on an electron-degenerate carbon-oxygen (C–O) core. Through a combination of nuclear burning and mass loss, the H envelope continues to thin, resulting in a

gradual increase in the effective temperature of the central star while maintaining a constant luminosity determined by the mass of the core (Paczynski 1971). The discovery of extensive mass loss on the AGB phase prior to the planetary nebulae phase led to the realization that the well-defined shell-like morphology of the nebulae is the result of the interaction between the remnant of the AGB wind with a later-developed fast wind from the central star (Kwok et al., 1978).

Development in infrared and millimeter-wave astronomy in the 1970s show that planetary nebulae are also strong sources of emissions from molecules and solid-state materials, and the true extent of planetary nebulae encompasses more than just the optical nebulae. A large fraction of the energy output from planetary nebulae is in the form of infrared continuum radiation emitted by solid dust grains (Zhang and Kwok 1991). Mapping of the molecular distribution in planetary nebulae shows that planetary nebulae contain a large amount of neutral matter, and in some cases, neutral matter mass exceeds the mass observed in the ionized nebulae. We now recognize that planetary nebulae contain matter in the forms of ionized, neutral atomic, molecular, to solid-state, and emit radiation throughout the electromagnetic spectrum from radio to X-ray. A modern view of the origin and evolution of planetary nebulae is given by Kwok (2000).

PLANETARY NEBULAE AS SOURCES OF HEAVY ELEMENTS

Although nuclear burning can theoretically occur in the core of AGB stars through to the synthesis of iron (Fe), for most stars their core masses never grow large enough to ignite carbon (C) (under either electron-degenerate or electron-non-degenerate conditions) due to surface mass loss. For stars in the Galaxy with initial masses under $8 M_{\odot}$, the star will undergo H and He shell burning on the AGB, evolve through the planetary nebulae stage, and end as white dwarfs. Since this mass range covers >95% of all stars in the Galaxy, C is the last element synthesized by direct fusion (through the triple- α process) for most stars. Heavy elements such as Y, Zr, Ba, La, Ce, Pr, Nd, Sm, Eu are synthesized through neutron capture followed by beta decay.

Because of their strong emission-line spectrum, abundance of heavy elements can be determined from their recombination or collisionally excited lines. The elemental abundances deduced are useful checks on stellar nucleosynthesis models. A recent review on elemental abundance determination in planetary nebulae is given by Kwitter and Henry (2022).

PLANETARY NEBULAE AS SOURCES OF MOLECULES

As a star evolves on the AGB, its H envelope expands, resulting in a size hundreds of times larger than the Sun. This is accompanied by an increasing luminosity to thousands of times that of the Sun, and a corresponding decreasing surface effective temperatures to

as low as 3000 K. Such low atmospheric temperatures allow the formation of molecules in the photosphere. Beyond the common diatomic molecule CO, molecules such as C_2 , C_3 , and CN can form in stars that are C-rich (elemental abundance of C exceeding that of O). For O-rich stars (elemental abundance of O exceeding that of C), the surplus O atoms are tied into OH, H_2O , SiO, and other oxides.

The development of millimeter-wave astronomy led to the detection of interstellar and circumstellar molecules through their rotational transitions. With infrared spectroscopy, the vibrational transitions of molecules can also be detected in absorption against the stellar photospheric or dust continuum. These molecules can be used to probe the physical conditions as well as kinematic structures of planetary nebulae.

Molecular Synthesis During the AGB Stage

A large variety of molecules including 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 , etc.), molecular ions (HCO^+), chains (e.g., HCN, HC_3N , HC_5N , etc.), and rings (C_3H_2) are detected in the circumstellar envelopes of AGB stars (Ziurys, 2006; Ziurys et al., 2016). The spatial distribution of these molecules in the circumstellar envelopes can be mapped by interferometric observations, showing that these molecules are synthesized in the stellar wind under very low density conditions. AGB stars are prolific molecular factories.

Molecules detected in the circumstellar envelopes of AGB stars include molecules involving heavy elements such as Si, Mg, Fe, Ti, and Al and detected molecules include SiH_4 , MgCN, FeCN, TiO_2 , and AlOH. The biologically important element phosphorus (P) (Maciá-Barber, 2019) is detected in the forms of CP, PN, PO, HCP, CCP, PH_3 (Agúndez et al., 2007; Agúndez et al., 2008; Halfen et al., 2008; Tenenbaum and Ziurys, 2008; Agúndez et al., 2014).

