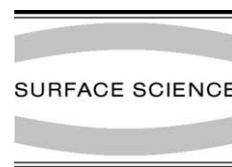




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# Cosmic dust and our origins

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## Abstract

The small solid particles in the space between the stars provide the surfaces for the production of many simple and complex molecules. Processes involving the effects of ultraviolet irradiation of the thin (hundredth micron) mantles are shown to produce a wide range of molecules and ions also seen in comets. Some of the more complex ones inferred from laboratory experiments are expected to play an important role in the origin of life. An outline of the chemical evolution of interstellar dust as observed and as studied in the laboratory is presented. Observations of comets are shown to provide substantial evidence for their being fluffy aggregates of interstellar dust as it was in the protosolar nebula, i.e. the interstellar cloud which collapsed to form the solar system. The theory that comets may have brought the progenitors of life to the earth is summarized. © 2001 Published by Elsevier Science B.V.

*Keywords:* Molecule–solid reactions; Photochemistry; Semi-empirical models and model calculations; Desorption induced by photon stimulation; Surface diffusion; Surface chemical reaction; Chemical vapor deposition; Porous solids

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## 1. Introduction

Pervading all the space between the stars are clouds of gas and dust which often appear as dark nebulae such as that which appears in the shape of a horse's head in the region of the constellation Orion (see Fig. 1). Over 100 organic and inorganic molecules have been detected in the gas but it is the dust that contains the largest and most complex organic molecules; these dust grains are very, very small. Even the large ones are only tenths of microns in size and there are myriads of smaller ones which may be more like large molecules, such as polycyclic aromatic hydrocarbons (PAHs) and perhaps fullerenes. The role of interstellar dust in

the cosmic scheme of things is fundamental to comets and other primitive solar system objects and is believed by many to provide the key to life's origins. The 'large' tenth micron sized particles are generally very cold with temperatures approaching as low as 5–6 K (–268 °C). Interactions on their surfaces with atoms, molecules, energetic photons and cosmic rays provide a major source of the chemical evolution in space. This is as much as we know today. But the subject of dark nebulae and what makes them dark has a patchy history. The earliest relevant ideas go back 100 years. Looking at the sky in the direction of the constellation Sagittarius, it is clear that there are tremendously dark lanes especially in the region toward the center of our Milky Way. This observation inspired Herschel in 1884 to say that there was undoubtedly a hole in the sky. Barnard started to

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\* Deceased.



Fig. 1. The Horsehead nebula, so called because in projection it looks like a horse's head, is a dark cloud of dust and gas in the Orion nebula in the region where much star formation is currently taking place. Its darkness is simply explained by the dust blocking of the starlight behind it.

take pictures and reported vast and wonderful cloud forms with their remarkable structure, lanes, holes and black gaps some of which are now called Bok globules. Clerke [1], in an astrophysics text she authored around the turn of the century, stated. "The fact is a general one, that in all the forest of the universe there are glades and clearings. How they come to be thus diversified we cannot pretend to say; but we can see that the peculiarity is structural that it is an outcome of the fundamental laws governing the distribution of cosmic matter. Hence the futility of trying to explain its origin, as a consequence, for instance, of the stoppage of light by the interposition of obscure bodies, or aggregations of bodies, invisibly thronging space". It was not until the work of Trumpler in 1930 [2] that the first evidence for interstellar reddening was found; which would imply that many stars were cooler than predicted. This reddening has nothing to do with the Doppler shift of receding objects. His observations indicated reddening even where he saw no clouds. In 1948 Whitford [3]

published measurements of star colors versus spectral types over a wavelength range from about 350 nm (ultraviolet) to the near infrared. Spectral types characterize the size and temperature of stars. The relation was not the expected straight line, but rather, it showed curvature at the near ultraviolet and infrared regions. This was later updated in 1958 [4]. Things were beginning to make some physical sense from the point of view of small particle scattering. In 1935 Lindblad [5] published an article in *Nature* indicating that interstellar elemental abundances made it seem reasonable to grow particles in space. Eddington had long before hypothesized that it was so cold in space that anything that hits a small particle will stick. But the earliest attempts to explain interstellar extinction were not in terms of something that could grow in space but rather in terms of meteors [6,7]. Interstellar extinction is the apparent reduction of starlight.

