Interstellar Extinction – A revisit

Chandra Wickramasinghe

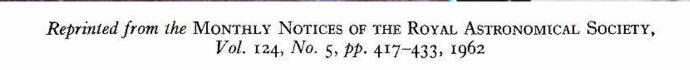


THE UNIVERSITY OF **BUCKINGHAM**

BUCKINGHAM CENTRE FOR ASTROBIOLOGY (BCAB)

 The total mass of "dust" in the universe is a fair fraction of 1% of the total mass of baryonic matter.

 So its chemical characterisation is a matter of profound importance to astronomy – and arguably also to our very existence on this planet Review is centred on a collaboration with the late Sir Fred Hoyle that started in 1962 and lasted till 2001



ON GRAPHITE PARTICLES AS INTERSTELLAR GRAINS

F. Hoyle and N. C. Wickramasinghe

(Received 1962 June 13)

Summary

The interstellar reddening curve predicted theoretically for small graphite flakes is in remarkable agreement with the observed reddening law, suggesting that the interstellar grains may be graphite and not ice. This possibility is not in contradiction with the high albedos of reflection nebulae at photographic wave-lengths, provided the particles have sizes of order 10^{-5} cm.

The origin of graphite flakes at the surfaces of cool carbon stars is con-



HE INTERNATIONAL ASTROPHYSICS SERIES

Interstellar Grains

N. C. Wickramasinghe

The very first review on grains was the first monograph on the subject published in 1967.....

To recap - a succession of models have been proposed since 1939.....

- Iron grains radii ~ 0.01 micron (C. Schalen, 1939)
 Dirty ice grains (J. Oort and H.C. Van de Hulst, 1946)
 Graphite grains (F. Hoyle and N.C. Wickramasinghe, 1962)
- •Graphite-silicate grain mixtures (Hoyle-Wickramasinghe, 1970)
- Iron, graphite whiskers contributing to far uv and neutral extinction

In 1962 popular theory of grains – dirty ice grains, condensed in interstellar clouds

We argued that.....

Nucleation of grains cannot occur in the diffuse interstellar clouds with densities in the range $10 - 100 \text{ cm}^{-3} => \text{higher density venues} - \text{cool stars}$

Atmospheres of giant stars

R Cor Bor

•N stars \Rightarrow carbon grains

•Nucleation and grain growth in cool star atmospheres and stellar mass flows

•Expulsion by radiation pressure

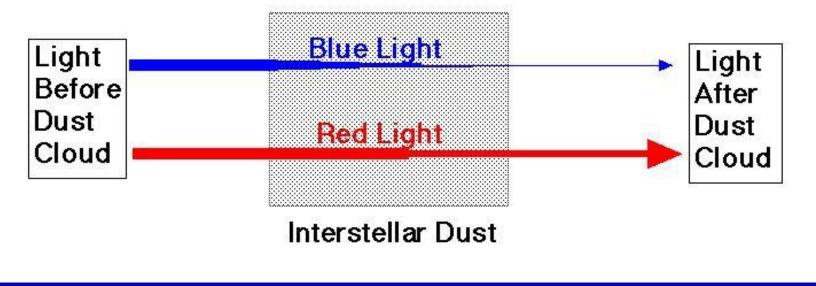
•Mira variables \Rightarrow mineral grains

Refractory grains from supernova explosions, planetary discs

•Volatile molecular mantles can form in dense clouds

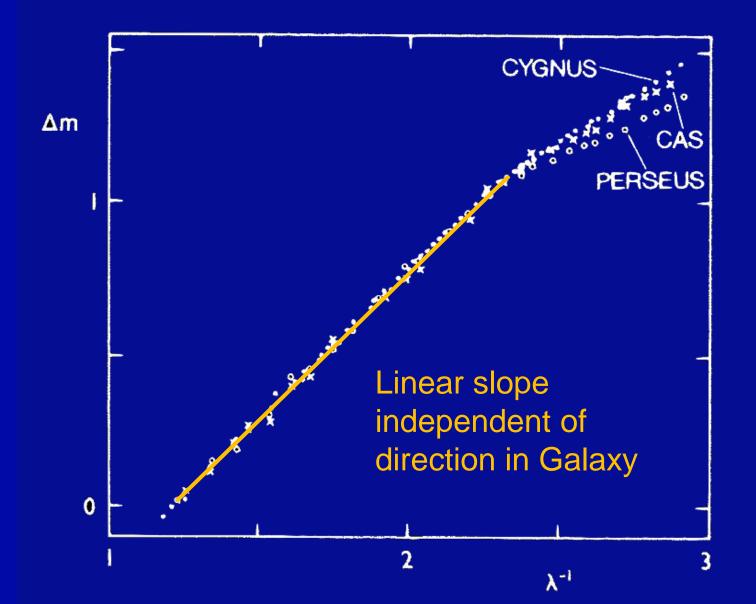
Interstellar Extinction Law

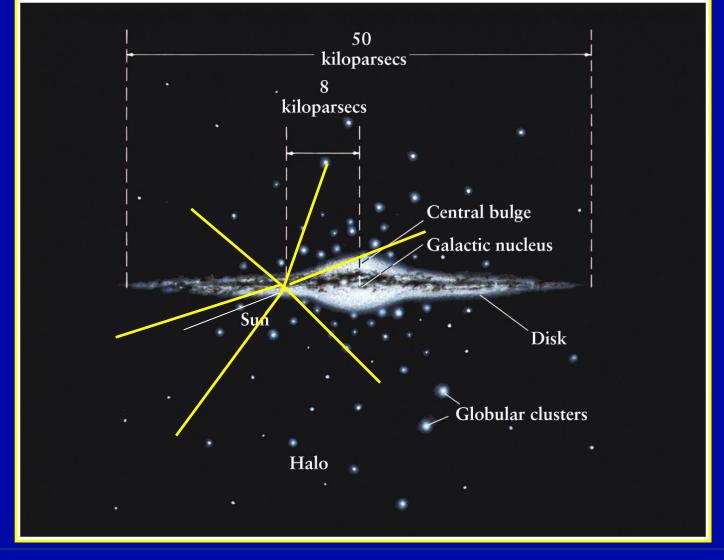
Strongest effect of the interstellar grains is the reddening of starlight



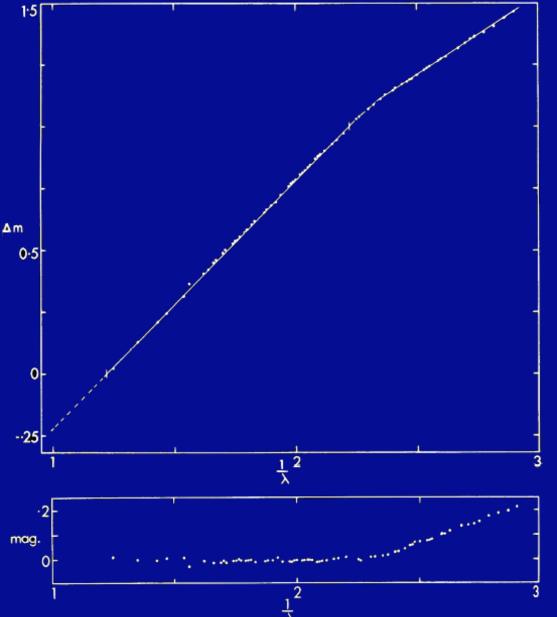
Reddening data + theoretical modelling gives the best information we can get on the nature of interstellar grains
Models require m(λ) for material => Qe (λ)
n(a)da for size distribution => normalised extinction curves

Most extensive set of data on visual extiinction curve due to K. Nandv. 1964. 1965





An unsolved mystery from the 1960's was to understand why the extinction curve at visual wavelengths is precisely the same (linear) in all directions



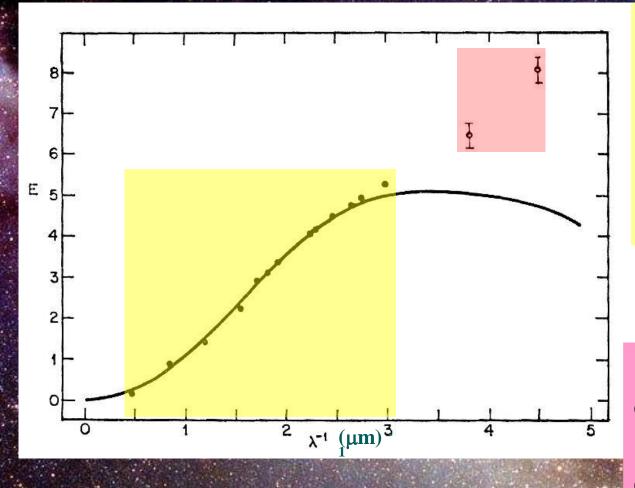
DEPARTURES FROM THE LINEAR LAW ARE NEGLIGIBLE

•Demands identical size distribution of icy grains *everywhere* n(a) ~ a⁻³

•Mean radius ~ 0.3µm

•No reasonable physical reason is offered

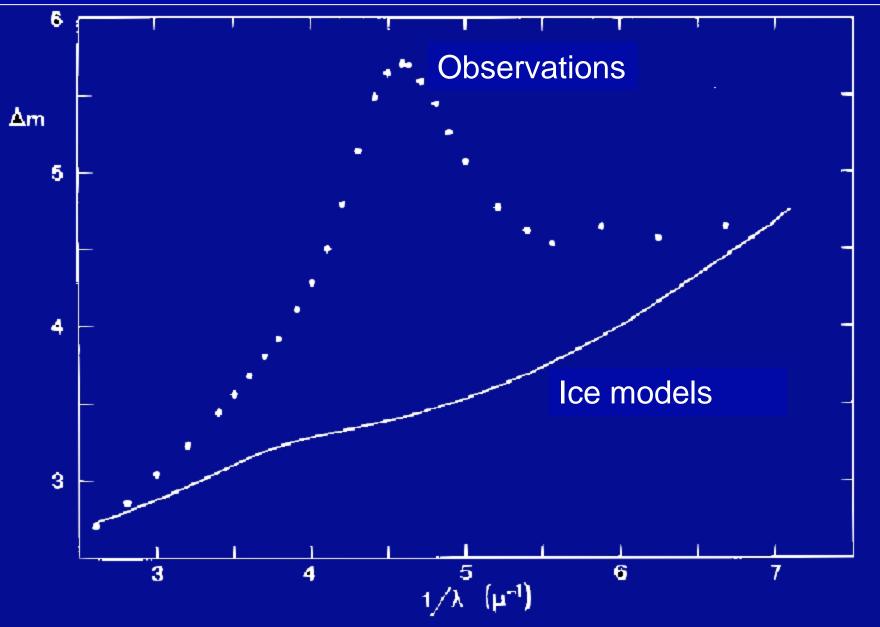
In 1965 - ice grain theory (Oort-Van de Hulst model) begins to fail



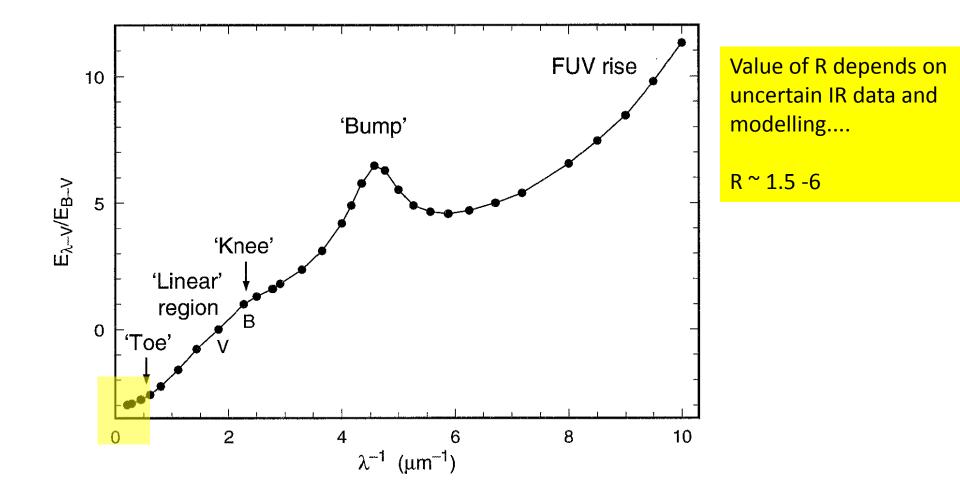
Visual extinction curve over λ =9000-3300A, accorded well with the ice grain model

