

Synthesis of Organic Compounds in the Late Stages of Stellar Evolution

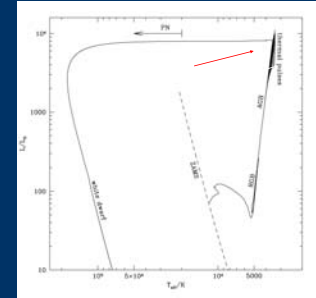
Sun Kwok

International conference on interstellar dust, molecules, and chemistry
Pune, November 22, 2011

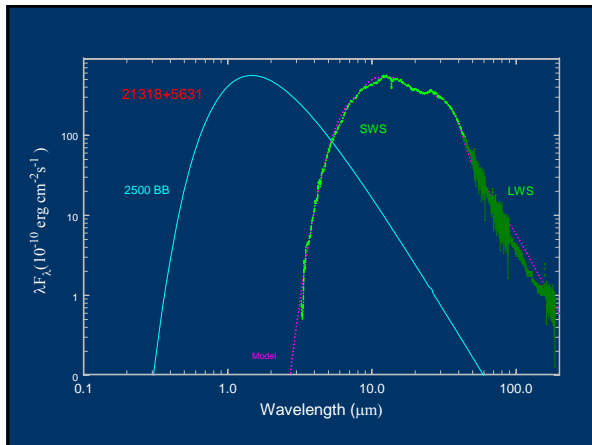


Evolution of intermediate mass (1-8 M_⊙) stars

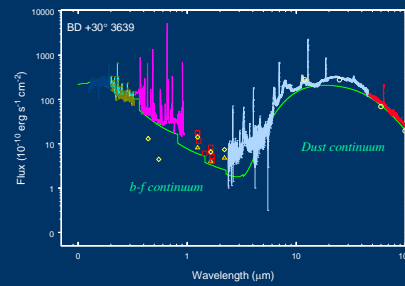
- Triple- α reaction (He \rightarrow C)
- Slow neutron capture (s-process) (Y, Zr, Ba, La, Ce, Pr, Nd, Sm, Eu, etc)
- Thermal pulse and dredge up



3 M_⊙ track



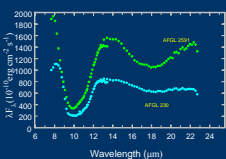
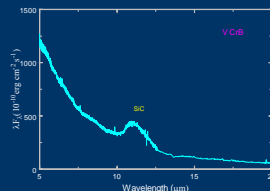
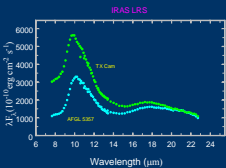
Remnant AGB dust envelope in PN



In young PN,
~1/3 of flux emitted in IR
(Zhang & Kwok 1991)



Amorphous Silicates & silicon carbide

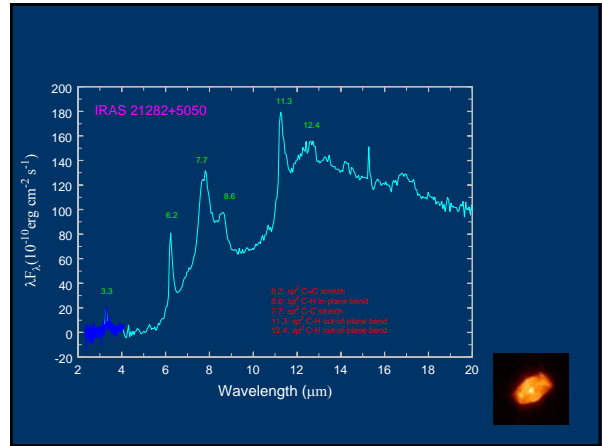
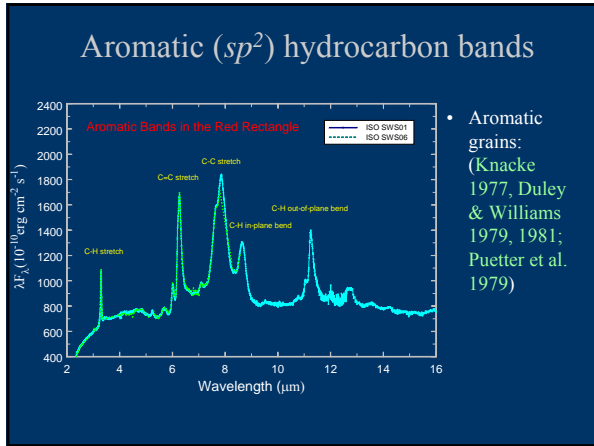