Molecular species detected in O- and C-rich AGB stars are also different. The proto-typical C-rich molecular source is IRC+10216 (CW Leo), where over 50 molecules have been detected (Ziurys 2006; McGuire 2022). The most common molecules in C-rich stars are CO, HCN, HC_3N , CN, and CS. The number of molecules detected in O-rich stars is more limited, with OH, H_2O , SiO being the most common. Recent surveys of the O-rich star VY CMa has expanded the list of molecules detected (Tenenbaum et al., 2010). The versatility of carbon chemistry is illustrated by the fact that only diatomic and triatomic compounds were observed in VY CMa, while species with four or more atoms are common in IRC+10216.

Molecular Synthesis During the Planetary Nebulae Stage

The largest molecule detected in planetary nebulae is fullerene (C_{60}). Fullerene was discovered in the planetary nebula Tc-1 through its vibrational bands at 7.0, 8.5, 17.4 and 18.9 μm (Cami et al., 2010). Further detections of C_{60} are found in H-rich planetary nebulae (García-Hernández et al., 2010), proto-

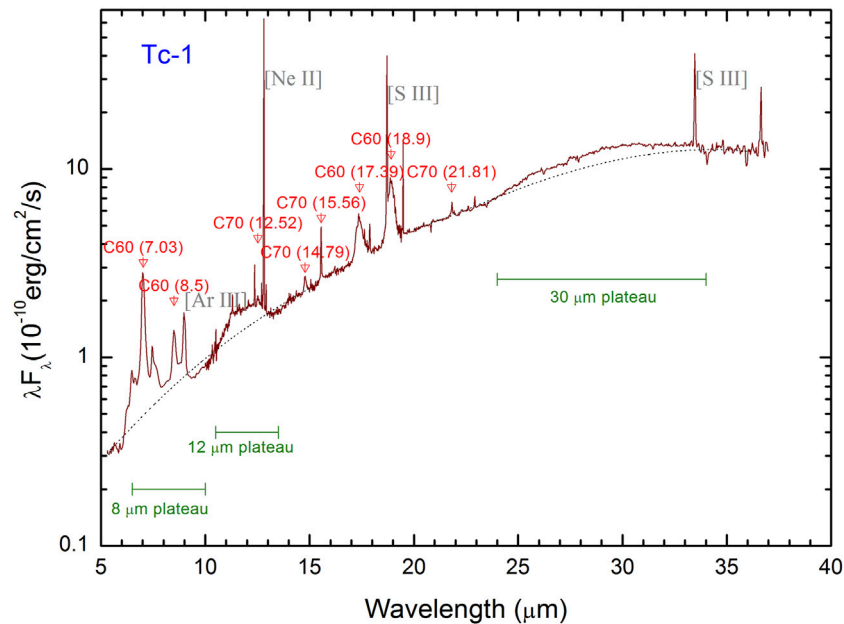


FIGURE 1 | *Spitzer* IRS spectrum of planetary nebula Tc-1 shows C_{60} and C_{70} emission bands (in red) as well as broad emission plateau features at 8, 12, and 30 μm (in green). The narrow lines are atomic lines (in grey). The dotted line represents an approximate fit to the continuum. No UIE bands are seen in this object.

planetary nebulae (Zhang and Kwok 2011), and reflection nebulae (Sellgren et al., 2010).

Also seen in the spectrum of Tc-1 are strong broad plateau features around 8, 12, and 17 μm (Figure 1). These plateau features are commonly seen in planetary nebulae and proto-planetary nebulae showing unidentified infrared emission (UIE) bands. These plateau features cannot be associated with any specific molecule and the 8 and 12 μm plateau features have been suggested to arise from superpositions of in-plane and out-of-plane vibrational modes of aliphatic side groups attached to aromatic compounds (Kwok et al., 2001). The presence of 8 and 12 μm plateau features in C_{60} sources (Otsuka et al., 2013; Zhang and Kwok 2013) suggests that amorphous carbonaceous solids could be precursors of fullerenes (Bernard-Salas et al., 2012; García-Hernández et al., 2012).