It was in the 1940s that van de Hulst [8] broke with tradition and published the results of making

particles out of atoms that were known to exist in space: H, O, C, and N. He assumed these atoms combined on a surface of some kind to form frozen saturated molecules. The surface was left as ‘to be determined’ (TBD). This is what later became known as the ‘dirty ice’ model and was the first application of surface physics to interstellar dust. The dirty ice model of dust was a logical follow up to the then existing information about the interstellar medium and contained the major idea of surface chemistry leading to the ices  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{NH}_3$ . But it was not until the advent of infrared astronomical techniques, making it possible to observe silicate particles emitting at their characteristic  $10\ \mu\text{m}$  wavelength in the atmospheres of cool stars, that we had the cores (surfaces) on which the matter could form. TBD was now determined. It is interesting to note that their presence was predicted on theoretical grounds by Kamijo in 1963 [9]. As van de Hulst said, he chose to ignore the nucleation problem and just go ahead (where no one had gone before) with the assumption that ‘something’ would provide the seeds for the mantle to grow on. What a great and creative guess! So it was that by 1945 we had many of the theoretical basics to help us understand the sources of interstellar dust ‘ices’ but it was not until about 1970 that the silicates were ascertained. However, having a realistic dust model, van de Hulst developed the scattering tools to provide a good idea of dust properties.

After the extinction curve—how the light blockage increases from the red to the blue—and the inferred particle size had been well established, two investigators, Hall [10] and Hiltner [11], inspired by a prediction of Chandrasekhar on intrinsic stellar polarization, discovered instead, the general interstellar linear polarization. It turns out that the blockage of starlight by the dust produces a partial linear polarization of the starlight as if the clouds were polarizers. The implication of the linear polarization was that the extinction was caused by nonspherical particles aligned by magnetic fields.

The past 40 years have seen a revolution in the study of interstellar dust. This has been a threefold process. First of all, the observational access to the ultraviolet and the infrared clearly drove home the

fact that there had to be a very wide range of particle sizes and types to account for the blocking of the starlight. Secondly, the infrared provided a probe of some of the chemical constituents of the dust. Thirdly, laboratory techniques were applied to the properties and evolution of possible grain materials. It was the advent of infrared techniques that made it possible to demonstrate conclusively that something like rocks (but very small, of course) constituted a large fraction of the interstellar dust. However the initial attempt to find the  $3.1\ \mu\text{m}$  feature of  $\text{H}_2\text{O}$  predicted by the dirty ice model was unsuccessful [12]. This was, at first, a total surprise to those of us who had accepted the dirty ice model. However, it supplied the incentive to perform the early experiments on the ultraviolet photoprocessing of low temperature mixtures of volatile molecules which would simulate the ‘original’ dirty ice grains [13]. By doing this we hoped to understand how and why the predicted  $\text{H}_2\text{O}$  was not clearly present. These experiments gave rise to predictions of a new component of interstellar dust in the form of complex organic molecules, as well as mantles of all sorts of ices on the silicates. The grain surfaces were becoming much more interesting.

Present studies of interstellar dust lead us in many directions; from chemical evolution of the space between the stars, to comets, to solar systems. I will try to present an overview of our current knowledge of the dust which brings many related astrophysical problems to the fore. Where and how small particles form and grow and evolve in the space between the stars, involve interactions between the solid dust and the gas atoms, molecules, the ultraviolet photons, and cosmic rays which drive the processes. The questions posed by our present information and the suggested needs for the future are discussed in the last section. The space age has ushered in some of the most dramatic developments and will ultimately give us the data we need to understand how solar systems are born out of collapsing clouds; how comets are made and whether comets are the carriers of the seeds of life’s origins. The ‘comet revolution’ occurred when the Russian space probes VEGA 1/2 and the European space probe GIOTTO were sent out to intercept comet Halley and returned their

remarkable results to earth [14]. Until 1986 no one had ever seen what a comet looked like close up and for the first time we were able to actually photograph the nucleus of a comet, which is always obscured by the gas and dust which it releases when it is heated by sunlight and produces the spectacular comet tail. Both the VEGA and the GIOTTO satellites passed between the comet and the sun so that the dust scattered light was minimized. Among other experiments on these satellites was a time-of-flight mass spectrometer which analyzed the dust which impacted the instrument at  $70 \text{ km s}^{-1}$ . From this it was discovered that a major fraction of the comet dust consisted of complex organic molecules as predicted from the interstellar dust—not just the minerals which many had anticipated. But it all starts with the interstellar dust.