- 4000 stars detected to have amorphous silicates by IRAS LRS
- 700 stars detected in SiC

Unidentified infrared emission bands



- 11.3 μ m: Gillett et al. 1973
- 3.3 μ m: Merrill et al. 1975
- 6.2, 7.7, 8.6 μ m: Russell et al. 1978 (from KAO)



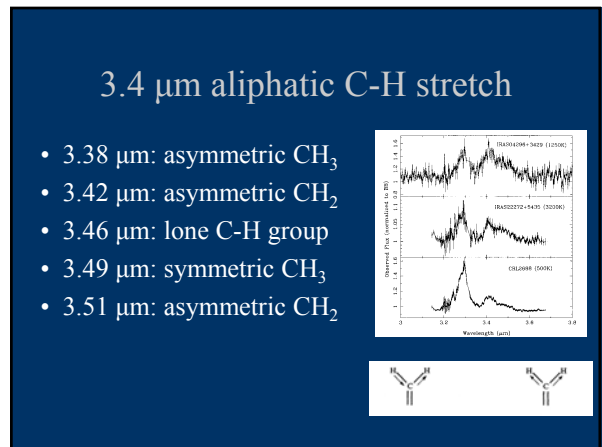
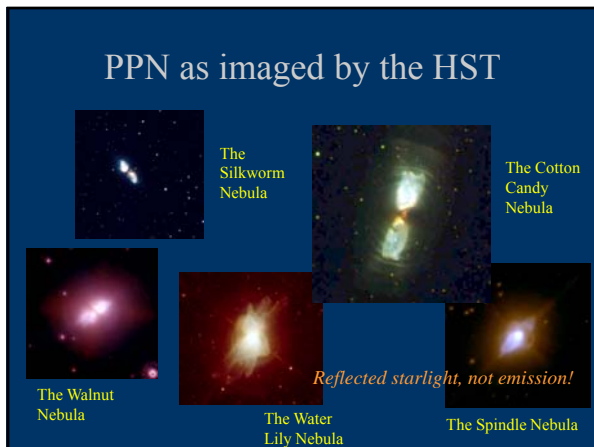
When are the aromatic compounds synthesized?

