

# The synthesis of organic and inorganic compounds in evolved stars

Sun Kwok

*Institute of Astronomy & Astrophysics, Academia Sinica, PO Box 23-141, Taipei 106, Taiwan*

**Recent isotopic analysis of meteorites and interplanetary dust has identified solid-state materials of pre-solar origin. We can now trace the origin of these inorganic grains to the circumstellar envelopes of evolved stars. Moreover, organic (aromatic and aliphatic) compounds have been detected in proto-planetary nebulae and planetary nebulae, which are the descendants of carbon stars. This implies that molecular synthesis is actively happening in the circumstellar environment on timescales as short as several hundred years. The detection of stellar grains in the Solar System suggests that they can survive their journey through the interstellar medium and that they are a major contributor of interstellar grains.**

**W**ork on stellar nucleosynthesis in the 1950s has led to our current realization that most of the chemical elements are synthesized in stars. Helium is made by hydrogen burning in the core during the main sequence and in a shell above the core in the red giant phase. The element carbon is created by helium-burning (the triple- $\alpha$  process), first through core burning and later through shell burning above an electron-degenerate carbon-oxygen core. For massive (more than ten solar masses,  $>10 M_{\odot}$ ) stars, direct nuclear burning continues with the production of oxygen, neon, magnesium, silicon and so on, cumulating in the synthesis of iron, the heaviest element possible through direct nuclear burning. The other heavy elements, from yttrium and zirconium to uranium and beyond, are produced by neutron capture followed by  $\beta$  decay<sup>1</sup>.

For the majority of stars ( $\sim 95\%$ , corresponding to stars with initial masses of less than  $\sim 8 M_{\odot}$ ), direct nuclear burning does not proceed beyond helium, and carbon is never ignited. Most of the nucleosynthesis occurs through slow neutron capture (the  $s$  process) during the asymptotic giant branch (AGB), a brief phase ( $\sim 10^6$  yr) of stellar evolution where hydrogen and helium burn alternately in a shell. These newly synthesized elements are raised to the surface through periodic 'dredge-up' episodes, and the observation of short-lived isotopes in stellar atmospheres provides direct evidence that nucleosynthesis is occurring in AGB stars<sup>2</sup>.

However, the atomic form is not the only form in which chemical elements can occur. Molecules are major constituents of planetary atmospheres and the Solar System contains many solid bodies, such as asteroids and terrestrial planets. Since the late 1960s, advances in millimetre-wave observation have led to the detection of over 120 molecules in the interstellar medium. Although a variety of chemical models have been developed to explain how molecular synthesis could occur in the interstellar medium, we have no direct observational knowledge of the timescales on which these reactions occur. The discovery of a large number of gas-phase molecules as well as submicrometre-sized solid-state particles of various chemical compositions in the circumstellar envelopes of AGB stars has led to the realization that extensive molecular synthesis occurs during this brief phase of stellar evolution. These envelopes are expanding and have dynamical timescales of several thousand years only, providing the first definite indication that production of molecules and solids of high complexity can occur rapidly in the circumstellar environment.

Although it was commonly assumed that stellar grains are destroyed during their journey through the interstellar medium by radiation and shocks<sup>3</sup>, the recent discoveries of the chemical richness of circumstellar grains have raised the possibility that

circumstellar molecular synthesis may have significant implications for the chemical enrichment of the Galaxy, or even of the early Solar System. The exploration of this new perspective is the subject of this review.

## The asymptotic giant branch and beyond

The approximately ten thousand years of evolution following the end of the AGB phase represents a most fascinating 'laboratory' for astrochemistry. A large variety of organic species have been observed to emerge in the circumstellar environment of stars evolving through this stage, following the formation of gas-phase molecules and inorganic solid-state compounds in the previous AGB phase. The well-defined conditions of the environment approximate a controlled laboratory as closely as is possible in space, providing severe constraints on any model of gas-phase and solid-state chemistry.

Stars on the galactic disk (population I) begin their AGB phase with more oxygen than carbon. As more and more carbon is made in the core and dredged up to the surface, the abundance of carbon in the stellar photosphere will eventually exceed that of oxygen. Most of the carbon will combine with oxygen to form the stable molecule carbon monoxide (CO). The excess carbon atoms will be available to form other carbon-based molecules such as  $C_2$ ,  $C_3$  and CN. The presence of these molecular bands in the photospheric spectrum distinguishes these stars from normal oxygen-rich AGB stars, and stars that show these spectral characteristics are called carbon stars.