## 2. The dust environment

Interstellar dust is coupled to and carried around the Milky Way by the gas clouds. These clouds come in a vast variety of shapes, sizes, densities and temperatures. They can, however, be qualitatively classified in two basic categories—diffuse clouds and molecular clouds. The diffuse clouds are not clearly distinguishable on a photograph and are limited in density to less than about 300 hydrogen atoms per cc and are at a temperature of 50–100 K. The molecular clouds can have kinetic temperatures as low as 20 K (even 10 K) and any density above 300 per cc including the densities at which clouds collapse to form stars. Diffuse clouds contain hydrogen in atomic form while molecular clouds are dominated by molecular hydrogen. They can be very dark, as commonly illustrated by the Horsehead nebula (see Fig. 1), and also by isolated blank regions in the sky commonly called Bok globules (see Fig. 2). These latter were suggested as concentrations of dust and gas which were collapsing to form stars.

The material environment is dominated by hydrogen which is the most abundant atom in the galaxy. But it is the condensable elements which are needed to make the solid dust. The most abundant ones are the ‘organics’ O, C, N which,

all together, account for one atom for each 1000 H atoms. Down by another factor of 10 are the ‘rockies’ Si, Mg, Fe. Table 1 shows the abundances of these in the solar system. Now, if we add these all together the total mass of the dust is at most about 1% of the gas.

The energetic environment affecting the dust (other than that associated with phenomena like star formation and even more explosive supernovae) consists of the ultraviolet radiation from stars and the cosmic ray particles. One of the principal effects of the ultraviolet is that it heats the dust. As a result of a kinetic balance between absorption and emission of radiation the dust temperature in diffuse clouds is about 15 K but in molecular clouds where it is shielded, the temperature may be as low as 5–10 K [15,16]. The dust and gas temperature can be very different from each other, with the dust generally being at the lower temperature.

## 3. What do observations tell us about dust?

The main features which characterize interstellar solid particles are described by their size (sizes), shape, their chemical composition, and amount. All of these must be determined by remote observations using telescopes in space as well as on the ground, with a variety of optical wavelengths. It is only by combining all these observations that we can come to any valid description. Even then there remain disagreements on what dust really is. Nevertheless, there are some firm conclusions. The first of these has to do with size as deduced from the way the dust blocks the light of stars.

### 3.1. *Interstellar extinction*

The most obvious evidence for the dust is that it blocks the light of stars in a very special way. As illustrated in the average interstellar extinction curve, shown in Fig. 3, the light in the red is reduced less than the light in the blue and in the ultraviolet. It can be shown from the basic electromagnetic scattering properties of particles that the blockage is most effective when there is an approximate match of particle size to wavelength, whether the particles be interstellar dust or atmo-