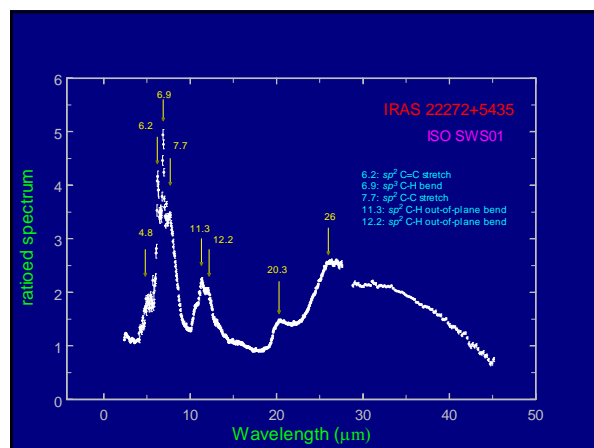
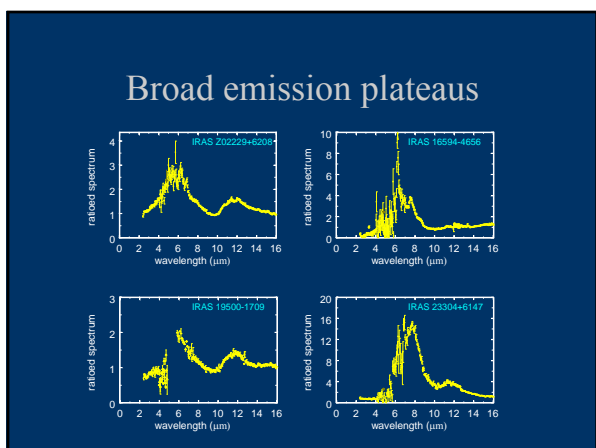
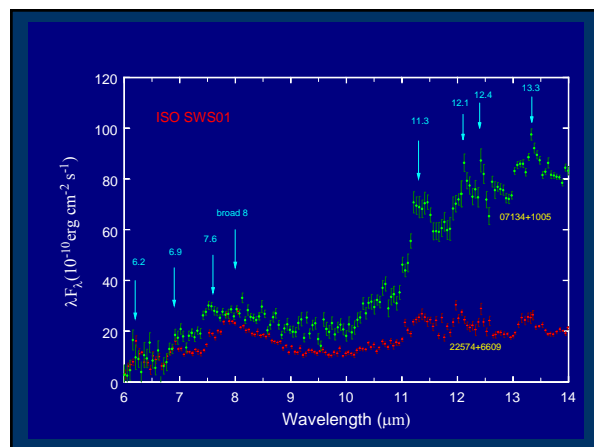
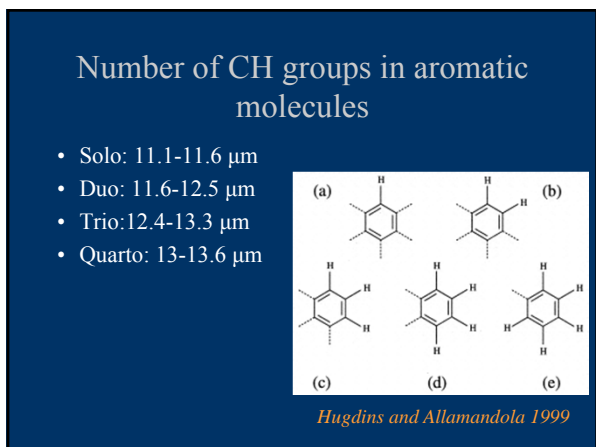
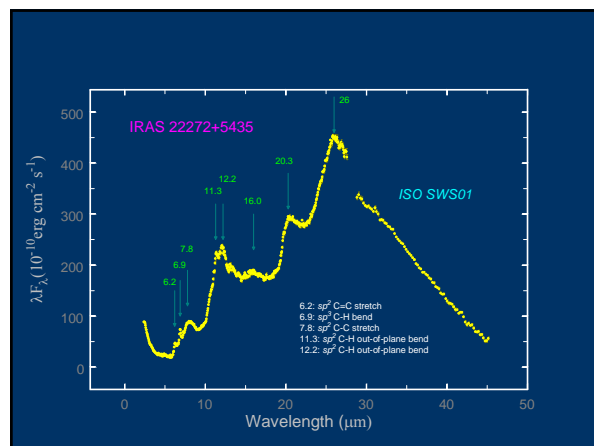
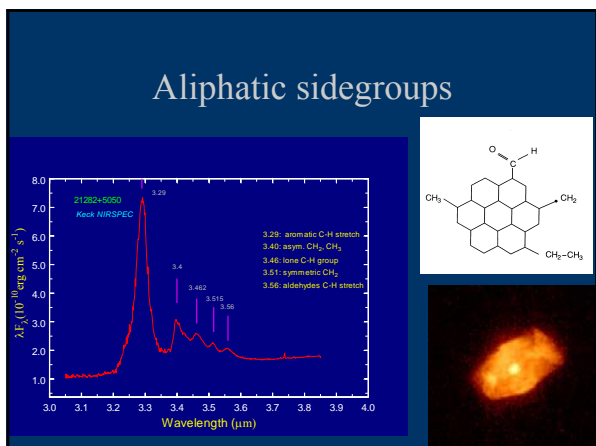
- AIB features not seen in AGB stars
- AIB features are strong in young planetary nebulae
- Have to study the missing link between AGB and PN phases