First rocket observations in 1965 showed major discrepancy with ice model

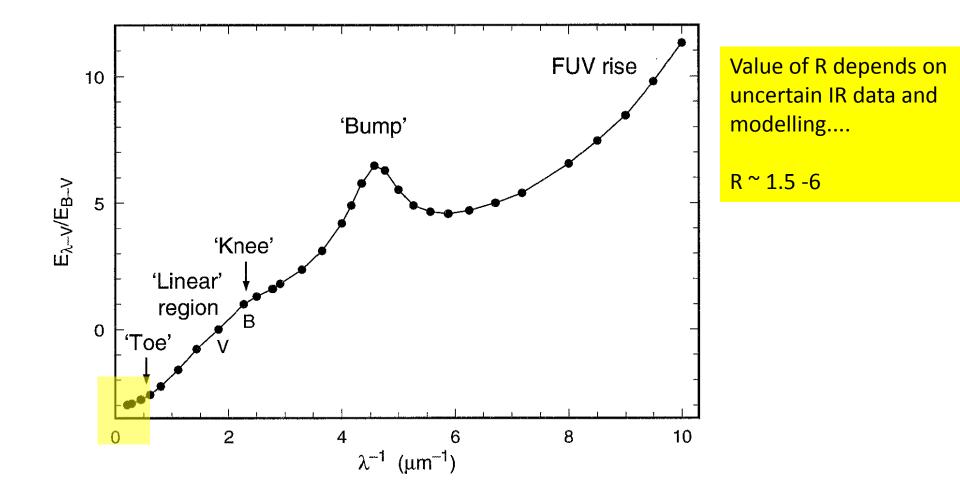
More decisive failing when 2175A feature discovered



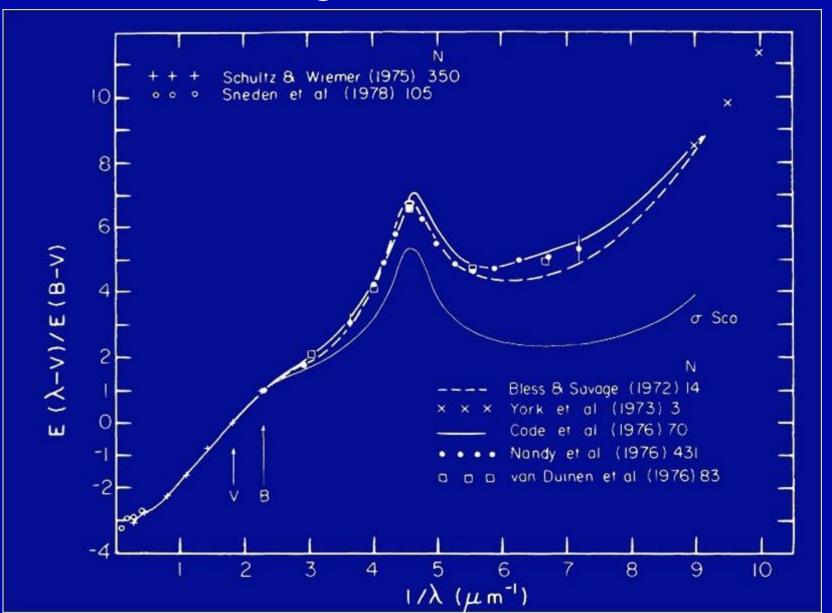
Average Extinction Curve (2011)



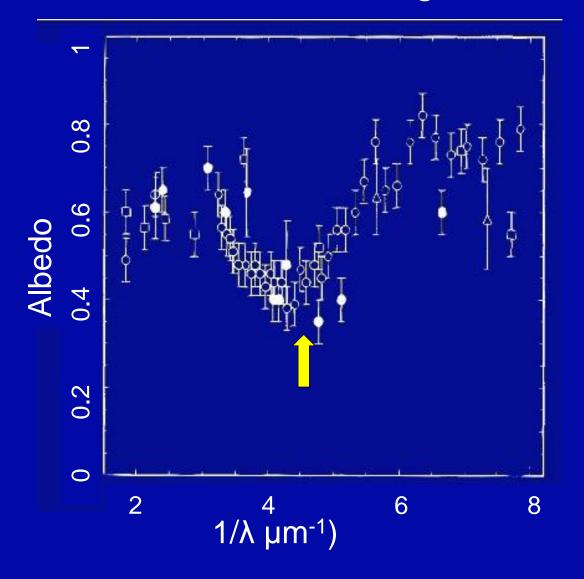
How invariant is this entire curve?



2175A hump and rise into the far UV can vary but linear visual segment is maintained



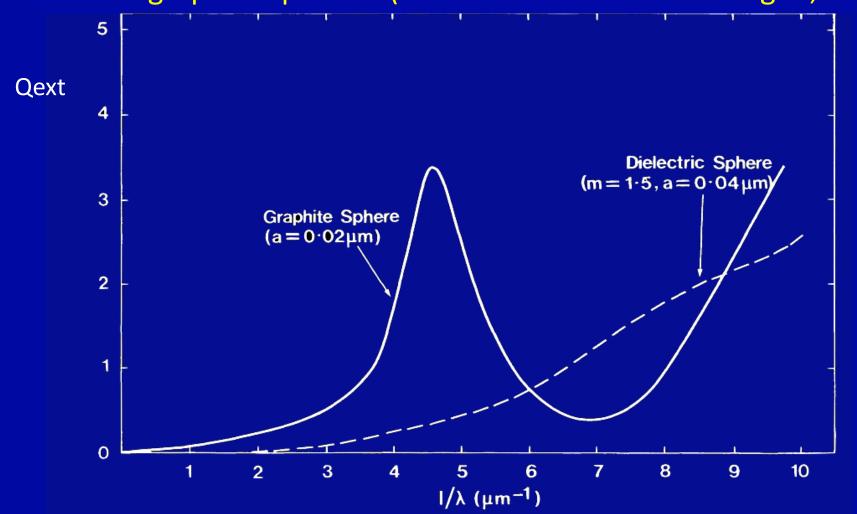
Albedo of grains at various wavelengths Diffuse Galactic Light & Reflection Nebulae



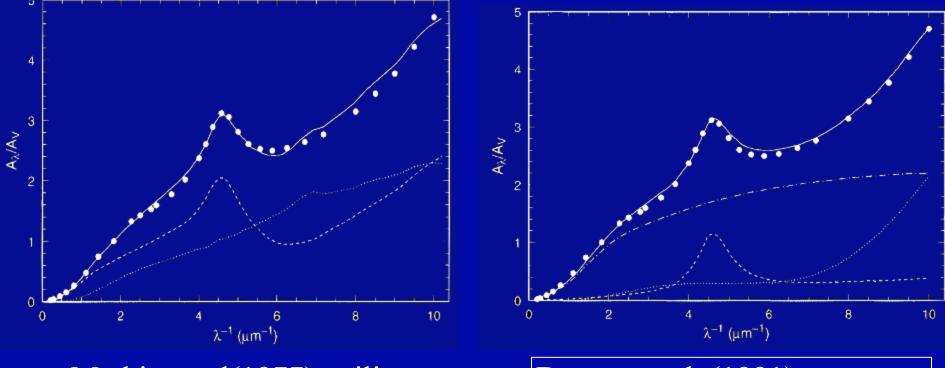
Low albedo shows 2175A band is due to pure absorption

Summing up

•UV extinction - pure absorption at 2175A
•Far uv scattering by small dielectric grains
•Small graphite spheres (Guillame and Wickramasinghe, 1965)

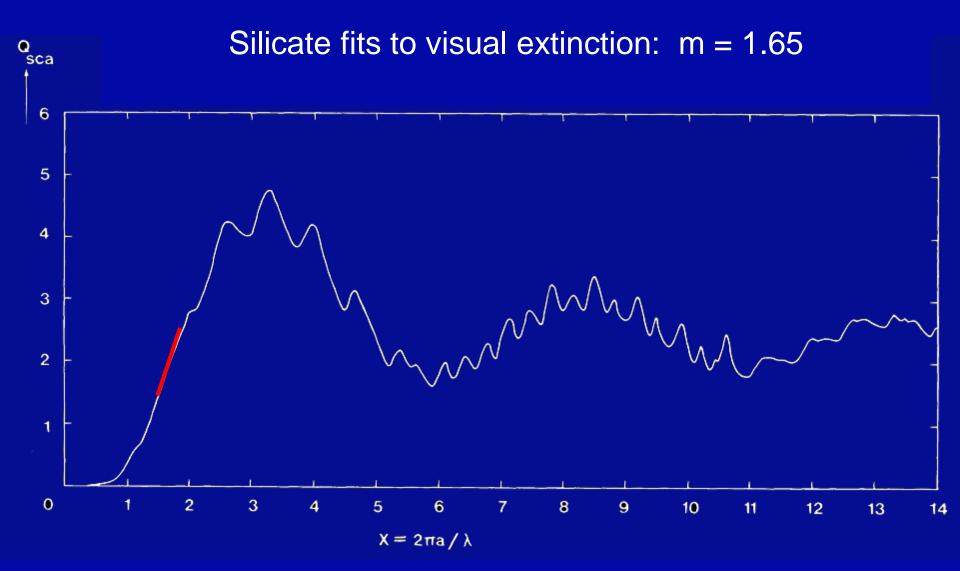


In addition to graphite, currently fashionable grain models include silicate particles to account for both the visual extinction and the far uv extinction rise



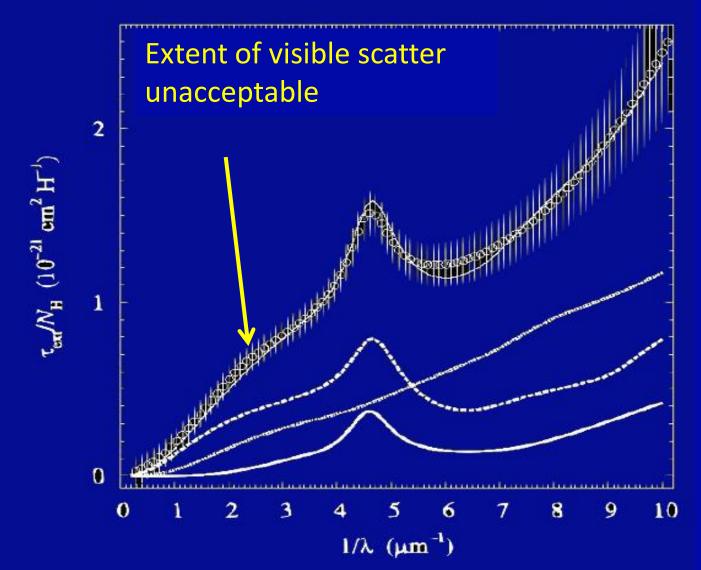
Mathis, et al(1977) - silicates and graphite $n(a) \sim a^{-3.5}$