The Molecular Component of Planetary Nebulae

Although planetary nebulae are usually known for their optical appearances and their optical nebulae are the most extensively studied, millimeter and submm-wave interferometric observations can map the distribution of the molecular component (Dinh et al., 2008; Nakashima et al., 2010; Santander-García et al., 2017; Andriantsaralaza et al., 2020). For the CO molecule, entire ladder of rotational transitions (up to $J = 37-36$) have been measured, making possible the estimate of the total molecular masses (Justtanont et al., 2000). In the near infrared, the $\nu = 1-0$, $J = 3-1$ S (1) vibrational-rotational transition of H_2 at 2.121 μm is widely observed in planetary nebulae. Assuming that this line is shock or UV excited, the

molecular mass in the H_2 -emitting region can be estimated (Rosado and Arias 2003). From single-dish CO observations, masses of the molecular envelopes of NGC 7027 and IRAS 21282 + 5050 are found to be 1.3 and 4.7 M_{\odot} respectively (Santander-García et al., 2022), much larger than the masses of their ionized components (0.03 and 0.16 M_{\odot} for NGC 7027 and IRAS 21282 + 5050, respectively).

PLANETARY NEBULAE AS SOURCES OF SOLID MINERALS

Solid Condensations in Stellar Winds

The most common solid-state condensate observed in the stellar winds of O-rich AGB stars is amorphous silicates. This mineral can be detected through their Si–O stretching mode at 9.7 μm and the Si–O–Si bending mode at 17 μm and is widely present in the spectra of O-rich AGB stars. Also seen in the spectra of O-rich stars are crystalline silicates (pyroxenes and olivines, Jäger et al., 1998) and various kinds of refractory oxides (corundum $\alpha\text{-Al}_2\text{O}_3$, spinel MgAl_2O_4 , rutile TiO_2 , Posch et al., 1999, 2002).

In C-rich stars, the most common feature is the 11.3 μm feature of silicon carbide (SiC). The strong featureless continuum emission is commonly attributed to amorphous carbon.

As the strength of the stellar wind increases as the star ascend the AGB, the amount of solid-state condensate in the circumstellar environment can begin to obscure the photosphere of the star. In some cases, the entire photospheric visible output of the star is absorbed by circumstellar material and the star will only appear as an infrared object.

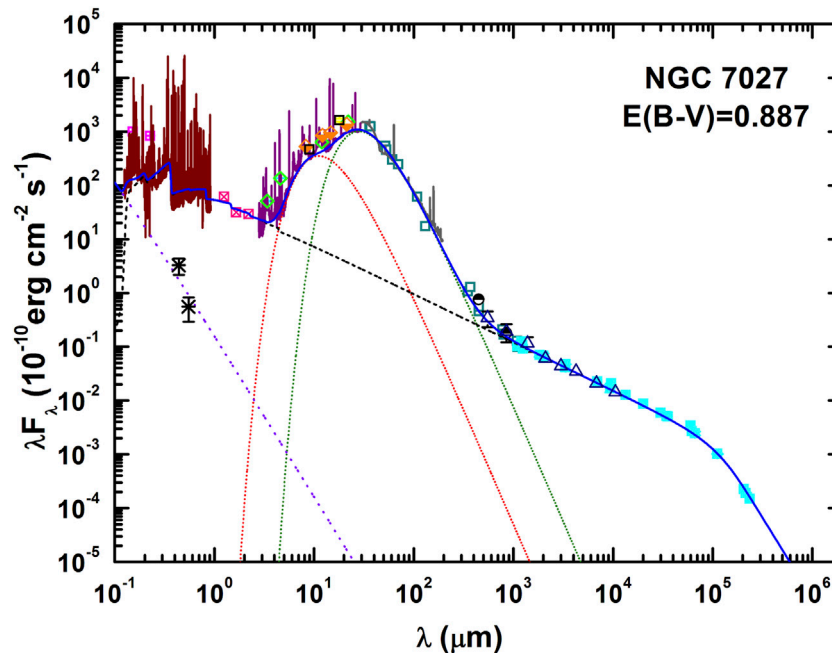


FIGURE 2 | Spectral energy distribution of the planetary nebula NGC 7027 from wavelength 0.1 to 1 m. Various symbols represent photometric measurements and the lines are spectroscopic observations. The red and green curves are approximate fits to the dust continuum. The dashed line covering the entire spectrum is a model bound-free and free-free emission from the ionized nebula. The dashed line in the visible and UV region is an approximate fit to the central star continuum. The UV and optical photometry and spectroscopy has been corrected for circumstellar/interstellar reddening with $E(B-V) = 0.887$. Figure courtesy of C.H. Hsia.