Proto-planetary nebulae

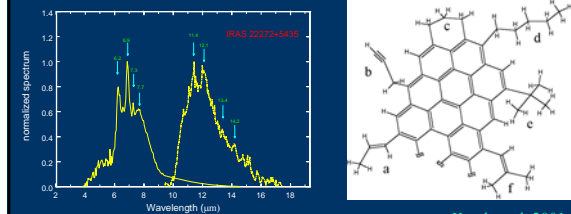
- Objects in transition between AGB and PN stages
- ~30 PPN are known, most discovered as the result of follow up of the IRAS survey (Kwok 1993, *Ann. Rev. Astr. Ap.*, 31, 63)

AFGL 2688, the Egg Nebula



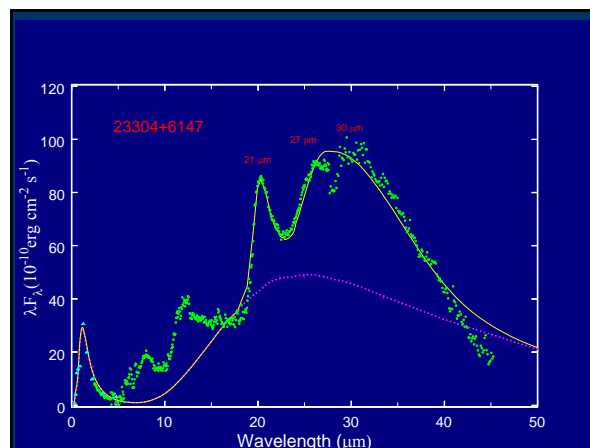


Aliphatic bending modes

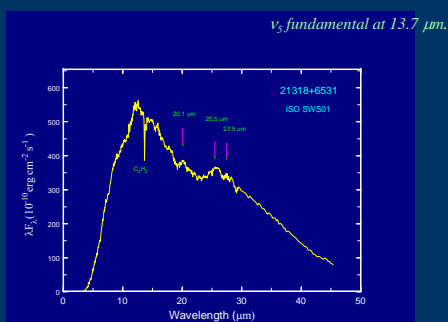
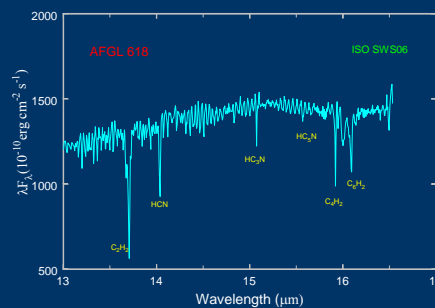


Kwok et al. 2001

- 8 μm plateau: $-\text{CH}_3$ (7.25 μm), $-\text{C}(\text{CH}_3)_2$ (8.16 μm , "c"), $=(\text{CH}_2)_2$ (8.6 μm , "f")
- 12 μm plateau: C-H out-of-plane bending modes of alkene ("a", "b"), cyclic alkanes (9.5-11.5 μm , "c"), long chains of $-\text{CH}_2-$ groups (13.9 μm , "d").



Acetylene: first step to organic synthesis

 v_3 fundamental at 13.7 μm .Polymerization of C_2H_2 in Post-AGB evolution

Chemical evolution from AGB to PN

- Extreme carbon stars ($t \sim 10^4$ yr): $\text{C}_2\text{H}_2 \Rightarrow \text{C}_6\text{H}_6$
- PPN ($t \sim 10^3$ yr): clusters of aromatic rings with peripheral aliphatic bonds
- PN ($t \sim 10^4$ yr): loss of H and a progressive formation of clusters of rings into more structured units

Advantages of circumstellar chemistry

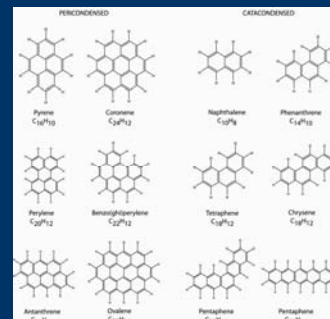
- Single energy source
- Simple geometry
- Well-determined physical environment (density $\rho(r)$, temperature $T(r)$, radiation background $I(r)$)
- Chemical time scale defined by dynamical time scale (AGB: 10^4 yr, PPN: 10^3 yr, PN: 10^4 yr)

What is the carrier of the UIR features?