Dessert et al. (1991) silicate/carbon, small graphite, and PAHs

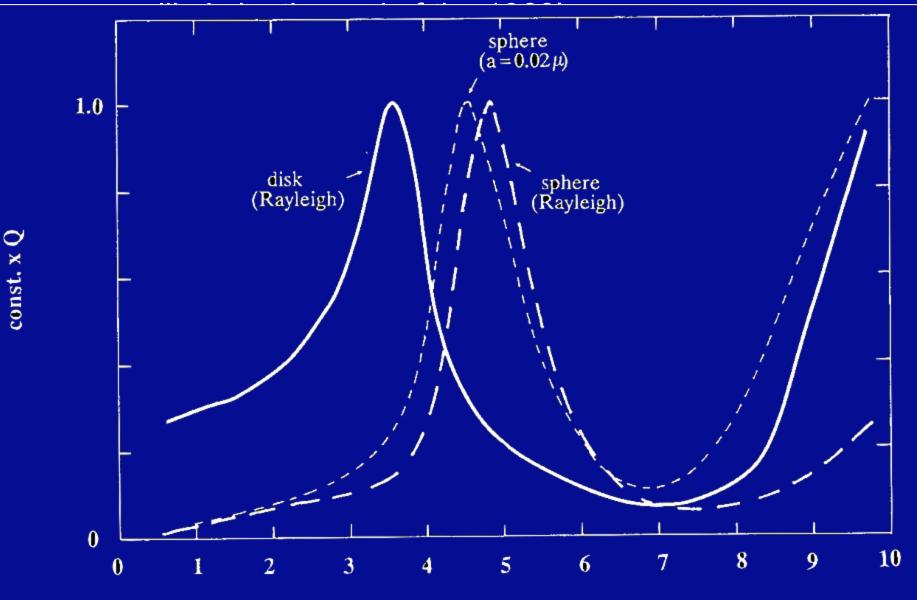


This very short linear segment scaled to fit linear visual extinction requires very stringent constraints

Model including silicates, graphite particles of radii 0.02 micron and a hypothetical PAH - all with arbitrarily fixed sizes and weighting factors (Zubko, *et at*, *ApJ*, 152, 211 (2004)



Graphite OK for 2175A band - but sensitivity to size and shape of particle renders it implausible



WAVENUMBER (inverse micron)

Alternative Models Emerge

These papers in *Nature*, are the first arguments for aromatic hydrocarbons in the ISM, and in comets and meteorites

(Reprinted from Nature, Vol. 21), No. 5635, pp. 323-324, November 24, 1977) C Macmillan Journals Ltd., 1977

Identification of the $\lambda 2$, 200A interstellar absorption feature

A BROAD absorption feature centred on 22,200Å with a halfwidth of ~300Å appears in the spectra of reddened stars1-3. This conspicuous feature in the interstellar extinction curve, might hold an important clue to the identity of a major component of interstellar matter, but it has defied identification for over a decade. Here we identify this band as representing the integrated effect of a set of hicyclic compounds, each with the empirical formula C_{*}H₄N₂. Such nitrogenated structures could form in stellar mass flows of the type which we have also discussed4. A significant mass fraction of all interstellar material might exist in this form.

Graphite particles have been considered the most plausible candidate for the 22,200 Å absorption feature. Whilst a small particle resonance in graphite can occur close to 22,200Å, the central wavelength of this feature is sensitively dependent on particle shape'. Spherical particles with sizes small compared to the wavelength are necessary to produce agreement with observational data, but a more realistic distribution of shapes would produce a considerably broader absorption feature than is required. It therefore seems that a narrower molecular absorption must be superimposed on an underlying broader extinction hump which could be caused by extinction from graphite grains with a wide spread in their shapes.

We have discussed a possible molecular origin for the λ 2,200Å band due to $\pi - \pi^*$ electronic transitions in a wide class of molecules involving conjugated double bonds^e. We now limit our search to the nitrogonated heterocyclic compounds listed in Table 1. The first four compounds represent all possible arrangements of two N atoms in a bicyclic structure, with the hetero-atoms confined to one ring only. The fifth compound is an isomer where there is one N atom in each of the two rings.

An average molar absorptivity function $\varepsilon(\lambda)$ was computed for these materials from available spectroscopic data". A normalised absorptivity $A(\lambda)$ given by

 $\varepsilon(\lambda) = \varepsilon(\lambda_0)$

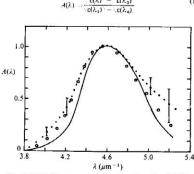


Fig. 1 Normalised average molar absorptivity for CaHeNa isomers (solid curve) compared with interstellar extinction data in the waveband 3.8 μ m⁻¹ < λ^{-1} < 5.4 μ m⁻¹. Normalisation is to 0.0 at λ^{-1} = 3.8 μ m⁻¹, 1.0 at λ^{-1} = 4.55 μ m⁻¹. Vertical bars give indication of spread of astronomical data. Dotted curve is the mean extinction curve of Bless and Savage* normalised according to equation (1). Open circles give mean extinction $(E(\lambda - V)/E(B - V))$ relative to extinction data for 9-Orionis, and normalised as above.

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(1)

Compound	Structural formula	$\lambda_m(\dot{A})$	ε (molar absorptivity)
Cinnoline		2,250	40,000
Quinazoline		2,220	35,500
Quinoxaline	(\mathbf{x}_{n}^{n})	2,340	23,400
Phthalazine	CC:N	2,150	56,000
1,5 Naphthyridine	(\mathcal{X})	2,060	54,000

with $\lambda_0^{-1} = 3.8 \ \mu m^{-1}$, $\lambda_1^{-1} = 4.55 \ \mu m^{-1}$ is plotted in Fig. 1. Our computed curve for C_sH₆N₂ isomers agrees exactly with the interstellar extinction data with respect to the central wavelength, but the 'average' interstellar band is apparently ~ 30°, wider. The latter departure could easily be ascribed to an underlying graphite particulate extinction (scattering + absorption) peak upon which the narrower molecular absorption band is superposed. Since 0-Orionis shows a broad extinction hump centred on 22,200Å rather than the sharper band which is more common, we can reasonably attribute this extinction curve to an underlying graphite component. The mean extinction curve relative to the extinction data for 0-Orionis (Fig. 1) provides much closer agreement with the molecular absorption data, as we would expect. The mass density of molecules necessary to produce the observed strength of the 22,200Å interstellar band (~1.5 mag kpc -1) is ~10 -27 g cm -3 implying that only ~10°, of interstellar C and N is in this form,

An identification of ring compounds of the type listed in Table 1 may have important consequences. Linear molecules such as HCN, HC3N, HC3N, HCN which have already been observed in interstellar space may result from the break-up of these more complex structures. It would now be worthwhile to search systematically for ring molecules by radioastronomical techniques.

Sakata et al." have reported the detection of an absorption feature at 22,200Å in soluble organic material extracted from the Murchison meteorite. In view of the possible connection of this material with interstellar matter, a chemical analysis of the molecules responsible for the meteoritic 2,200Å band will also be valuable. It is interesting that several nitrogen heterocyclic compounds, including purines, pyrimidines and pyrroles have recently been identified in carbonaceous chondrites*-11.

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Primitive grain clumps and organic compounds in carbonaceous chondrites

We show here that the physical conditions in prestellar molecular clouds favour the condensation of complex organic polymers, including amino acids, within a matrix of smaller refractory particles. Such composite grain clumps with dimensions exceeding 1 µm could be expelled along with gaseous material in protostellar cocoons, causing the widespread dispersal of biological activity in the Galaxy. We argue that grain clumps of the type considered here may be identified with um-sized inclusions in carbonaceous chondrites.

Carbonaceous chondrites, with a carbon content of several per cent mainly in the form of aromatic polymers, and including amino acids in trace quantities, are generally believed to be among the most primitive solid bodies in the Solar System. The compaction of mineral particles with a substantial admixture of trapped volatiles must have occurred at temperatures in the range 350-500 K, with no subsequent reheating above ~ 500 K. trefs 1 and 2).

Several striking isotopic anomalies have been discovered in mineral separates from carbonaceous chondrites3-7. Such anomalies have tentatively been attributed to inclusions of interstellar grains which condensed in novae or supernovae rence of heavily irradiated um-sized mineral separates rich in "Ne in the Orguel meteorite". The presence of µm-sized inclusions, each comprised of closely packed aggregates of grains of 100 Å (ref. 11), is also suggestive of interstellar grain clumps within carbonaceous chondrites.

An understanding of the origin of carbonaceous chondrites may have an important bearing on the early history of the solar nebula, and in particular on theories of planetary formation. The efficient adhesion of relatively cold refractory grains (for example, graphite or silicate particles) in low velocity graingrain collisions could occur if these grains possessed mantles composed of organic polymers which are adhesive at temperatures - 300 K. Such organic polymers have been tentatively identified by their infrared spectral features in cometary as well as interstellar dust12.13.

We argue here that interstellar molecular clouds which are the most probable sites for the condensation of polymeric mantles around grains are also likely to provide suitable venues for the formation of composite grain aggregates, by the adhesion of such coated grains in grain-grain encounters. Such grain clumps of sizes ~1 µm pre-existing in the solar nebula could have served as aggregation centres for the growth of carbonaceous chondrites, perhaps representing the earliest stage of planet formation.

Large molecular clouds with masses in the range ~104-10" W are widespread in the galactic disk. Such clouds, typified by W3, OMC-2, NGC2024, Sg B2, are generally believed to be progenitors of OB associations. In a typical extended cloud of diameter ~ 10 pc, observations of molecular CO at millimetre wavelengths leads to an estimate $n_{\rm H_{2}} \simeq 3 \times 10^3$ cm ³ for the smeared out hydrogen density11. More complex molecules, including HCN. H CO, tend to be more localised in their spatial distribution, generally associated with infrared knots, OH masers and presumably protostellar clouds. Molecular densities in such clouds are difficult to estimate. The requirement for collisional excitation of optically thin lines of H₂CO, HCN by neutral particles gives a lower limit $n_{\rm H_2} > 10^5$ (ref. 14), but densities ~ 10° cm 3 or higher are most probably appropriate to protostellar clouds.

One may also argue that molecular clouds are not in a state of free-fall collapse14. Condensation may be slowed down by several processes, including effects of magnetic pressure, rotation and turbulence. We assume here that typical collapse times for an entire cloud, as well as for fragments within it, are of the general order of 104 yr. Such a condensation time, together with the estimated total mass of protostellar clouds, gives a rate of star formation which is consistent with observations.

A molecular cloud fragment collapsing towards a protostellar situation will contain a mass fraction of ~10⁻¹ of refractory grains such as graphite, silicate and iron particles of mean radius $a_1 = 2 \times 10^{-8}$ cm. The first stages of collapse will be accompanied by accretion of organic molecules on to these grains. Since a significant mass fraction of C and O is initially in solid grains, the maximum extent of mantle growth is not likely to exceed 50% of the original radius. This gas phase accretion would proceed to effective completion on a time scale which is short compared with the estimated collapse time of ~10° yr. The grain radius may now be assumed to be 3 · 10-6 cm (50°, increase) in accord with our earlier remarks. The precise composition of molecular mantles is uncertain, but a hybrid mixture of organic polymers is likely to ensue.