As an AGB star evolves, both its luminosity and size increase. A typical AGB star has a luminosity several thousand times that of the Sun, and a radius several hundred times the solar radius. The combination of high luminosity and large size causes envelope pulsation, and when aided by radiation pressure, an AGB star will eject its outer layers in the form of a stellar wind, with ejection rates as high as  $10^{-4} M_{\odot} \text{ yr}^{-1}$  (ref. 4). A star can therefore lose a major fraction of its original mass through these stellar winds, creating a thick, dense envelope around the central star.

Because of the low temperatures, most of the gas in the circumstellar envelopes is in molecular form, and can be detected through their rotational or vibrational transitions. In the past 30 years, millimetre-wave and near-infrared spectroscopy has detected the rotational and vibrational stretching mode transitions of  $\sim 60$  molecules in the circumstellar envelopes of AGB stars. The detected molecular species include inorganics (CO, SiO, SiS,  $NH_3$ , AlCl), organics ( $C_2H_2$ ,  $CH_4$ ,  $H_2CO$ ,  $CH_3CN$ ), radicals (CN,  $C_2H$ ,  $C_3$ ,  $HCO^+$ ), cyclic molecules ( $C_3H_2$ ), and cyanopolynes (HCN,  $HC_3N$ , ...  $HC_9N$ ) (ref. 5).

In addition to molecules, solid-state species, both amorphous and crystalline, are also found in the circumstellar envelopes of AGB stars. The chemical composition of solids can be identified through their lattice vibrational modes. The most common solid-state condensate is amorphous silicates and silicon carbide (SiC). These solid particles are believed to condense directly from gas-phase molecules, as the gas temperature cools during the envelope expansion<sup>6</sup>.

Because solid particles have a high opacity to visible light, the condensation in the circumstellar envelope can cause large obscuration to the light from the central star. The intercepted starlight heats up the dust particles, which in turn cools by self-radiating in the infrared. As the ejection rate increases in the late stages of AGB evolution, the envelope can contain so much dust that the star is completely obscured by dust extinction. Such extremely evolved AGB stars have no optical counterpart and can only be identified by infrared observations (Fig. 1).

The high rate of mass loss on the AGB will eventually deplete the envelope of the star and gradually expose the hot core. As the envelope thins to below  $10^{-3} M_{\odot}$ , the star will begin to increase in temperature. Through a combination of hydrogen shell burning and mass loss, the envelope becomes thinner, leading to an increase of stellar temperature. When the stellar temperature reaches 25,000 K, the ultraviolet photon output from the star will begin to photo-ionize the circumstellar envelope, creating a planetary nebula (PN). The intervening phase between the end of AGB and the onset of photo-ionization is called the proto-planetary nebula (PPN) phase<sup>7,8</sup>.

Although PNe are bright visible objects because of their emission-line spectrum, recent observations of PNe in the infrared and millimetre wavelengths have shown that they also possess thick molecular envelopes mixed with solid-state particles. Mid- and far-infrared observations from the Infrared Astronomical Satellite (IRAS) and Infrared Space Observatory (ISO) missions have found that dust emission represents a major fraction of energy output from PNe<sup>9</sup>. The detection of molecular/dust envelopes in PNe clearly establishes the link to their progenitor AGB stars.

By observing the spectral changes of the envelope as a function of evolution between AGB stars and PNe, we are able directly to

determine the chemical steps through which complex organic and inorganic compounds are made in the circumstellar environment. In comparison to interstellar clouds, there are many advantages to using circumstellar envelopes to study the process of chemical synthesis. First, there is only one single energy source—the central star, whose temperature and luminosity are well known. The envelope often has a well-defined symmetry, which simplifies the geometry of the system. By using molecular lines and infrared continuum radiation as probes, the physical conditions of the envelope, such as density, temperature and radiation background, are well determined as a function of distance from the star. Most importantly, the chemical reaction times are constrained by the dynamical and stellar evolution times, which are  $\sim 10^4$  yr for AGB stars,  $10^3$  yr for PPNe, and  $10^4$  yr for PNe. These timescales therefore give us a precise knowledge of the chemical time needed to form one species from another and thus rigorously constrain the chemical models<sup>10,11</sup>.

### Infrared features of inorganic compounds

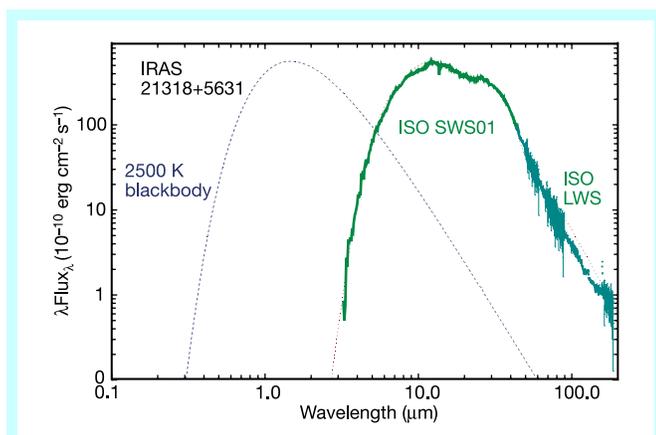
By comparing the spectral features of known minerals with astronomical spectroscopic observations, we are able to identify inorganic solid-state materials that are synthesized in stars. However, the circumstellar envelopes of stars may harbour new substances made under conditions different from those of the terrestrial environment. Through the discovery of new spectral features and the subsequent identification of their carriers, we may learn about new chemical processes or materials that have not previously been considered in the laboratory setting.