- Aromatic features: 3.3, 6.2, 7.7, 8.6, and 11.3 μm
- Aliphatic features: 3.4 and 6.9 μm
- Features at 15.8, 16.4, 17.4, 17.8, and 18.9 μm
- Broad plateau features at 8, 12, and 17 μm .

Polycyclic aromatic hydrocarbons (PAH)

- Fused ring molecules made up of pure C and H



The PAH hypothesis

(Allamandola et al. 1989, Puget & Léger 1989)

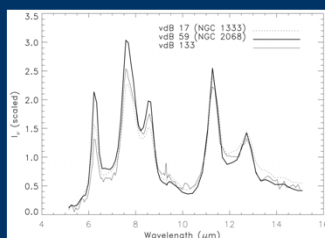
- the UIR features are the result of infrared fluorescence from small (~ 50 C atoms) gas-phase PAH molecules being pumped by far-ultraviolet photons (Tielens 2008)
- The central argument for the PAH hypothesis is that single-photon excitation of PAH molecules can account for the 12 μm excess emission observed in cirrus clouds in the diffuse interstellar medium by *IRAS* (Sellgren 1984, 2001).

Problems with the PAH model

- PAH molecules have well-defined sharp features but the UIR features are broad
- PAHs primarily excited by UV, with little absorption in the visible
- UIR features seen in PPN and reflection nebulae with no UV radiation
- Shapes and peak wavelengths independent of stellar temperature
- The strong and narrow predicted gas phase features in the UV are not seen in interstellar extinction curves
- No PAH molecules have been detected in spite of the fact that the vibrational and rotational frequencies are well known
- In order to fit the astronomical observations, the PAH model has to appeal to a mixture of PAH of different sizes, structures (compact, linear, branched) and ionization states, as well as broad intrinsic line profiles.

Reflection nebulae

- The UIR features have consistent profiles and peak wavelengths in spite of the fact that the nebulae are heated by central stars of 11000, 19000 and 6800 K
- No UV background



Uchida et al. (2000)

Excitation problem

- The 3.3 and 7.7 μm radiate at too short a wavelength for the grains to be in thermal equilibrium
- Stochastic heating by single photon
- Alternate explanation: sudden release of chemical energy as a source of transient heating (Duley and Williams 2011).

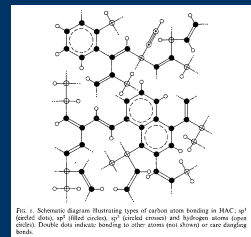
If not PAH, then what is it?

Laboratory Simulations of Cosmic Dust

- Quenching of plasma of 4-torr methane (Sakata et al. 1987)
- Hydrocarbon flame or arc-discharge in a neutral of hydrogenated atmosphere (Colangeli et al. 1995)
- HAC films prepared by laser ablation of graphite in a hydrogen atmosphere (Scott and Duley 1996)
- Infrared laser pyrolysis of gas phase molecules (C_2H_4 , C_4H_6) \Rightarrow C-based nanoparticles (Herlin et al. 1998)
- HAC polymers: photolysis of methane at low temperatures (Dartois et al. 2004)
- Flame combustion forming soot (Pino et al. 2008) (C_2H_2 , C_2H_4 , C_3H_6 mixed with O_2)

Hydrogenated Amorphous Carbon

- Aromatic rings of various sizes bonded peripherally to polymeric of hydrocarbon species
- A mixture of sp^2 and sp^3 bonded carbon
- Formed when H content exceeds 0.1 relative to C
- Similar to soot formed from the combustion of hydrocarbons