Refractory grains with such tar-like polymeric coatings tend to stick to one another in low velocity grain-grain collisions at temperature $T \simeq 300$ K. Suppose $n_{\rm H}$ (= $2n_{\rm H}$) is the total hydrogen density and n, is the grain density at this stage of protostellar collapse. Assuming an initial grain mass fraction of ~ 1%, we have (for any reasonable grain specific gravity)

$$\frac{n_{\rm w}}{n_{\rm H}} \simeq 3 \cdot 10^{-10}$$
 (1)

(2)

The rate of growth of a grain clump of radius r by this process is given by

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\alpha n}{s} \left[\frac{kT(\frac{4}{3}\pi a_{s}^{2})}{2\pi} \right]^{\frac{1}{2}}$$
$$= \alpha n_{t} \left[\frac{2kTa_{s}^{2}}{3s} \right]^{\frac{1}{2}}$$

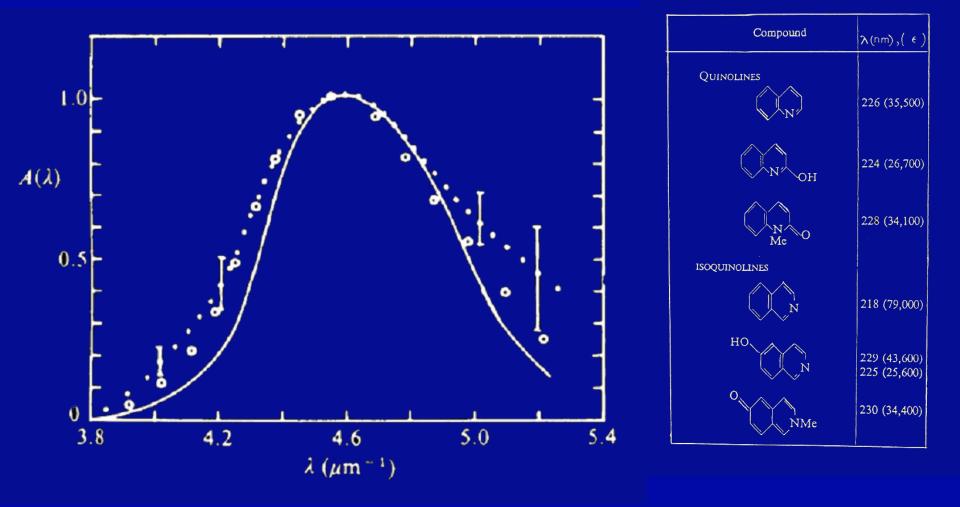
where a is the sticking probability, s is the mean specific gravity of the grain clump material, $a_1 (= 3 \times 10^{-4} \text{ cm})$ is the radius of polymer coated grains, n_{i} is the number density of grains, and Tis the kinetic temperature. We assume in equation (2) equipartition of energy between grains and gas and a Maxwellian distribution of grain velocities. Sticking of grains occurs by collisions during their Brownian motion with relative speeds of ~ 10 cm s⁻¹. With $\alpha \simeq 1$, $T \simeq 300$ K, s = 1, $a_1 = 3 \times 10^{-6}$ cm and using equation (1) we obtain

$$\frac{dr}{dt} = 8.2 \times 10^{-18} n_{\rm H} \,{\rm cm} \,{\rm yr}^{-1} \tag{3}$$

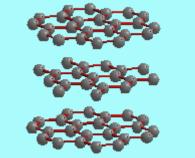
In the available time, ~ 10° yr, we obtain clump diameters $2r \sim 1 \ \mu m$ for a typical value of the molecular density $n_{\rm H_2} \simeq$ 3 x 10⁴ cm⁻³. Larger clumps could arise from higher density regions.

The ultimate dispersal of a protostellar cocoon, including large grain clumps, may have a role in the removal of angular momentum from a central protostellar condensation, thus permitting further contraction and evolution on to the main sequence. A large fraction of composite grain clumps in such cocoons could probably survive the 'switching on' of the stars in an OB

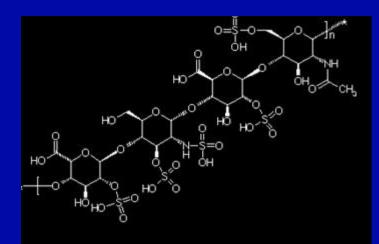
H-W, 1977 Nature - bicyclic aromatic molecules



Progression from graphite to complex organics polymers



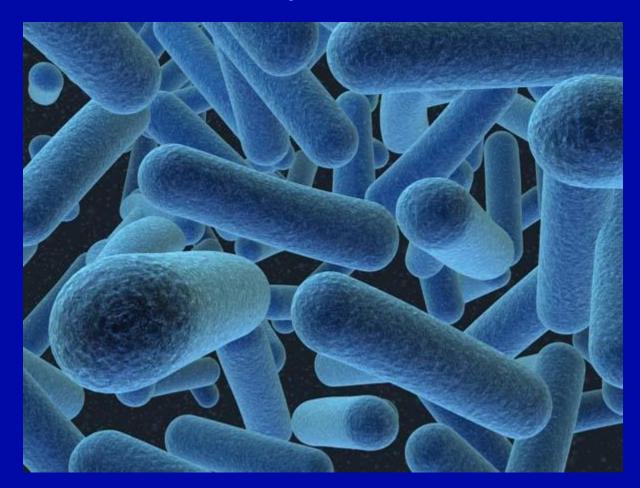
Graphite particles, 1962



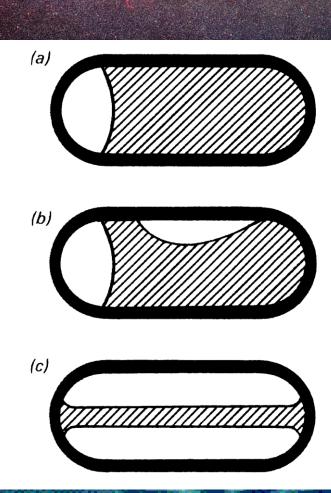
Heteroaromatic molecules, 1977



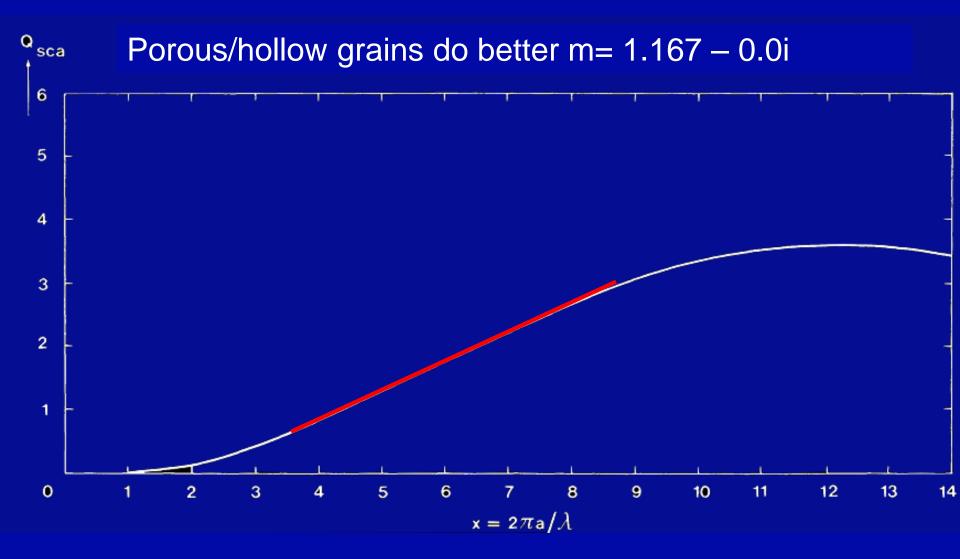
Heterodox hypothesis – bacteria In 1980 we began exploring the seemingly outrageous hypothesis that interstellar dust may be bacteria – dehydrated in the vacuum of space



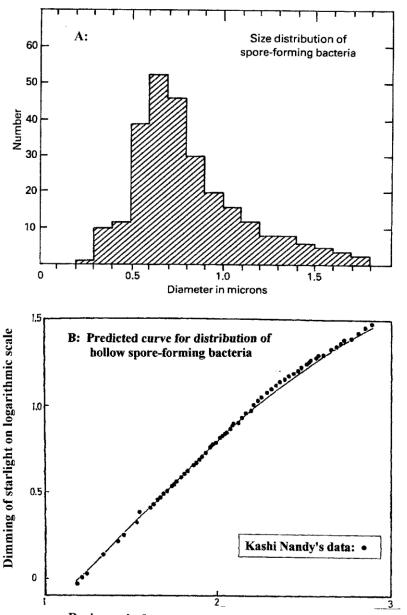
To test the hypothesis that a large fraction of interstellar dust starts off as viable bacteria – perhaps in comets....



In the interstellar medium, free water in a bacterium evaporates leaving a structure with an average visual refractive index n=1.167



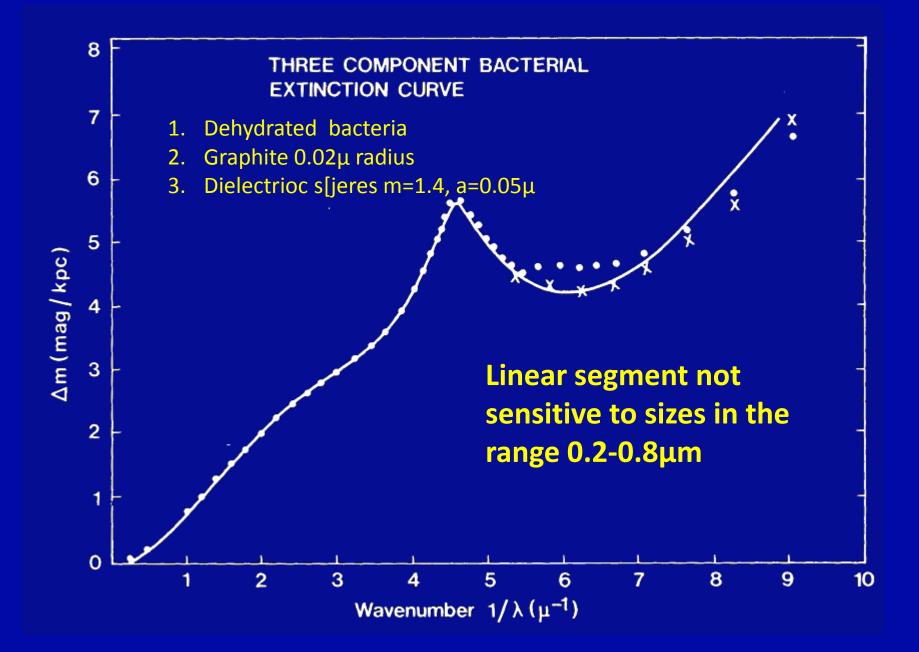
Extent of linear segment over factor of 3 in x helps to explain why the visual extinction curve is invariant across the sky



Reciprocal of wavelength in inverse micrometres

For a size-distribution of particles consistent with laboratory data for spore-forming bacteria we have perfect match with the visual extinction without any need for parameter fitting

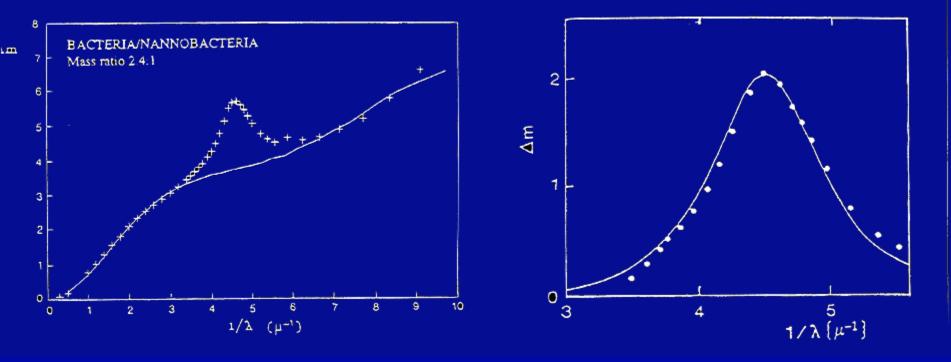
This was a triumph for the hypothesis of bacteria-like dust



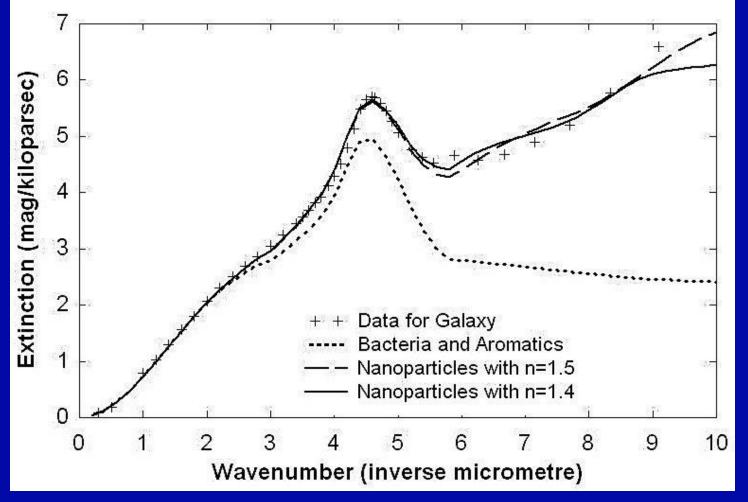
Replacing graphite with organic chromophores provided a much better option