The Solid-State Component of Planetary Nebulae

Since planetary nebulae evolve from their AGB progenitors, remnants of the dust envelopes of AGB stars should still be detectable in planetary nebulae (Kwok 1982). **Figure 2** shows the spectral energy distribution of the planetary nebula NGC 7027 over the wavelength range of 0.1 μm –1 m. In the long wavelength region ($\lambda > 1$ mm), the spectrum is dominated by free-free emission from the ionized nebula. Between 3 μm and 1 mm, thermal radiation from solid-state grains dominates. The UIE bands and the 30 μm feature can be seen in emission above the dust continuum. In the optical region, nebular emission is due to atomic line emission and bound-free continuum emission from the ionized nebula. The central star is heavily obscured by circumstellar dust and is very faint in the visible. The molecular lines are not plotted in this diagram.

Planetary nebulae can be classified as O- or C-rich based on the respective strengths of the atomic lines in the ionized component (Zuckerman and Aller 1986; Delgado-Inglada and Rodríguez 2014). A similar independent classification is also possible using their infrared spectra of their solid components (Kwok et al., 1997). The presence of silicate feature is a signature of O-richness, and the UIE and 30 μm features are generally only seen in C-rich nebulae (Cohen et al., 1986; Cohen et al., 1989). The *Spitzer Space Telescope* was used to survey a large sample of galactic and extragalactic planetary nebulae and their spectra have been used to classify planetary nebulae as O- or C-rich types (Stanghellini et al., 2007; Bernard-Salas et al. 2009; Stanghellini et al., 2012; García-Hernández and Górný 2014).

PLANETARY NEBULAE AS SOURCES OF ORGANICS

Before the mid-20th century, organics were commonly believed to be within the sole domain of the Earth, and the existence of organic matter in space was not expected. The discovery of complex organics in planetary nebulae came as a surprise and represents a new beginning of our understanding of abiotic synthesis of organics in space.

Observational Evidence of Aromatic and Aliphatic Organics in Planetary Nebulae

A family of broad unidentified infrared emission (UIE) bands at 3.3, 6.2, 7.7, 8.6 and 11.3 μm was first found in the spectrum of the planetary nebula NGC 7027 (Russell et al., 1977), and later found to be commonly present in C-rich planetary nebulae. By comparison with laboratory spectra of organic compounds, these bands are suggested to arise from stretching and bending modes of aromatic compounds (Duley and Williams 1981). Also present in spectra are emission features around 3.4 μm , which correspond to the symmetric and anti-symmetric C–H stretching modes of aliphatic methyl and methylene groups (Puetter et al., 1979; Geballe et al., 1992). The bending modes of these groups manifest themselves at 6.9 and 7.3 μm (De Muizon et al., 1990; Chiar et al., 2020). In addition, there are weaker unidentified emission features at 15.8, 16.4, 17.4, 17.8, and 18.9 μm which may be due to C skeleton vibrational modes of aromatic structures.