The kinds of molecules and solid particles that form in the circumstellar envelopes of AGB stars are dependent on the chemical composition of the stars. Because CO molecules take up most of the elemental form of whichever is less abundant of oxygen and carbon, oxides are generally found in oxygen-rich AGB stars, whereas organic compounds are generally limited to carbon-rich AGB stars.

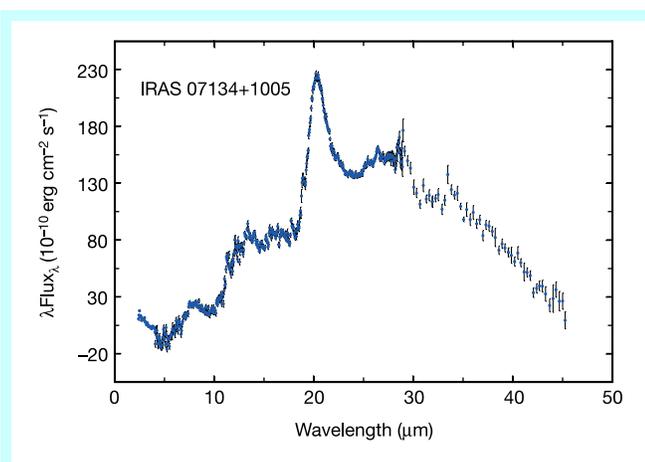
The first solid-state condensate detected in the circumstellar envelopes of AGB stars is composed of silicates. Because silicates make up the most common group of minerals in the Earth's crust and both oxygen and silicon are among the most abundant elements in the Universe, it is reasonable to expect that silicates of stellar origin may also be common. Although most of the terrestrial silicates are in crystalline form, most of the silicates found in AGB stars are amorphous. This is consistent with the expectation that amorphous structures result from rapid condensation from the gas phase in AGB winds. The 9.7- and 18- $\mu\text{m}$  features of amorphous silicates are detected in over 4,000 oxygen-rich AGB stars<sup>12</sup>. During the ISO mission, a rich family of narrow emission bands was found in the spectra of AGB stars and PNe and they are identified as originating from crystalline silicates<sup>13</sup>. Crystalline silicates can be in the form of olivine ( $\text{Mg}_{2-2x}\text{Fe}_{2x}\text{SiO}_4$ , where  $0 \leq x \leq 1$ ) or pyroxene ( $\text{Mg}_{1-x}\text{Fe}_x\text{SiO}_3$ ). Analyses of the ISO observations suggest that the crystalline silicates in AGB stars are magnesium-rich ( $x \approx 0$ ). From the strengths of the crystalline silicate features we can estimate that the abundance of crystalline silicates is small in comparison to amorphous silicates.

In addition to silicates, a variety of refractory oxides may also be present in circumstellar envelopes of AGB stars. A broad feature centred around 13  $\mu\text{m}$ , first discovered by the IRAS Low Resolution Spectrometer (LRS)<sup>14</sup>, could be due to corundum ( $\alpha\text{-Al}_2\text{O}_3$ , which has a feature at 12.7  $\mu\text{m}$ ), glass (amorphous  $\text{SiO}_2$ , 12.3  $\mu\text{m}$ ), spinel (12.95  $\mu\text{m}$ ), or rutile (13.4  $\mu\text{m}$ )<sup>15</sup>. An emission feature at 19.5  $\mu\text{m}$  observed by ISO has been attributed to mixture of Mg-Fe oxides (such as  $\text{Mg}_{0.1}\text{Fe}_{0.9}\text{O}$ )<sup>16</sup>.

In carbon-rich AGB stars, the most common solid-state condensate is SiC, whose 11.3- $\mu\text{m}$  feature due to the stretch mode of the Si-C bond is detected in emission in 700 carbon stars<sup>12</sup>. In more evolved carbon stars, the SiC feature becomes weaker, suggesting that the dust constituent is increasingly dominated by amorphous carbon.