L: Extinction by mixture of hollow bacteria and nanobacteria *R*: Deficit at 2175A filled by aromatic chromophores

Suite of 115 biomolecules produces interstellar UV extinction

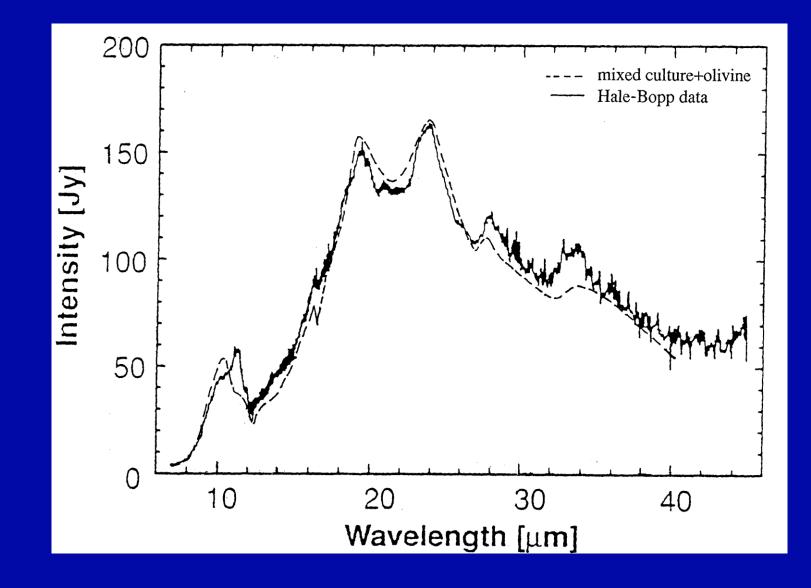


Composite extinction curves preserving strict linearity of visual extinction



Nanoparticles can include silicates from stars- but silicate fraction is small

Modelling of spectrum of Comet Hale Bopp implies 10% by mass of crystalline olivine 90% organics similar to biomaterial



Dust and extinction is not confined to our galaxy



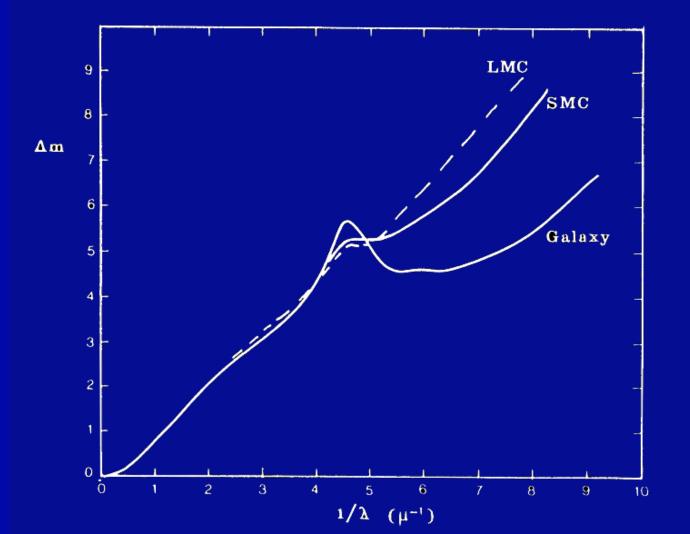




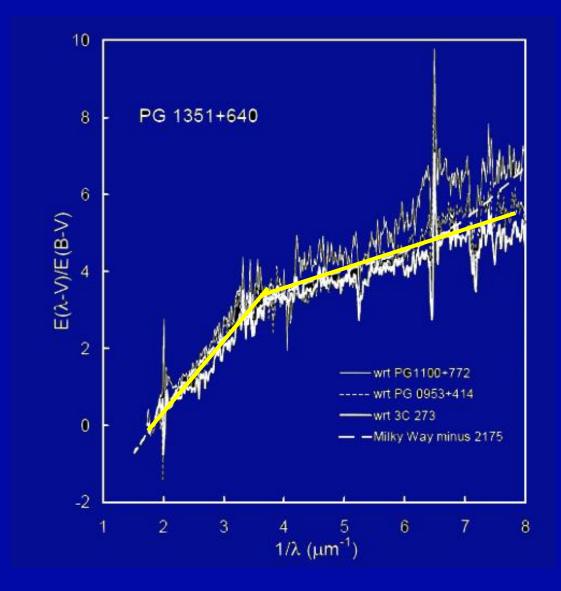


•Extinction law with a linear visible segment is not confined to the galaxy

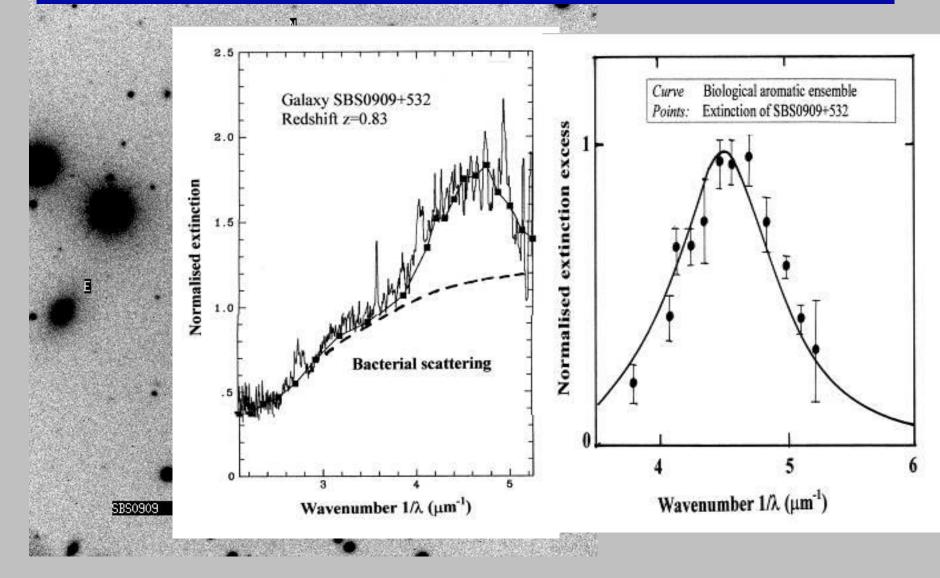
•This makes invariance even more difficult to explain



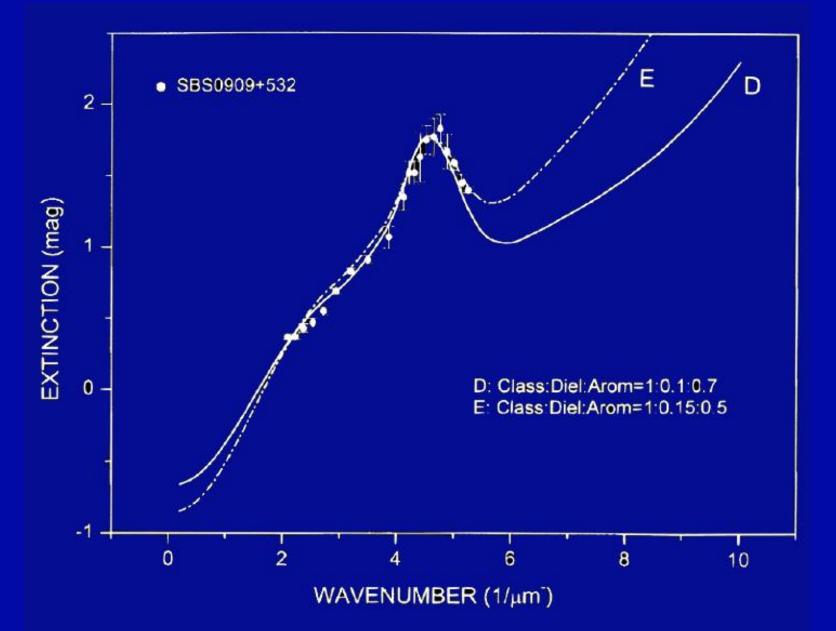
AGN extinction - Gaskell and Benker (ApJ 2007) – no 2175A feature, but linear segments



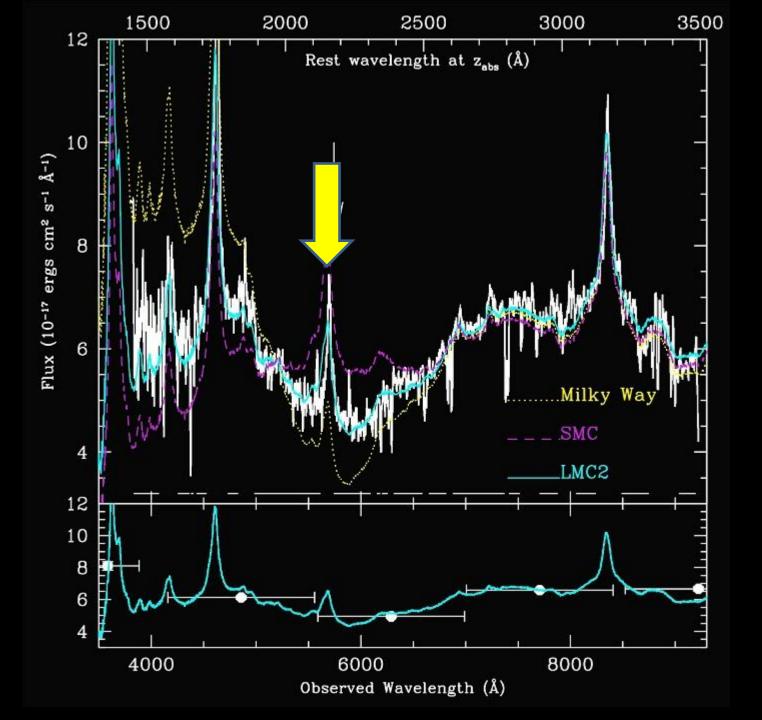
In a gravitational lens galaxy SBS0909+532, at a red-shift of z=0.83, we find an absorption signature of dust similar to biological aromatics (Motta *et al* Ap.J. 574, 719-725, 2002)



Gravitational lens galaxy at z=0.84



In a remarkable discovery the molecule CO and the 2175A band was discovered at z=1.6408 towards the quasar SDSSJ160457.50+220300.5P (Noterdaeme, et al 2011)



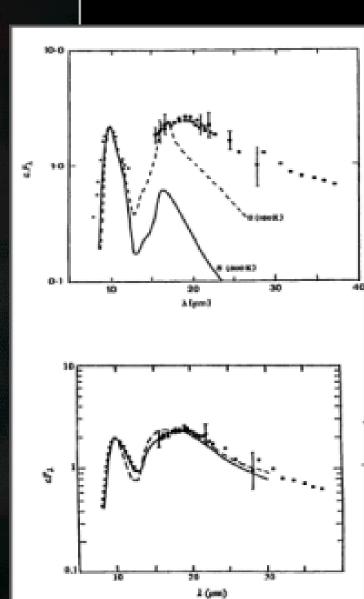
Infrared Characterisation

By 1969 infrared emission of heated dust showed silicates, but real silicates alone were deficient