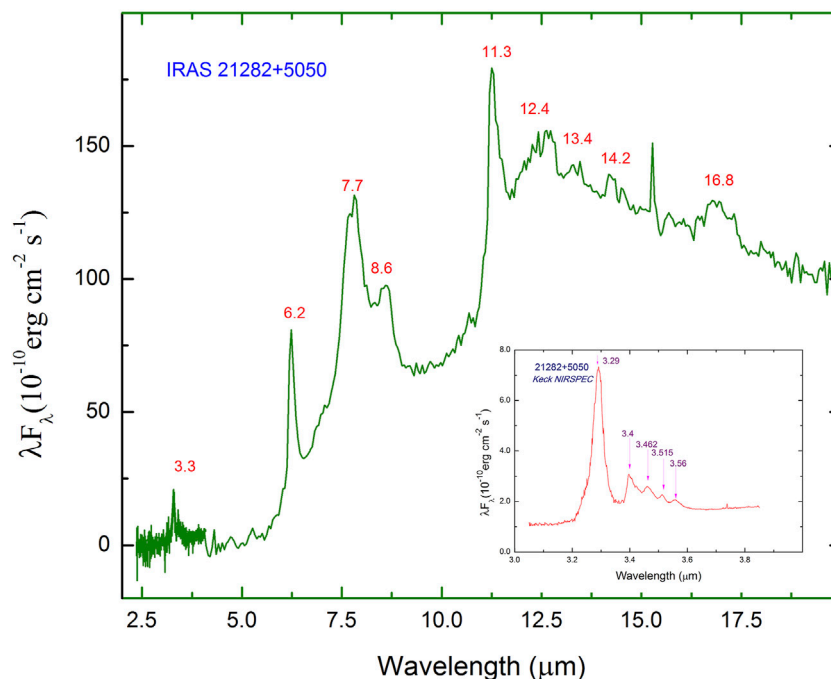


FIGURE 3 | *Infrared Space Observatory* spectrum of planetary nebula IRAS 21282 + 5050. The UIE bands (in units of μm) are marked in red. The insert box shows the expanded spectrum in the $3\ \mu\text{m}$ region obtained with the *Keck Telescope*, where both the aromatic and aliphatic C–H stretch emissions can be seen.

These discoveries represent the first discovery of stars as sources of organic matter in the Universe.

Figure 3 shows the infrared spectrum of the planetary nebula IRAS 21282 + 5050. In addition to the 3.3, 6.2, 7.7, 8.6, 11.3, 12.4, 13.4, and 16.8 μm UIE bands, emission bands around 3.4 μm due to aliphatic C–H stretching modes can also be seen (Hrivnak et al., 2007).

Circumstellar Synthesis of Complex Organics

Since the UIE bands are seen in planetary nebulae but not AGB stars, they are probably the product of circumstellar synthesis during the post-AGB phase of evolution. The dynamical age of planetary nebulae of $\sim 10^4$ yr places a limit on the time scale of chemical synthesis. The first signs of UIE bands are seen in proto-planetary nebulae, transition objects between the AGB and planetary nebulae phases before the onset of photoionization (Kwok et al., 1999). The first step to an aromatic compound is the formation of the ring molecule benzene (C_6H_6), which was detected in the proto-planetary nebula AFGL 618 through one of its bending modes in the infrared (Cernicharo et al., 2001). Acetylene (C_2H_2), a linear molecule and building block of benzene, is commonly detected in evolved carbon stars through its ν_5 fundamental band at 13.7 μm (Volk et al., 2000). Polymerization of C_2H_2 leads to the formation of diacetylene (C_4H_2) and triacetylene (C_6H_2) in proto-planetary nebulae, cumulating in the possible formation of benzene. Benzene molecules can group into multiple rings in the form

of aromatic islands, which can be linked to each other via aliphatic bridges of variable lengths and orientations. A possible structure of such mixed aromatic/aliphatic organic nanoparticles (MAONs) was proposed by Kwok and Zhang 2011, Kwok and Zhang 2013. Since MAONs are amorphous and have an extremely sturdy structure, they can survive journeys through the interstellar medium after their ejection during the planetary nebulae stage.

ENRICHMENT OF PLANETARY SYSTEMS

Planetary systems are formed from proto-stellar nebulae condensed from interstellar clouds. The chemical composition of the pre-solar nebula is therefore determined by the chemical composition of star-forming regions, which are enriched by ejecta from AGB stars and planetary nebulae. Supernovae, which occur much more rarely in the Galaxy, are responsible for heavy elements produced by rapid-process nucleosynthesis. A large part of condensed objects in the early Solar System are made of ice (H_2O , CO) and minerals made of heavy elements (O, Si, Fe, etc). The outer planets are results of condensation of gases and ices, and the inner planets are products of aggregation of solid particles in the primordial Solar Nebula.

Recent studies of meteorites, comets, asteroids, planetary satellites, interplanetary dust particles, have led to unexpected discoveries that complex organics are commonly present in the Solar System. The presence of organics is not only extensive, but also diverse. Almost every class of organic molecules (including

carboxylic acids, sulfonic and phosphonic acids, amino acids, aromatic hydrocarbons, heterocyclic compounds, aliphatic hydrocarbons, amines and amides, alcohols, aldehydes, ketones, and sugar related compounds) have been identified in the soluble component of carbonaceous chondrites (Schmitt-Kopplin et al., 2010; Remusat 2015).

Most interestingly, a 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). Laboratory analyses of IOM reveal a chemical structure consisting of small islands of aromatic rings connected by short aliphatic chains (Cody et al., 2001; Cody et al., 2002). Evidence for the interstellar origin of IOM can be found in its isotope anomalies (Busemann et al., 2006).