**Figure 1** Invisible stars. IRAS 21318+5631 is an example of an evolved carbon star so obscured by its own ejected circumstellar dust envelope that the central star suffers from 360 magnitudes of extinction in the visible ( $A_V$ ), and is undetectable in the optical region. Its infrared spectrum (solid lines: green, ISO SWS01; turquoise, ISO LWS) is completely due to dust emission and has a colour temperature of 300 K. The red dotted line represents the theoretical fit to the spectrum based on a one-dimensional radiation transfer model with a hidden 2,500 K central star (blue dashed line) as the energy source. The absorption feature near the peak of the spectrum is the 13.7- $\mu\text{m}$  band of acetylene. Infrared and millimetre-wave spectroscopic observations have shown that these stars are prolific molecular factories.



**Figure 2** The unidentified emission feature at 21  $\mu\text{m}$ . ISO SWS spectrum of the PPN IRAS 07134+1005 showing the very strong 21- $\mu\text{m}$  emission feature. The only reason this feature was not detected earlier is because it has been difficult to do mid-infrared spectroscopy from ground-based telescopes and because it is only present in PPNe, a new class of celestial object with very short lifetimes. The error bars are  $1\sigma$  deviation of data points from different scans and detectors over each wavelength resolution element.

In addition to spectral features that can be identified as originating from known minerals, there are strong emission features that remain unidentified. The 21- $\mu\text{m}$  feature was first discovered in four PPNe from observations by the IRAS LRS<sup>17</sup> (Fig. 2). As of 2004, there are 12 known 21- $\mu\text{m}$  sources; all are carbon-rich stars in the post-AGB phase of evolution<sup>18</sup>. The fact that all of the 21- $\mu\text{m}$  sources are carbon-rich strongly suggests that the carrier of this feature is carbon-based. High-resolution ( $\Delta\lambda/\lambda \approx 2,000$ ) ISO observations have found that all features have the same intrinsic profile and peak wavelength ( $\lambda = 20.1 \mu\text{m}$ )<sup>19</sup>. There is no evidence for any discrete substructure caused by molecular bands in the

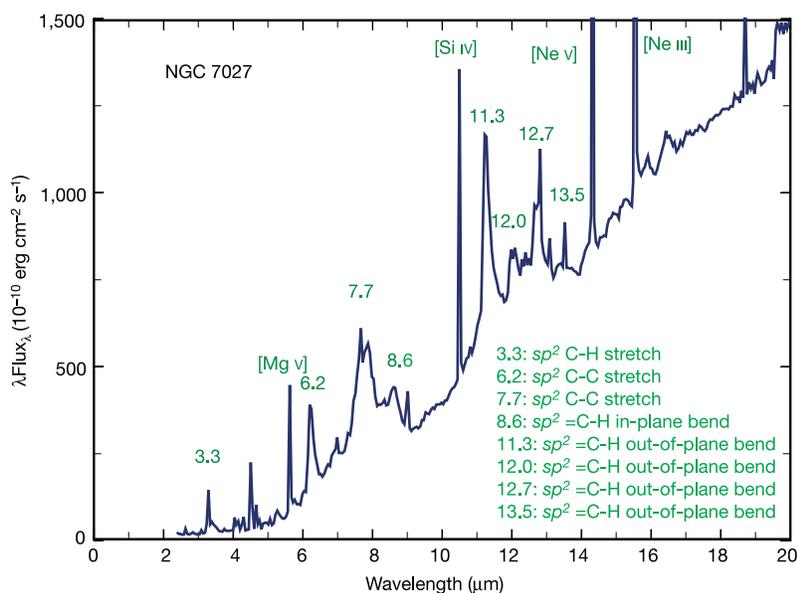
observed spectra, suggesting that the 21- $\mu\text{m}$  feature is either due to a solid substance or a mixture of many similarly structured large molecules. Possible candidates that have been proposed include large polycyclic aromatic hydrocarbon (PAH) clusters, hydrogenated amorphous carbon (HAC) grains<sup>20</sup>, hydrogenated fullerenes<sup>21</sup>, nanodiamonds<sup>22</sup> and TiC nanoclusters<sup>23</sup>, but none of these identifications has been found to be satisfactory. The recent suggestion that the feature is due to micrometre-sized  $\beta$  SiC or nano-SiC grains with carbon impurities may be the most plausible<sup>24</sup>, although this hypothesis requires an efficient suppression of the 11.3- $\mu\text{m}$  feature.