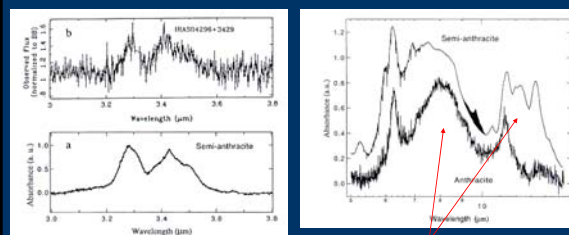


Duley

Pure C & H or with N?

- **QCC**: hydrocarbon plasma deposition
- **Tholins**: refractory organic materials formed by UV photolysis of reduced gas mixtures (N_2 , NH_3 , CH_4 , etc.)
- **HCN polymers**: amorphous hydrogenated carbon nitride, formed spontaneously from HCN

Infrared Spectrum of Coal

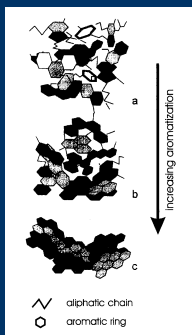


Guillois et al. 1996

Emission plateaus

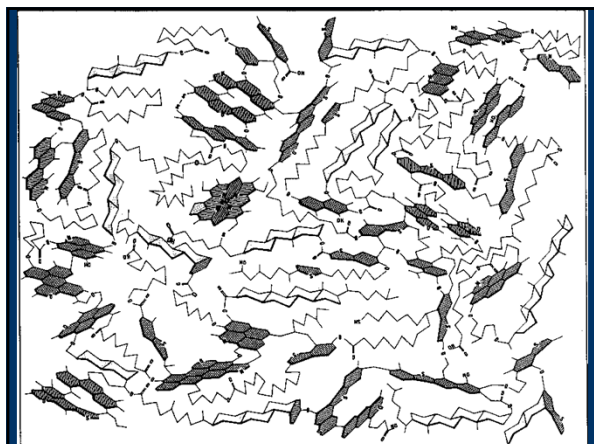
Coal

- The physical and chemical properties of coal are entirely controlled by the chemical evolution of the Earth's crust
- semianthracite \Rightarrow anthracite \Rightarrow semi-graphite
- Decreasing H and O content
- Change from aliphatic (sp^3) to aromatic (sp^2) bonds
- graphitization



Kerogen

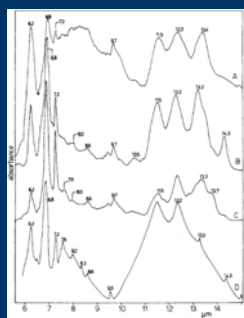
- random arrays of aromatic carbon sites, aliphatic chains ($-CH_2-$)_n, and linear chains of benzenic rings with functional groups made up of H, O, N, and S attached
- a solid sedimentary, insoluble, organic material found in the upper crust of the Earth



Origin of coal and kerogen

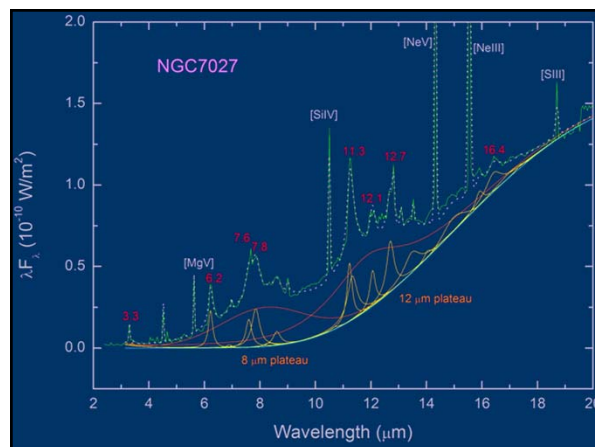
- Fraction of H, S, N, and O relative to C in kerogen are similar to those in lipids \Rightarrow *formed as the result of decay of living organisms*