Aromatic, aliphatic, and thiophenic (sulfur-containing rings) compounds have been found in Mars' Gale crater, with kerogen-like materials being their most likely precursor (Eigenbrode et al., 2018). The origin of organic plumes from Enceladus can be traced to complex macromolecular organics in subsurface oceans (Postberg et al., 2018). The atmosphere of Saturn's moon Titan is filled with organic haze and its surface is covered by lakes of liquid methane and ethane, as well as dunes made of organic particles (Lorenz et al., 2008).

The *Rosetta* mission to the comet 67P/Churyumov-Gerasimenko has revealed an array of organic compounds on the surface of the comet (Goesmann et al., 2015). The *Stardust* mission to Comet 81P/Wide 2 has detected amino acid glycine with a carbon isotopic ratio suggestive of extra-solar origin (Elsila et al., 2009). Infrared spectra of cometary dust show the 3.3 μm aromatic C–H stretch and 3.4 μm aliphatic C–H stretch, implying the presence of both aromatic and aliphatic materials like IOM in meteorites (Keller et al., 2006; Fray et al., 2016).

Complex organics are also found in interplanetary dust particles (IDP) collected in the Earth's stratosphere (Flynn et al., 2003). Since IDPs originated from comets and asteroids, this gives us indirect evidence of the presence of organics in comets and asteroids. The anomalous H and N isotopic ratios of IDP organics suggest that they are of pre-solar origin (Keller et al., 2004).

In the asteroid belt, the *Dawn* mission has detected the 3.4 μm aliphatic C–H stretch over a 1000 km^2 area near the Ernutet Crater of the dwarf planet Ceres, therefore confirming the presence of complex organics in the main belt asteroids (De Sanctis et al., 2017). The red color and low albedo of D-type asteroids have been attributed to kerogen-like macromolecular organics covering their surfaces (Cruikshank and Kerridge 1992).

In the outer Solar System, the *New Horizons* mission found the surface of Pluto to be covered with a range of colored regions, which could be the result of complex organics embedded in water ice on the surface or liquid organics in subsurface reservoirs (Cruikshank et al., 2019). The low albedo found in trans-Neptunian objects has also been suggested to be due to surface complex organics (Giri et al., 2016).

The origin of Solar System organics is a subject of active debate. They are either synthesized *in situ* from simple molecules, or they are remnants of stellar ejecta that were embedded in the primordial solar nebula. The Solar System is already known to have inherited pre-solar grains of AGB star origin (Zinner 1998). Pre-solar grains

of diamonds (Lewis et al., 1987), silicon carbide (Bernatowicz et al., 1987), corundum, and spinel (Nittler et al., 1997) have been identified by isotopic studies of meteorites. It is therefore quite conceivable that stellar organic grains were also embedded in the pre-solar nebula and later deposited into Solar System objects.

SUMMARY

Planetary nebulae have a long history of research on their morphology, structure, and evolution. They are also known to be sources of chemical elements that carry the chemical evolution of the Galaxy. However, it was not until the emergence of infrared and millimeter-wave observations that we realize that they are also major sources of molecules and solids in the Galaxy. The products synthesized in the outflows from evolved stars provide the primordial ingredients for the formation of next generation of stars and planetary systems.

A more significant implication of these recent discoveries is the possible organic enrichment of primordial planetary systems by planetary nebulae. Planetary nebulae (together with novae, Endo et al., 2021) are the only astronomical objects that the synthesis of complex organic compounds is directly observed. Although complex organics could have been synthesized *in situ* in the Solar System, their presence in carbonaceous chondrites, the most primitive of all Solar System objects, suggests that these organics are most likely previously embedded in the nebula from stellar ejecta materials. The delivery of these Solar System organics onto the early Earth could have implications on the origin of life on Earth.

Planetary nebulae therefore represent a crucial link in the lives of stars. Formed during the last stages of stellar evolution, planetary nebulae ejecta provide primordial ingredients for the formation of the next generation of stars and planetary system. The atomic elements, molecules, minerals, and organic solids are major constituents of the planetary systems. Observations of planetary nebulae show that abiotic organic synthesis can occur extremely efficiently under very low nebular density conditions and over very short (10^3 yr) time scales. This opens the possibility that organic matter is common in the Universe, and the chemical composition of the Universe is more complex than we previously believed. Since planetary nebulae are a common stage of evolution for most stars, the synthesis and distribution of stellar organics may have significant implications on the existence and distribution of life in our Galaxy.

AUTHOR CONTRIBUTIONS

SK is responsible for the research performed and writing of this article.

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