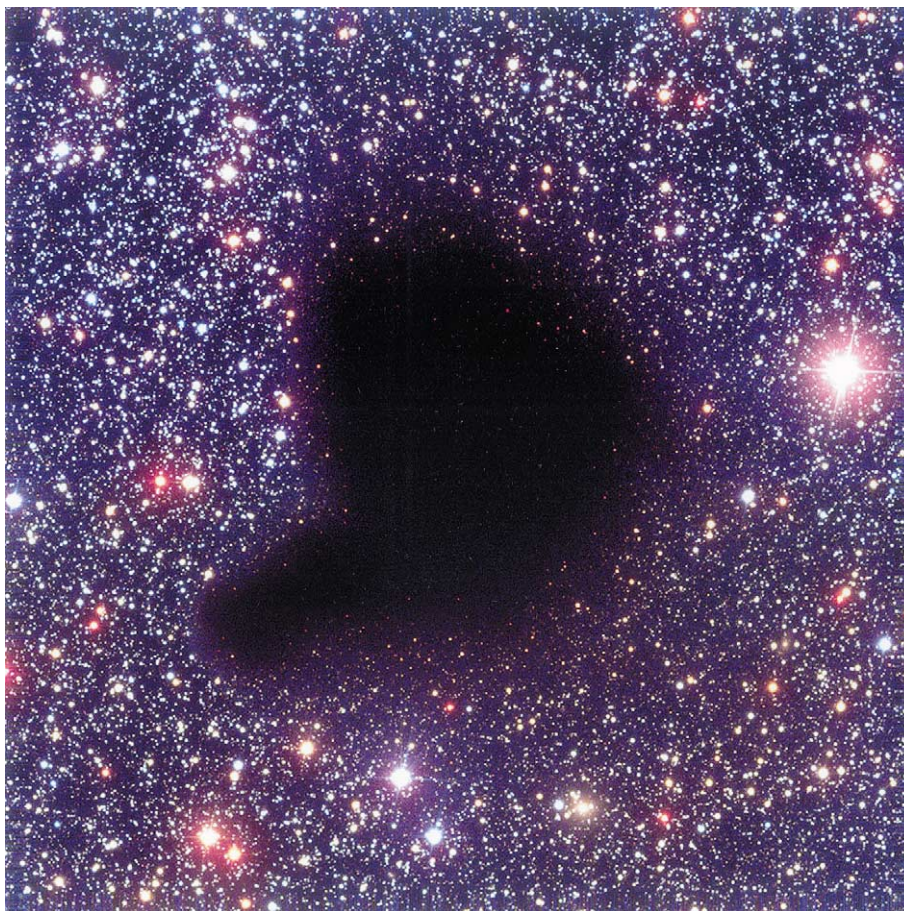


Fig. 2. An isolated cloud of dust called a Bok globule. No obvious star formation is taking place in its vicinity.

Table 1

Solar system abundances obtained by studies of solar spectra and presumed to represent the relative proportions of the elements which make up the solar system

Element	Relative number
H	1
He	0.0098
C	4.44(−4)
N	0.93(−4)
O	7.44(−4)
Mg	0.38(−4)
Si	0.355(−4)
S	0.214(−4)
Fe	0.316(−4)

The carbon abundance is a key factor in the composition of interstellar dust and the consequences are discussed in Ref. [16]. The numbers in parentheses denote powers of 10. Note that the organics O, C, N are 10 times as abundant as the rockies Mg, Si, Fe.

spheric aerosols which, when seen as smog, make the sun look so red when low on the horizon. From the shape of the extinction curve we can deduce that the particles responsible for the visual extinction are about the size of smoke particles (from a cigarette) being about  $0.1 \mu\text{m}$  in size (a mean radius) and those responsible for the hump and the far ultraviolet extinction are 10–100 times smaller [17].

### 3.2. Chemical composition

The principal molecular ingredients of the interstellar dust are deduced from the way they absorb or emit infrared radiation. Fortunately the so-called fingerprint region of the infrared