Another unidentified solid-state circumstellar feature is a strong feature at around 30  $\mu\text{m}$ . This feature was first discovered in the spectra of carbon stars and PNe from the Kuiper Airborne Observatory (KAO) observations<sup>25</sup>. More recently, the 30- $\mu\text{m}$  feature has been found to be common in carbon-rich PPNe, especially those showing the 21- $\mu\text{m}$  emission feature<sup>26</sup>. The fact that a significant fraction ( $\sim 20\%$ ) of the total radiative energy output of PPNe is emitted in this feature suggests that the carrier must be composed of abundant elements<sup>27</sup>. The first suggested identification was solid MgS based on a comparison with laboratory measurements<sup>28</sup>. The alternative suggestion that the carrier is a carbonaceous material continues to be popular because the feature is seen only in carbon-rich objects.

### The synthesis of organic compounds

Although many of the gas-phase molecules detected through their rotational transitions are organic molecules, the detection of complex organic compounds through their stretching and bending vibrational modes was totally unexpected. These organic compounds have dozens or hundreds of atoms, and their synthesis was not thought to be possible in a low-density environment. The detection of organic compounds in stellar winds gives us important information on how these species are formed. The evolution from AGB star to PPN to PN is very short, and this gives us precise knowledge of the timescale of chemical synthesis.

A family of strong infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7  $\mu\text{m}$  were first detected by the KAO in the young carbon-rich PN NGC 7027<sup>29</sup>, and have since been widely observed



**Figure 3** Stretching and bending modes of aromatic compounds. The ISO SWS spectrum of the PN NGC 7027 is dominated by a strong dust continuum (peaking at  $\sim 30 \mu\text{m}$ ), and atomic emission lines due to fine-structure transitions of heavy

elements (for example, the [Ne III] line at 15.6  $\mu\text{m}$ ). The AIB features are marked by their peak wavelengths and their identification is listed in the legend.

in PNe, H II regions, reflection nebulae and galaxies (Fig. 3). These features are identified with the aromatic C–H stretch (3.3  $\mu\text{m}$ ), aromatic C–C stretch (6.2 and 7.7  $\mu\text{m}$ ), aromatic C–H in-plane bend (8.6  $\mu\text{m}$ ), and aromatic C–H out-of-plane bending (11.3  $\mu\text{m}$ ) modes<sup>30</sup>. These features are collectively referred to as aromatic infrared bands (AIB). Since the AIB features first emerge in the PPN phase, what are the steps leading to the formation of ring molecules? Acetylene ( $\text{C}_2\text{H}_2$ ), believed to be the first building block of benzene, is commonly detected in evolved carbon stars through its  $\nu_5$  fundamental band at 13.7  $\mu\text{m}$  (see Fig. 1). Polymerization of  $\text{C}_2\text{H}_2$  leads to the formation of diacetylene ( $\text{C}_4\text{H}_2$ ) and triacetylene ( $\text{C}_6\text{H}_2$ ) in PPN, culminating in the formation of benzene<sup>31</sup>.

In addition to the AIBs seen in PNe, emission features at 3.4 and 6.9  $\mu\text{m}$  due to aliphatic C–H stretch and bending modes are found in the spectra of PPNe and young PNe<sup>20,27,32,33</sup>. Furthermore, emission features at 11.3, 12.1, 12.4 and 13.3  $\mu\text{m}$ , which can be identified as arising from out-of-plane vibrational modes of aromatic C–H bonds with respectively one, two, three or four C–H bonds per edge of an aromatic ring<sup>34</sup>, have also been detected<sup>35</sup>.

Aromatic and aliphatic bands are not the only emission features seen in the infrared spectrum of PPNe. Also present are broad emission features at 8 and 12  $\mu\text{m}$  (Fig. 4). Because the 6.9- $\mu\text{m}$  band is known to originate from a mixture of  $-\text{CH}_2-$  and  $-\text{CH}_3$  bending modes, associated bending modes of other side groups are likely to be present. Similarly, the 11.3- $\mu\text{m}$  aromatic C–H out-of-plane bending mode can be accompanied by a complex set of features due to out-of-plane vibrations of alkenes<sup>36</sup>. The existence of the 8- and 12- $\mu\text{m}$  broad emission features therefore suggests that the chemical structures of these carbonaceous compounds are complex, and probably include a variety of alkane and alkene side groups attached to aromatic rings.