Petroleum fractions

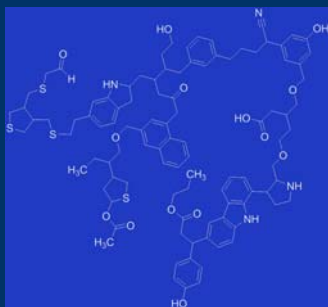


Anthracite coal
Modified fraction 2
Distillate aromatic extract
PPN 22272+5435

Cataldo et al. 2004



Complex organic solids with disorganized structures



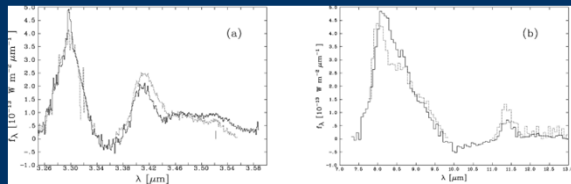
- Small units of aromatic rings linked by aliphatic chains
- Impurities of O, N, S
- A typical nanoparticle may contain multiple of this structures

Kwok & Zhang 2011

How do they form?

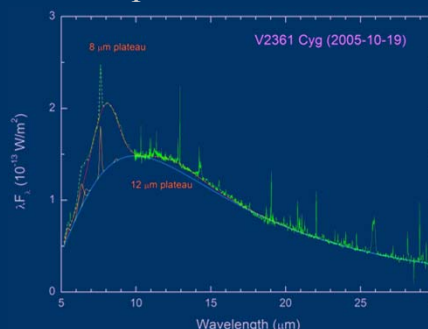
- Surface temperature of red giants: 3000 degrees
- Solid grains condensed from gas in the stellar wind under near vacuum conditions
- Theoretically impossible, especially during the PPN phase
- Observationally we see aliphatics and aromatics form in PPN on time scales as short as hundreds of years
- In novae, they form on a time scale of days

Aromatic & aliphatic features in novae



The 3.3 & 3.4 (left) and 8.2 and 11.4 μ m features of Nova V705 Cas at 253 (solid line) & 320 (broken line) days after outburst (Evans et al. 2005)

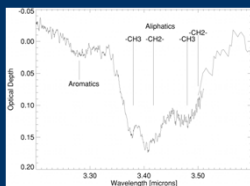
Aliphatics in novae



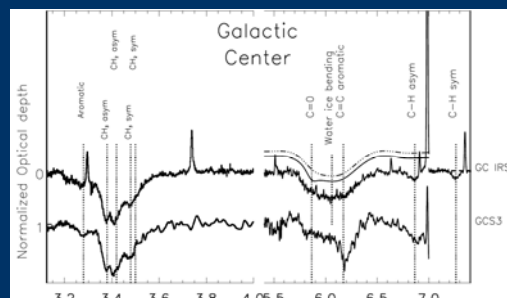
Kwok & Zhang 2011

Organic grains in the diffuse ISM

- 3.4 μ m C-H stretch observed along the line of sight to the GC (Wickramasinghe & Allen 1983)
- Other sources: Sandford et al. 1991, Pendleton et al. 1994, Chiar et al. 2000



Aliphatics in diffuse ISM



15% of C in sp^3 bonding

Dartois et al. 2004, Chiar et al. 2002, Dartois 2011

Organics in the Solar System

- Planets and their satellites, asteroids, comets, minor bodies in the outer Solar System
- Traditional picture: made up of minerals, metals, and ices

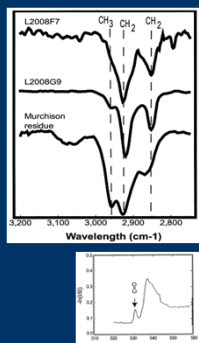
Interplanetary dust particles

- About 30,000 tons of IDP fall on Earth every year, higher in the early periods



Interplanetary Dust

- Few microns to tens of microns in size (Brownlee 1978)
- Silicates (olivine & pyroxene)
- 10-12% carbon content
- 3.4 μm aliphatic feature and sometimes C=O group (Flynn et al. 2003)