Amorphous Silicates \Rightarrow

 H_2CO polymers: Polyformaldehyde Polysaccharides \Rightarrow

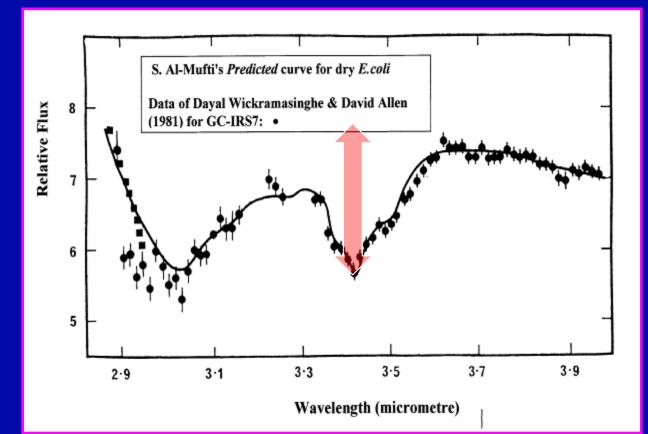
So 1% in form of grains could be in form of complex organic polymers



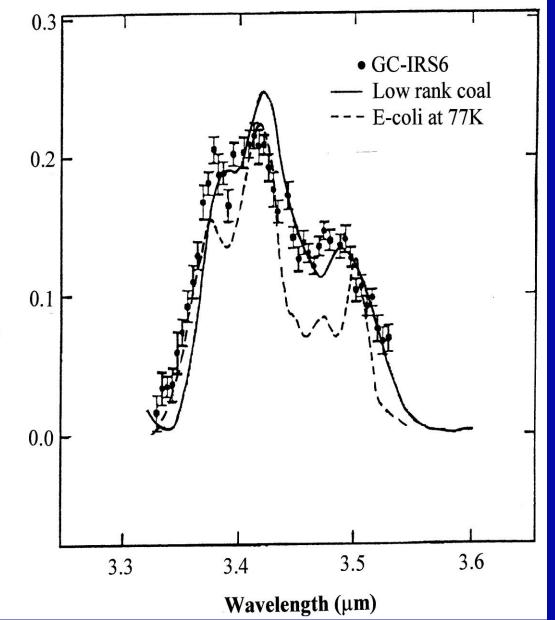
Sources at galactic centre had longest path length through interstellar dust

Center of galaxy

In 1982 a newly discovered 3.4 micron absorption in dust to the galactic centre confirmed that large fraction of dust was complex organic, and spectroscopically identical to bacterial-type material

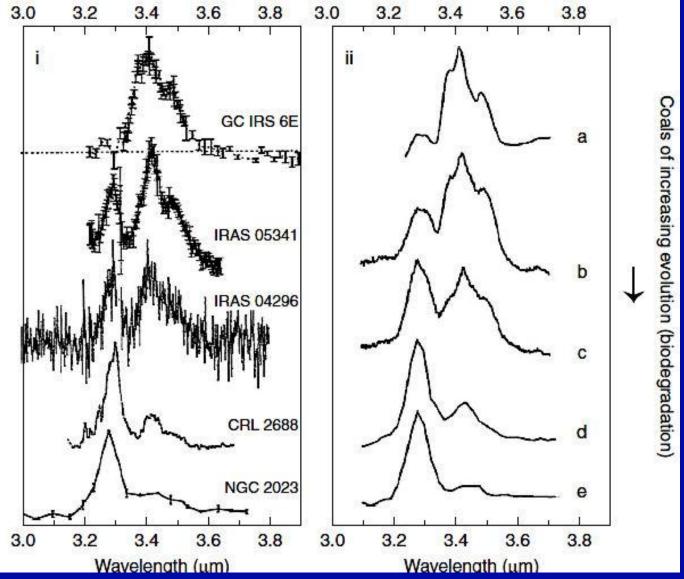


Absorption of 0.3 mag at 3.4µm with organic grains with κ =1000 cm²/g gives ρ = 10⁻²⁶g cm⁻³

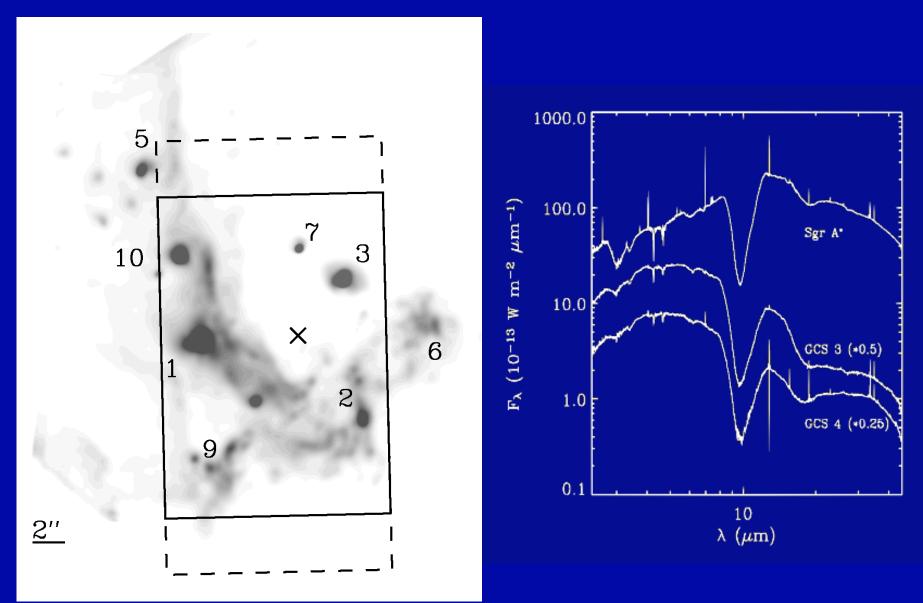


Low rank coal and cryogenic *Ecoli* have similar spectra so spectrum of GC-IRS7 was consistent with degraded biomaterial

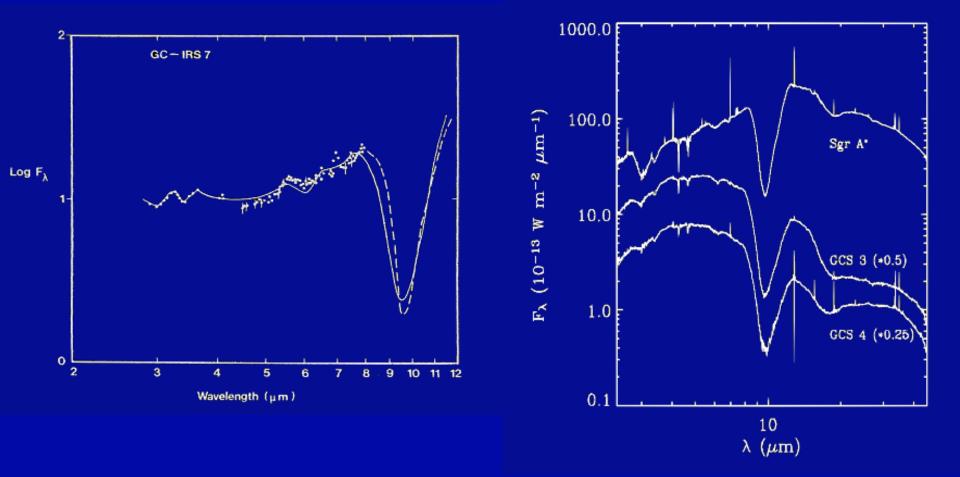
Other astronomical spectra matching coals of varying degrees of biodegradation



10micron Band Toward the Galactic Center

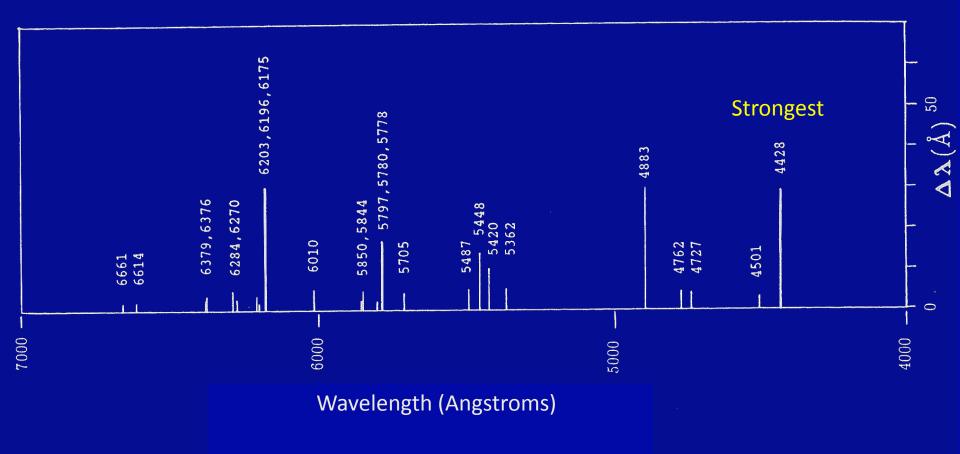


10micron Band Toward the Galactic Center Not necessarily due to silicates alone

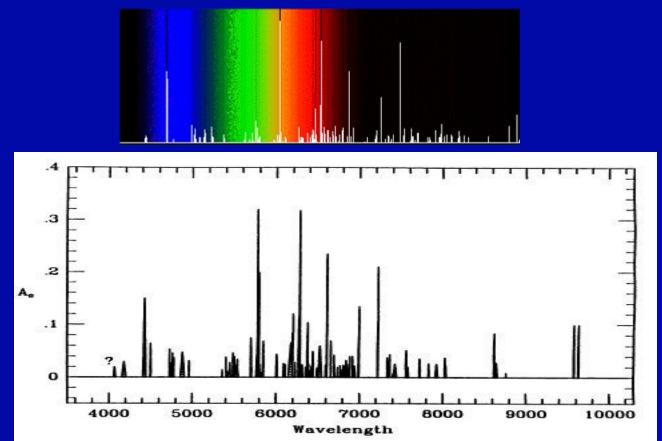


Diffuse Interstellar Bands

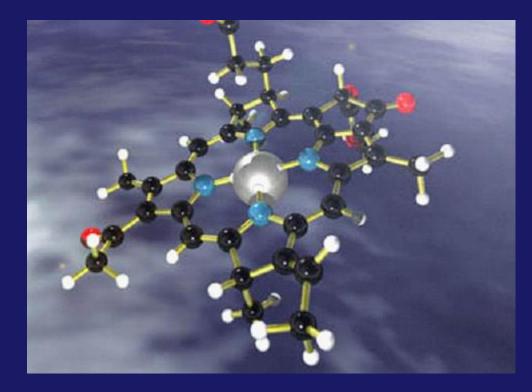
Diffuse Interstellar Bands discovered in 1922



Evidence of aromatic molecules existed since the discovery of the diffuse interstellar bands in the visual spectral region – strongest centred at 4430A with a half width of 30A



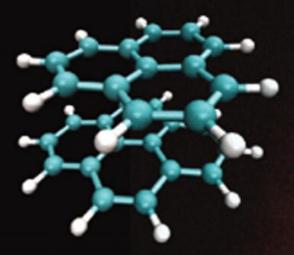
Dispyridyl magnesium tetrabenzoporphine Related to Chlorophyll fits 90% of visible diffuse bands



F.M. Johnson: Spectrochim Acta A Mol Biomol Spectrosc. 2006. Dec;65(5):1154-79 Extended red emission (ERE) is a widely observed interstellar photoluminescence phenomenon in the 500-900 nm spectral range and is seen

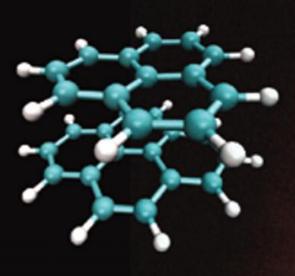
Reflection nebulae
H II regions (Perrin & Sivan 1992),
Planetary nebulae (Furton & Witt 1990, 1992)
Also recently found in the diffuse interstellar medium