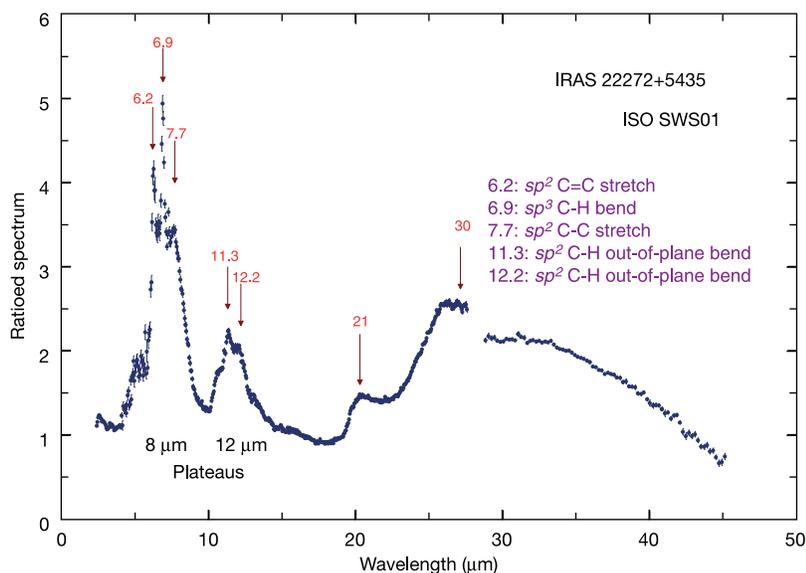
The discovery of aromatic features has led to vigorous discussions in the literature on the nature of the carriers. Most of the suggestions centre on aromatic hydrocarbons of both natural and artificially created varieties. Carbonaceous compounds have been produced in the laboratory by a variety of techniques, including chemical vapour deposition<sup>37</sup>, combustion<sup>38</sup>, laser ablation<sup>39</sup>, and laser pyrolysis of

hydrocarbons<sup>40</sup>. The most widely discussed candidates for the carrier of the AIB are polycyclic aromatic hydrocarbon (PAH) molecules. PAH molecules are benzene rings of  $sp^2$ -hybridized C atoms linked to each other in a plane, with H atoms or other radicals saturating the outer bonds of peripheral C atoms. PAH molecules were first proposed as the carrier of the AIBs in the diffuse interstellar medium because their small sizes (<1 nm) allow them to be heated to high temperatures ( $\sim 1,000$  K) by stochastic heating<sup>41–43</sup>.

However, small gas-phase PAH molecules are unlikely to be the carrier of the AIBs seen in PPNe and PNe. The AIBs in these objects always sit on top of a strong continuum, which cannot be provided by small PAH molecules. PPNe have no ultraviolet photon output, which would be required for the excitation of gas-phase PAHs. The width of the AIB features and the consistency of the peak wavelengths also argue against the idea that they are produced by a mixture of different PAH molecules. The carrier is more likely to be a solid-state compound, consisting of at least hundreds of carbon atoms.

The detection of aliphatic signatures in PPNe has greatly increased the interest in another natural substance: coal. Formed from fossilized hydrocarbon materials, coal contains a mixture of  $sp$ ,  $sp^2$  and  $sp^3$  bonds. The possibility that coal-like material (for example, kerogen) can be responsible for the AIB was first suggested by R. Papoular<sup>44</sup>. Structurally, kerogen can be represented by random arrays of aromatic carbon sites, aliphatic chains ( $-\text{CH}_2-$ )<sub>n</sub>, and linear chains of benzenic rings with functional groups made up of H, O, N and S attached. Stellar synthesis of organic compounds is unlikely to be pure, involving only H and C, so the presence of other elements in carbonaceous material is to be expected. Comparison of the infrared spectra of kerogen shows that they are very similar to those of PPNe<sup>45–47</sup>.

The AIBs can also arise from artificial substances not common in the natural terrestrial environment. Examples of such compounds include hydrogenated amorphous carbon (HAC) and quenched carbonaceous composites (QCC). HAC consists of islands of aromatic ( $sp^2$ ) bonded C atoms joined together with a variety of



**Figure 4** Broad emission features in PPNe. This continuum-removed ISO SWS01 spectrum of the PPN IRAS 22272+5435 shows the 8- and 12- $\mu\text{m}$  emission plateaus due to the in-plane and off-plane bending modes of aliphatic side groups attached to an aromatic carbonaceous compound, for which the narrow emission features and

their peak wavelengths are marked on the spectrum. Also shown are the unidentified emission features at 21 and 30  $\mu\text{m}$  (ref. 36). The error bars are  $1\sigma$  deviation of data points from different scans and detectors over each wavelength resolution element.

peripheral  $sp^2$  and  $sp^3$  bonded hydrocarbons<sup>48</sup>. HAC can be formed in the laboratory by direct condensation of carbon vapour from an H-rich atmosphere, and has been observed to show similar spectral features as in PPNe<sup>49</sup>. QCC are produced by the technique of hydrocarbon plasma deposition. Methane gas is heated to 3,000 K with a microwave generator, allowed to expand into a vacuum chamber and condensed on a room-temperature substrate<sup>50</sup>. The resultant dark, granular material is shown by electron micrography to have an amorphous structure. Mass spectroscopy of QCC suggests that their aromatic component typically consists of one to four rings, and most have only one to two rings. Infrared spectroscopy of QCC reveals a mixture of  $sp$ ,  $sp^2$  and  $sp^3$  bonds. The conditions under which QCC are synthesized resemble the circumstellar environment of AGB stars, so its laboratory production may shed some light on the solid-state condensation process in the envelopes of AGB and post-AGB stars.