O-XANES spectrum of IDP

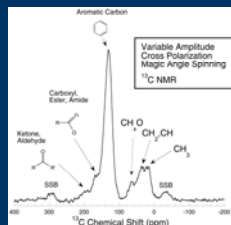
The soluble component

- Carboxylic acids, sulfonic and phosphonic acids, amino acids, aromatic hydrocarbons, heterocyclic compounds, aliphatic hydrocarbons, amines and amides, alcohols, aldehydes, ketones, and sugar related compounds
- Almost all biologically relevant organic compounds are present in carbonaceous meteorites

C and N isotopic ratios suggest interstellar origin (Martins et al. 2008; Nakamura-Messenger et al. 2006)

Carbonaceous Chondrite Meteorites

- Pre-biotic organic matter
- Insoluble macromolecular material similar to kerogen (Kerridge 1999), possibly of interstellar origin due to excess of D, ^{13}C , ^{15}N , etc.

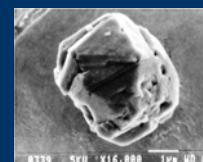


Functional groups identified in Murchison IOM (Cody 2008)

Spectral profiles of IOM similar to interstellar 3.4 μm features (Ehrenfreund et al. 1991)

Pre-solar grains

- Isotopic studies of meteorites have also identified grains of presolar origin, including diamonds (Lewis et al. 1987), SiC (Bernatowicz et al. 1987), corundum (Al_2O_3) and spinel (MgAl_2O_4) (Nittler et al. 1997).

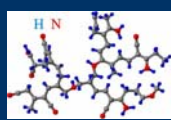
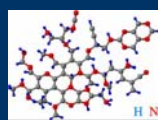


Scanning electron microscopic micrograph of a 4 μm pre-solar SiC crystal from the Murchison meteorite.

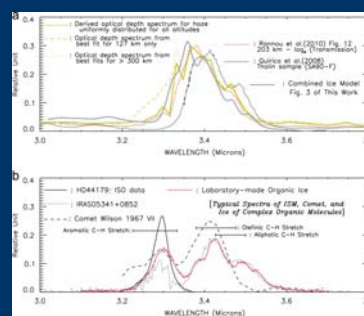
Burning down a haystack to find a needle

Planetary satellites

- Cassini-Huygens observations of the Saturnian satellite Titan
- Total amount of hydrocarbons on Titan is larger than the oil and gas reserves on Earth



Comparison between 3.4 μm features in Titan haze, comets, and PPNs



Kim et al. 2011

Primordial solids

- Most of the original solar nebula was incorporated in the Sun, with the remaining planetesimals aggregated into planets
- Small fractions of the pristine materials reside in comets and asteroids which were not subjected to extensive processing
- Effects of exogenous delivery (**Anders 1989, Chyba & Sagan 1992**)

Summary

- Organic compounds are everywhere in the Universe (from solar system to ISM to galaxies)
- Hydrocarbons with linear, aromatic and aliphatic structures are detected in the circumstellar envelopes of evolved stars
- These carbonaceous materials undergo a change from aliphatic to aromatic structures during the transition from PPN to PN
- Chemical evolution leading to complex organic compounds can take place over only a few thousand years in the circumstellar environment

Summary (cont.)

- The detection of pre-solar grains suggests that grains from AGB stars can survive the journey through the ISM and reach the Solar System
- Macromolecular organics in meteorites, IDP, comets, and planetary satellites show similarities with organics produced by planetary nebulae
- To what extent was the Early Earth chemically enriched by the early bombardment?

A star-Earth connection

References

- Kwok, S. 2004 The Synthesis of Organic and Inorganic Compounds in Evolved Stars, *Nature*, **430**, 985
- Kwok, S. & Zhang, Y. 2011, Mixed aromatic/aliphatic organic nanoparticles as carriers of the unidentified infrared emission features, *Nature*, **479**, 80