Many models proposed, none entirely satisfactory

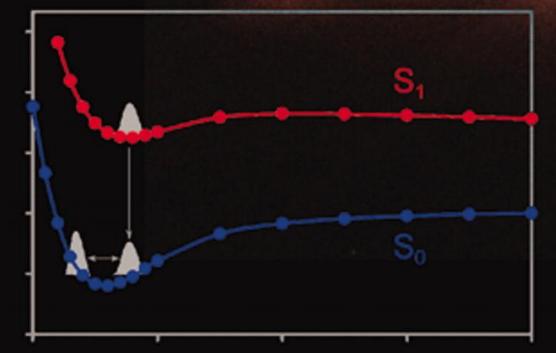


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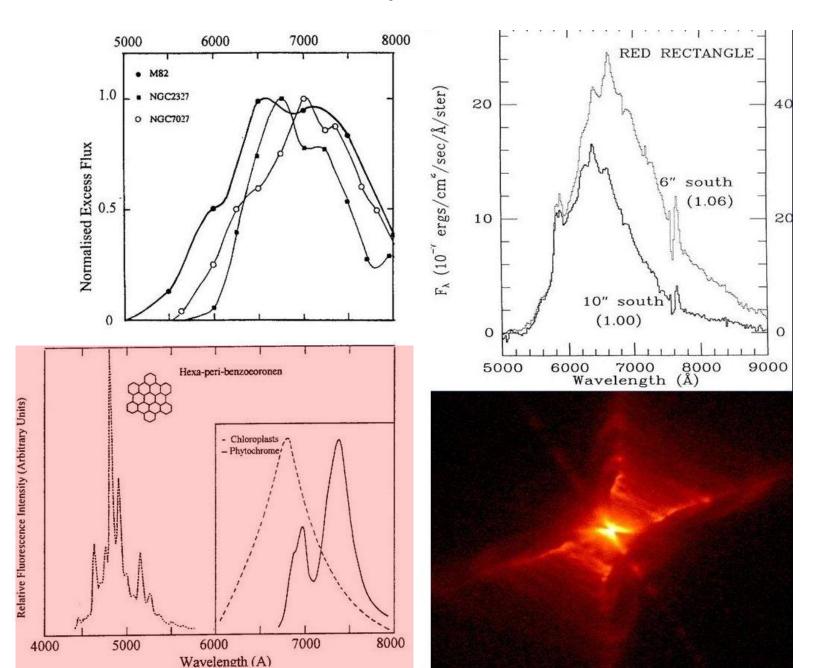
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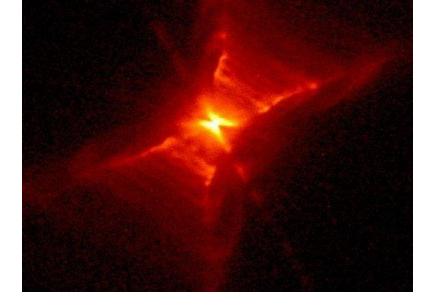


Charged PAH clusters proposed, but fit is not good

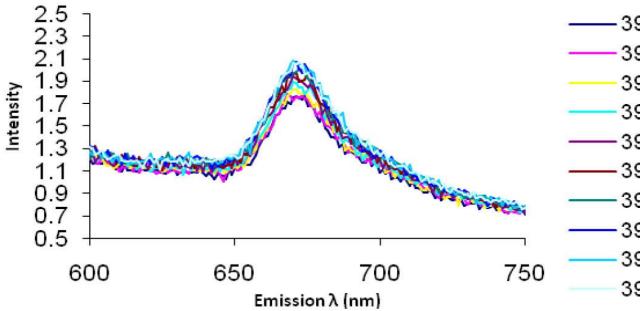


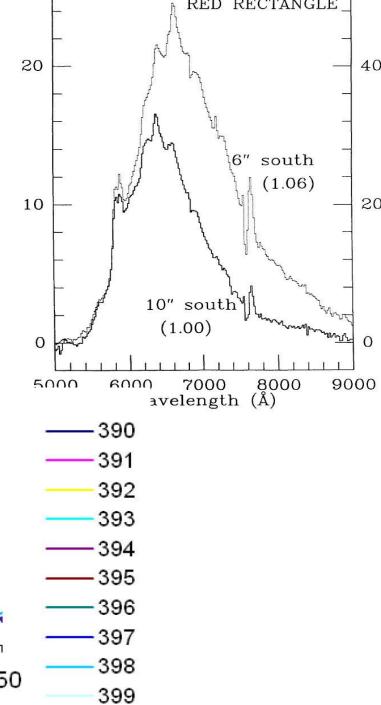
ERE due to complex biomolecules?





Red rectangle emission spectrum compared with Red Rain fluorescence



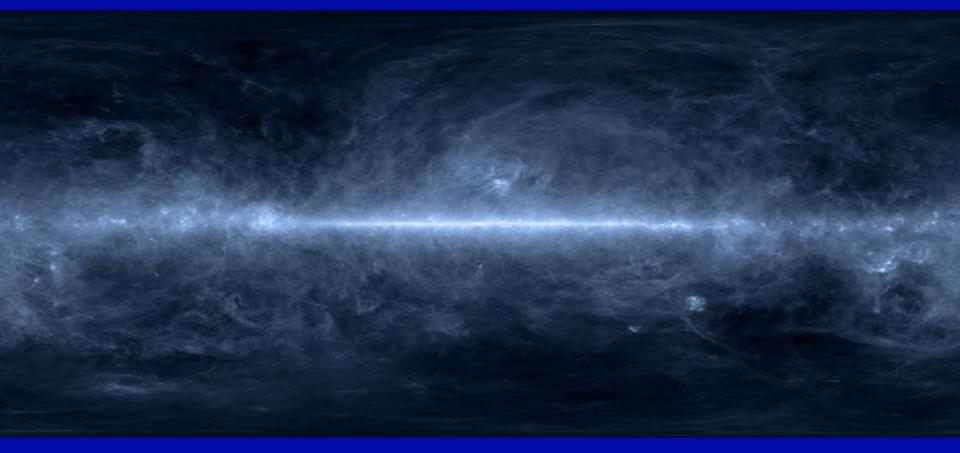


 F_{λ} (10^{-''} ergs/cm^{*}/sec/Å/ster)

Infrared Bands

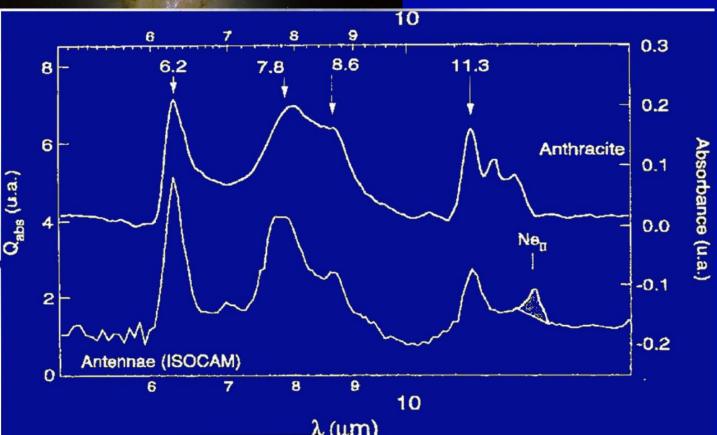
Infrared studies from the 1980's revealed a set of emission bands possibly related to the DIB's in the visible -3.3, 6.2, 7.7, 8.6, 11.3µm – particularly in the high latitude galactic cirrus

Strengths required substantial fraction of C tied up in such emitters

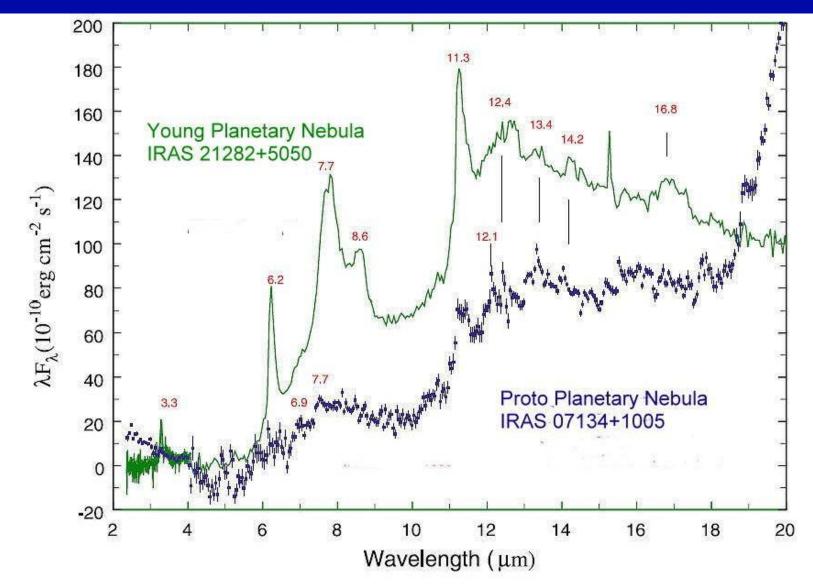


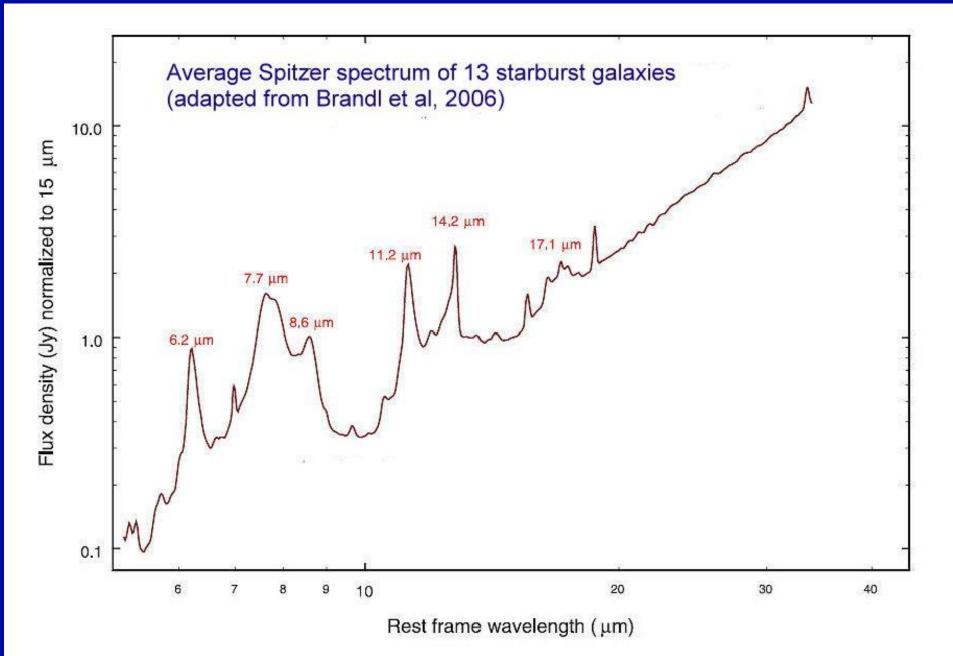


....and these were not confined to our galaxy

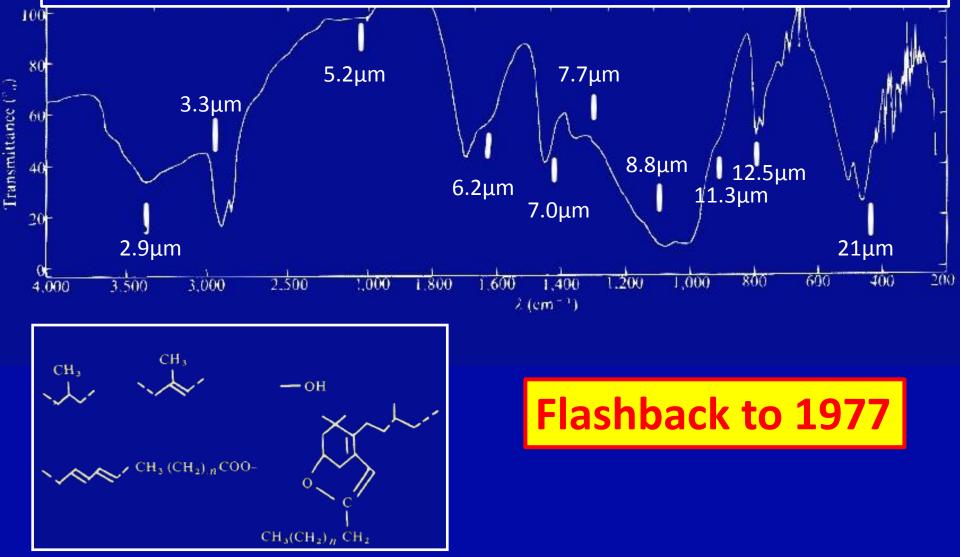


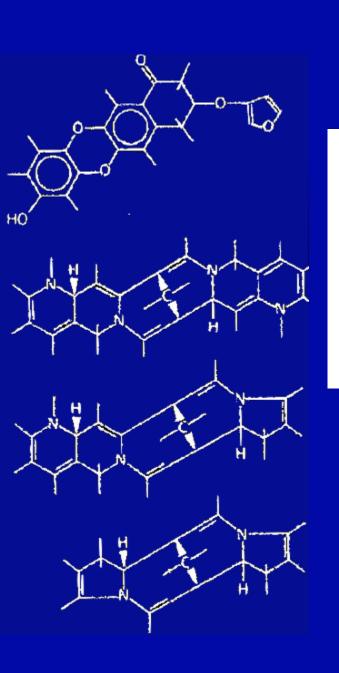
Spitzer telescope provides a wealth of data confirming aromatics everywhere