Although it is not yet certain whether coal, HAC or QCC gives the best approximation to interstellar carbonaceous dust, it is clear that such grains include both aromatic and aliphatic components. A schematic of possible chemical structure is given in Fig. 5.

### Stardust in the Solar System

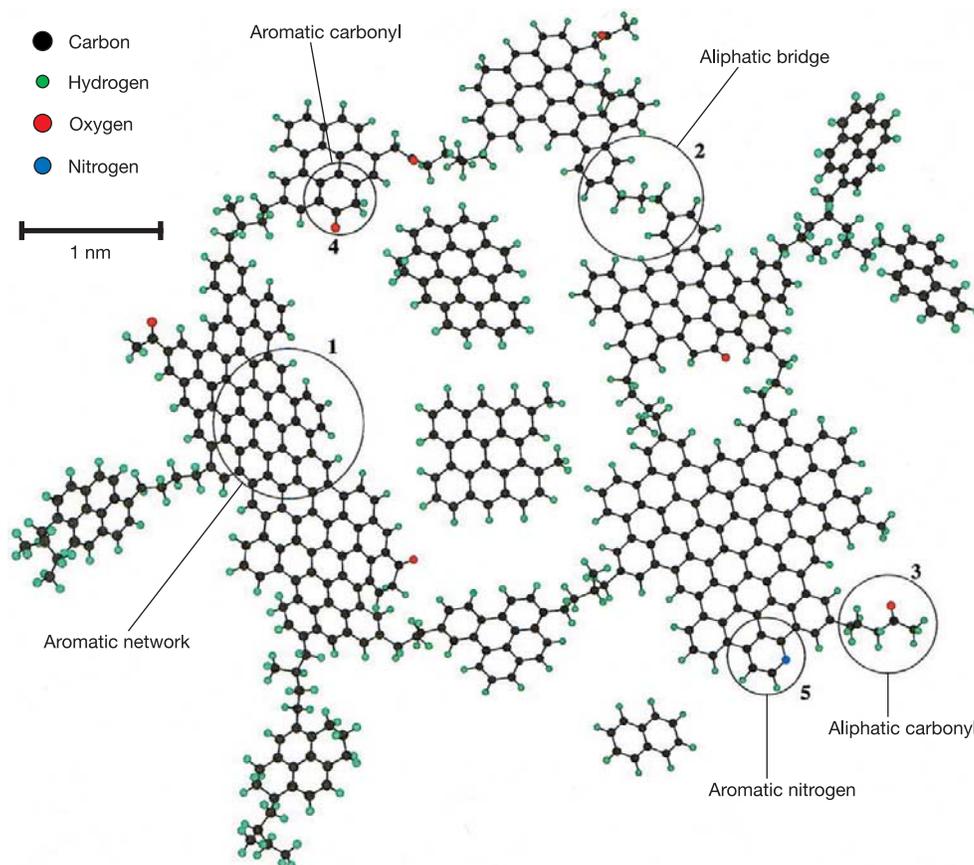
Spectral signatures of grains produced in AGB stars, PPNe and PNe are now found in Solar System objects. These results suggest that comets, interplanetary dust and meteorites preserve pristine stellar material not processed by the early solar nebula, and our ability to

perform laboratory analysis of these materials through mass spectroscopic and isotopic analysis has given us a direct link to inorganic and organic compounds produced by stars.

The silicate features, both amorphous and crystalline, are seen in comets<sup>51</sup>, interplanetary dust<sup>52</sup> and meteorites<sup>53,54</sup>. Infrared spectra of organic extract sublimate from the Murchison meteorite show the 3.4- $\mu\text{m}$  aliphatic features that are similar to those observed in PPNe<sup>55</sup>. This feature has also been observed in comets<sup>56</sup> and interplanetary dust<sup>57</sup>. Isotopic studies of meteorites have also identified grains of presolar origin, including diamonds<sup>58</sup>, corundum<sup>59</sup>, spinel<sup>59</sup>, and in particular SiC<sup>60</sup>, the most common and best-studied of the group. These grains therefore represent an important link between stars and the Solar System<sup>61</sup>. The dominant organic matter in carbonaceous chondrites is similar to kerogen<sup>62</sup> and aliphatic sidegroups constitute several per cent of the mass of interplanetary dust<sup>63</sup>.