Sporopollenin – Wickramasinghe, N.C., Hoyle, F., Brooks, J. and Shaw, G., Prebiotic polymers and infrared spectra of galactic sources, *Nature*, 269, 674-676 (1977)





Stardust collected flecks of interstellar dust in 1996 (Kissel and Kreuger)

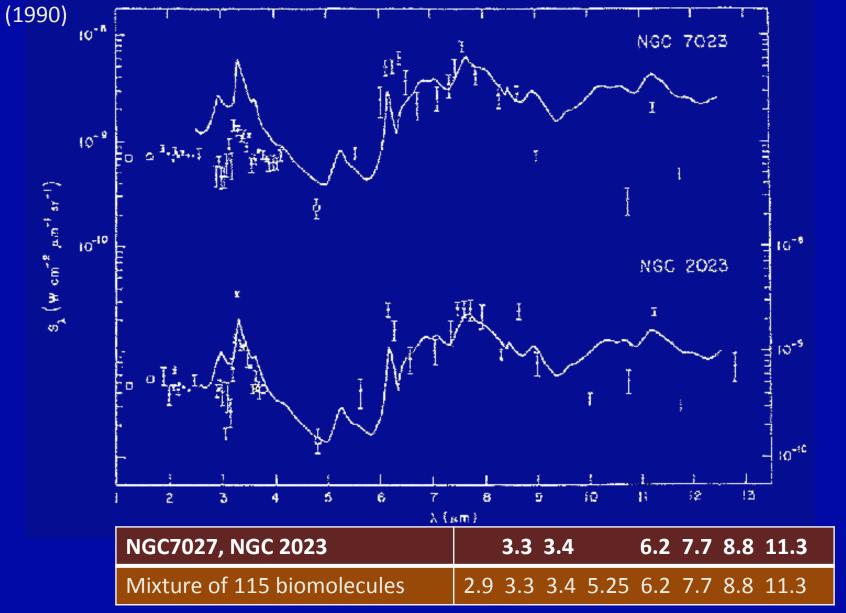
CROSS-LINKED HETERO AROMATIC POLYMERS IN INTERSTELLAR DUST

N.C. WICKRAMASINGHE^{1*}, D.T. WICKRAMASINGHE² and F. HOYLE¹ ¹ School of Mathematics, Cardiff University, P.O. Box 926, Senghennydd Road, Cardiff CF2 4YH, U.K.; *Author for correspondence; E-mail: wickramasinghe@cf.ac.uk ² Department of Mathematics, Australian National University, Canberra, ACT2600, Australia

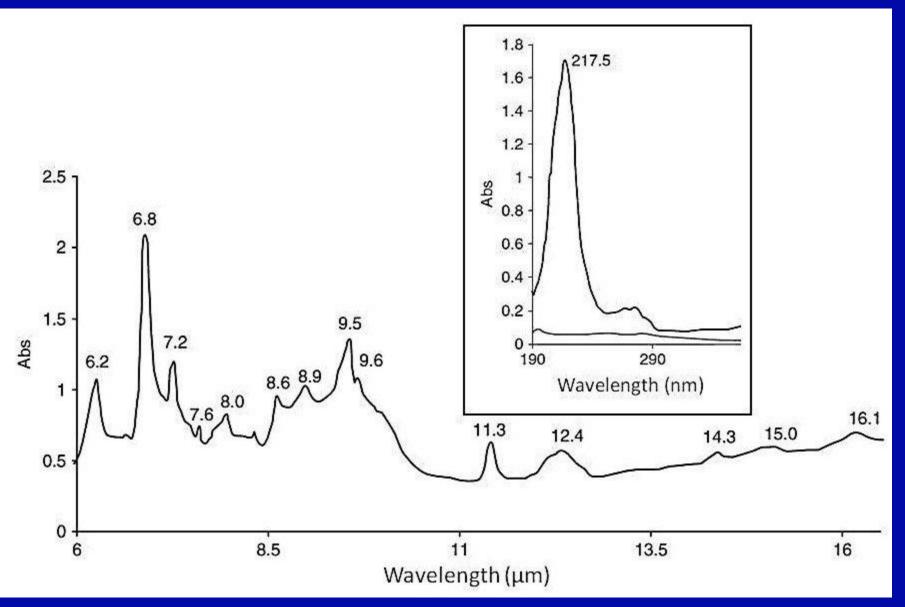
(Received 17 May 2000; accepted 22 May 2000)



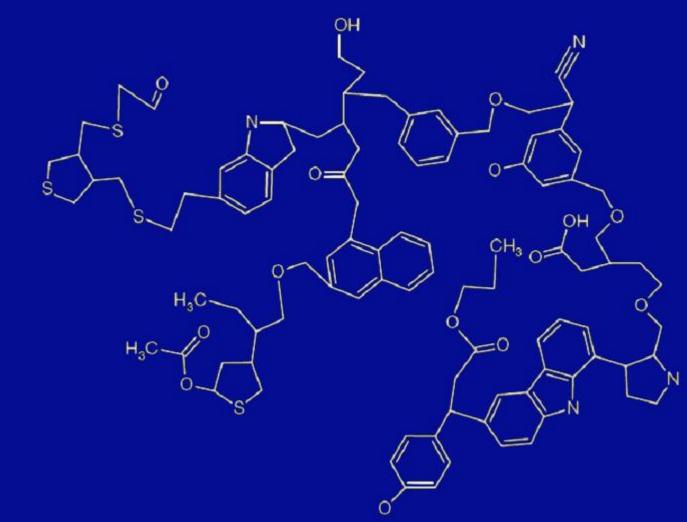
Wickrama **p**inghe, N.C., Hoyle, F. and Al-Jobory, T., An integrated 2.5-12.5µm emission spectrum of naturally-occurring aromatic molecules, *Astrophys.Space Sci.*, **166**, 333-335



Average spectrum of algae, grass extract (Rauf and Wickramasinghe, IJA, 2010)

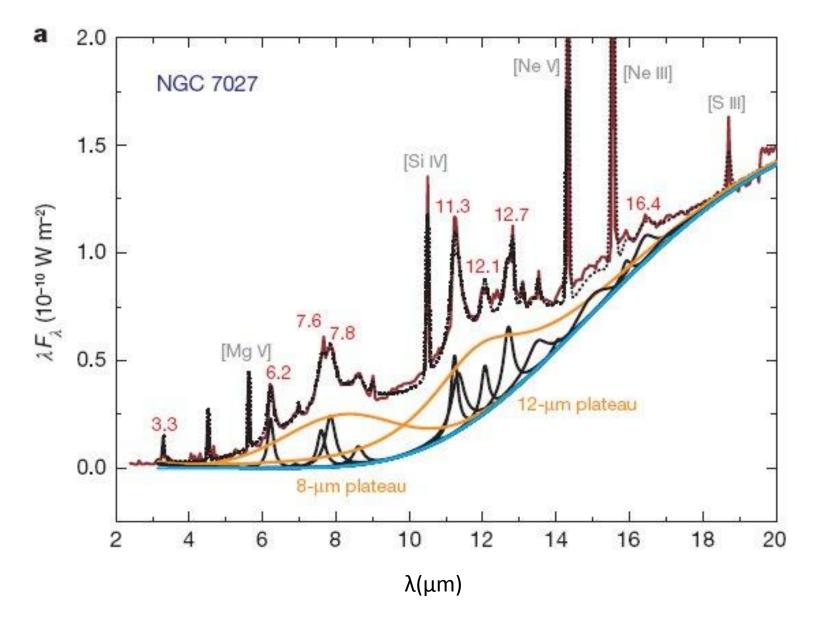


Kwok and Zhang, 2011



Kwok, S. and Zhang, Y. Mixed aromatic-aliphatic organic nanoparticles as carriers of unidentified infrared emission features. *Nature*, **470**, 80-83 (3/112011)

Kwok and Zhang, 2011



Infrared, ultraviolet and visual extinction/emission data

Huge quantities of exceedingly complex organic chemicals in ISM (~10% of interstellar carbon) have to be explained

Break-up of cells

Build-up from atoms

SENORGEF-COX

Break-up of cells arguably the more plausible!

Genetic information in life is robust and can be dispersed through the galaxy comet bombardment

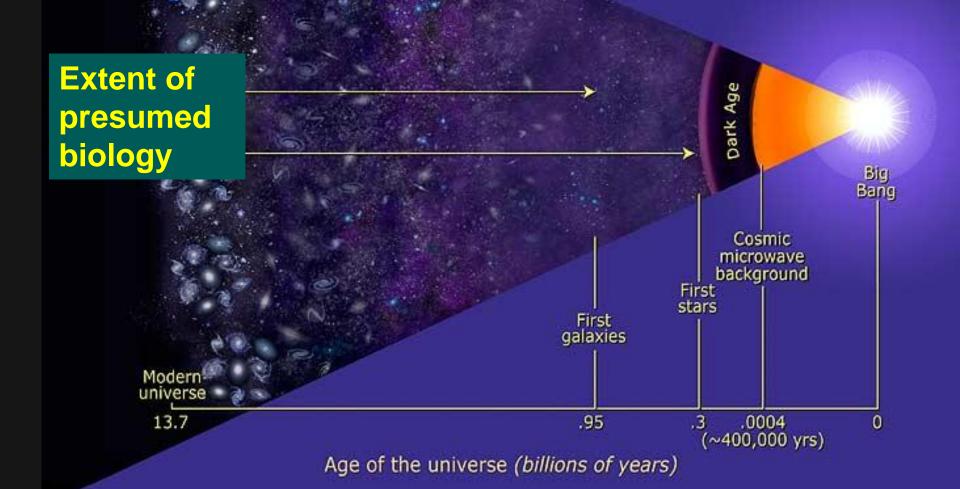
Primordial Microbes

Interstellar gas Stars and Planets

Amplified Microbes

An initial cosmic legacy of life is continuously amplified – inevitable degradation => astronomical observations

Seeing back into the cosmos



Reason for excluding biology:

Extraordinary claim

•Far more extraordinary is the claim that biology is confined on our planet



"When you have eliminated all which is impossible, then whatever remains, however *improbable*, must be the truth." Sherlock Holmes,