### Outlook

We have learned that chemical synthesis of complex organic and inorganic compounds can take place in the low-density circumstellar environment over very short ( $10^3$  yr) timescales during the late stages of stellar evolution. By tracing the change in the infrared spectra of carbon stars to PPNe to PNe, we found definite evidence for chemical evolution (Table 1). Infrared spectroscopic observations have clearly demonstrated that solid-state compounds of both organic and inorganic nature are produced in abundance in



**Figure 5** A model of carbonaceous interstellar dust consisting of various aromatic and aliphatic groups (after ref. 55). Examples of five basic units are shown, circled and labelled. The carbonaceous compounds seen in PPNe and PNe are likely to include both aromatic and aliphatic components as well as impurities such as O and N. Among the 470 C atoms in this structure, 400 are in aromatic units and 70 are in aliphatic

groups. The approximate volume of this structure is  $\sim 10^{-19} \text{ cm}^3$ , that is, approximately  $10^4$  of such structures could be contained in a typical grain of 0.1  $\mu\text{m}$ . The exact ratios of  $sp^2$  and  $sp^3$  sites will vary, depending on the state of evolution of the central star.

Table 1 Changes in relative strengths of infrared emission features as stars evolve from AGB to planetary nebulae

Infrared features ( $\mu\text{m}$ )	Origin	Carbon stars	Proto-planetary nebulae	Planetary nebulae
3.3, 6.2, 7.7, 11.3	Aromatic stretch and bending modes	No	Yes	Strong
3.4, 6.9	C-H aliphatic stretch and bend	No	Yes	Weak
12.1, 12.4, 13.3	C-H out-of-plane bend with two, three and four adjacent H atoms	No	Yes	Weak
Broad 8, 12	Bending modes from aliphatic sidegroups	No	Yes	Weak
Broad 21	–	Weak	Strong	No
Broad 30	–	Yes	Yes	Yes

The weakening of the 3.4 and 6.9  $\mu\text{m}$  features from PPNe to PNe suggests a change from aliphatic to aromatic structures. This could be the result of photochemistry where the onset of ultraviolet radiation modifies the aliphatic side groups through isomerizations, bond migrations, cyclization and ring closures and transforms them into ring systems<sup>36</sup>. Hydrogen loss can also result in fully aromatic rings that are more stable than alkanes or alkenes. Evidence for such H loss can also be found in the weakening of the 12.1, 12.4 and 13.3  $\mu\text{m}$  features and the strengthening of the 11.3  $\mu\text{m}$  feature from PPNe to PNe.

the circumstellar envelopes of evolved stars. The ejection of these grains into the interstellar medium suggests that circumstellar grains are a major source of interstellar grains, some of which have even survived the formation of the Solar System. The detections of pre-solar grains in meteorites and the detection of a high deuterium to hydrogen ratio in interplanetary dust particles<sup>64</sup> have supported this stellar–Solar System connection. Space missions to comets allow *in situ* analysis of dust compositions in comets through mass spectroscopy, yielding both size and elemental abundance determinations. Instead of being condensates out of a homogeneous solar nebula that has vaporized all pre-solar material, we now believe that the Solar System objects contain primordial materials that have been delivered to the solar nebula from stars. The possibility of sample gathering from interplanetary space and comets will allow us to obtain specific information on the structure of the grains and sheds light on the process of nucleation and condensation from the gas phase under non-equilibrium conditions.

With the analysis of meteoritic material and sample returned from comets and in the interplanetary medium<sup>65</sup>, we are now able to hold materials condensed in the stellar environment in our own hands, and perform a variety of analyses using all the laboratory techniques at our disposal. With techniques such as scanning transmission X-ray microscopy<sup>66</sup>, high-resolution transmission electron microscopy, nuclear magnetic resonance spectroscopy<sup>67</sup>, and ion microprobe scanning imaging<sup>68</sup>, we can make high spatial resolution measurements of the physical and chemical properties of stellar grains. These techniques allow precise determination of the geometry, size and shape of the aliphatic groups, as well as their exact chemical nature. All these properties are difficult to obtain from spectroscopy alone. Comparison of the actual isotopic ratios in these grains to their predicted values by theoretical nucleosynthesis models will help to constrain the nuclear processes in the interior of stars.

In the coming decade, laboratory astrophysics will expand beyond its traditional role of comparing laboratory measurements and astronomical observations to include the analysis of stellar-synthesized materials. For most of the history of the science, astronomy has been restricted to remote observations. Through a comparison between infrared spectroscopy of stellar ejecta and laboratory analysis of collected pre-solar grains, we have entered a new era of direct testing of theories of nucleosynthesis in the interior of stars and chemical synthesis of inorganic and organic compounds in the circumstellar environment. □

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**Correspondence** and requests for materials should be addressed to S.K. (kwok@asiaa.sinica.edu.tw).