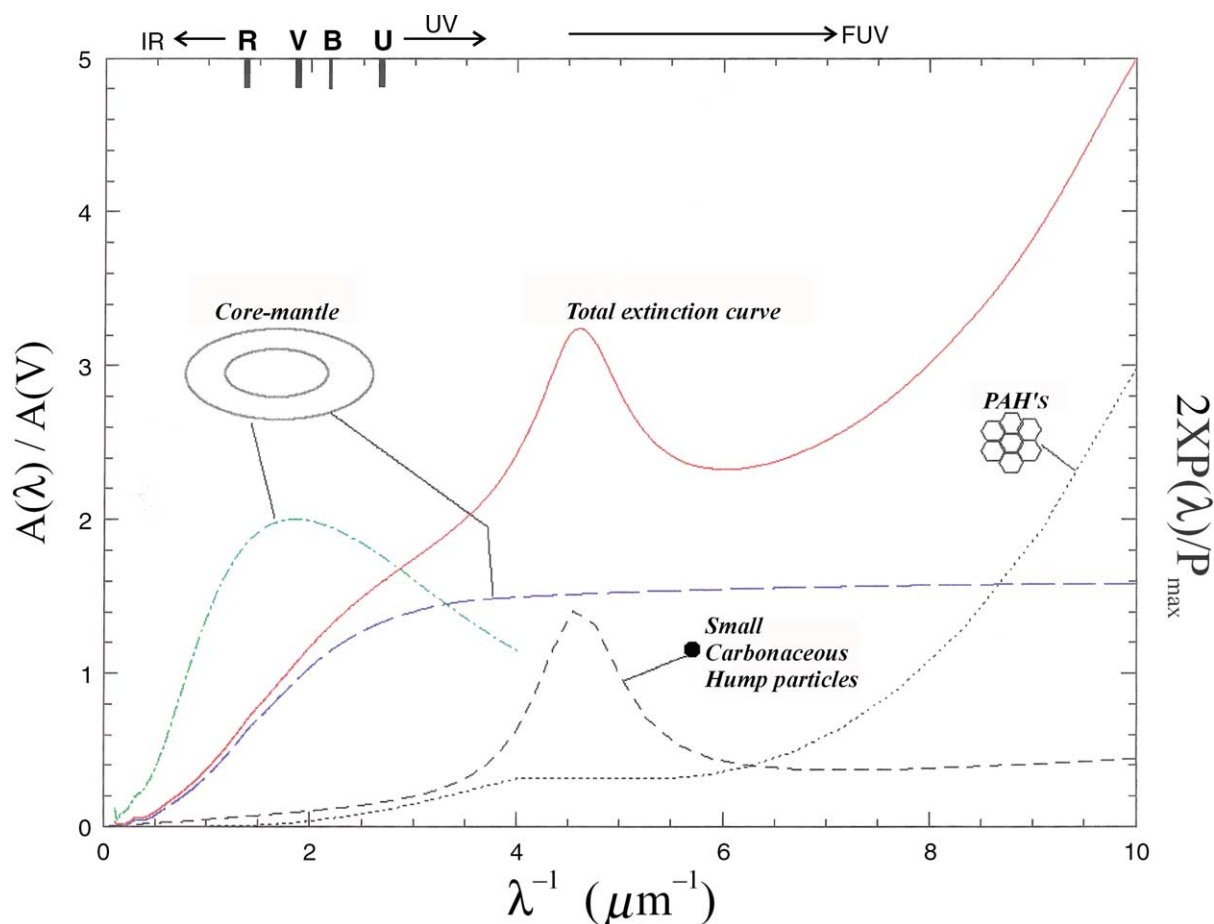


Fig. 3. The average extinction curve in the diffuse interstellar medium (solid line) and the mean polarization curve (dash-dot line) normalized to the maximum wavelength of polarization ( $P_{\max}$ ). The quantities  $A(\lambda)$  and  $A(V)$  are the amounts of blockage of starlight as a function of the wavelength ( $\lambda$ ) and specifically in the visual (V) region of the spectrum at about  $1.8 \mu\text{m}^{-1}$ . The various wavelength regions are indicated at the top: IR—infrared; R, V, B, U,—red, visual, blue, ultraviolet, FUV—far ultraviolet. If one compares the average extinction curve with the blocking of light by small solid particles, one finds that the long wavelength region (up to about  $4 \mu\text{m}^{-1}$ ) corresponds to the blocking of light by particles about  $0.1 \mu\text{m}$  in mean radius. So-called Rayleigh scattering which is proportional to  $\lambda^{-4}$  would be produced by particles much smaller than the wavelength. It turns out that the extinction of light by particles  $0.1 \mu\text{m}$  in size levels off (saturates) when the wavelength is significantly shorter than the particle size no matter what the material properties of the particle are. This implies that the extra rise in the extinction curve at  $\lambda^{-1}$  about  $4.6 \mu\text{m}^{-1}$  must be due to much smaller particles. The unified dust model [16] deconvolves the size distribution of the interstellar dust particles into three components: (1) the tenth micron silicate core-organic refractory mantle particles which provide all the polarization (dash-dot line) and a major fraction of the visible extinction (—); (2) very small ( $0.003 \mu\text{m}$ ) carbonaceous particles responsible for the 216 nm hump in the extinction (—); (3) a population of PAH like particles (large molecules) responsible for ultraviolet extinction ( $\cdots$ ). The polarization of starlight is produced as radiation passes through clouds of aligned interstellar dust particles which act like a polarizer.

spectrum from 2.5 to  $25 \mu\text{m}$ , where most vibrations of the molecular groups containing C, N, O and H occur, is accessible with modern telescopes. This region is indicated in Fig. 4. For example, the C–H stretching vibration is around  $3.4 \mu\text{m}$  and the

O–H stretch resonates at around  $3.1 \mu\text{m}$ . Similarly the Si–O stretch of silicates (rocks) is at about  $10 \mu\text{m}$ . Just knowing these features does not guarantee that we can identify the molecule in which the group exists. There are an infinite number of

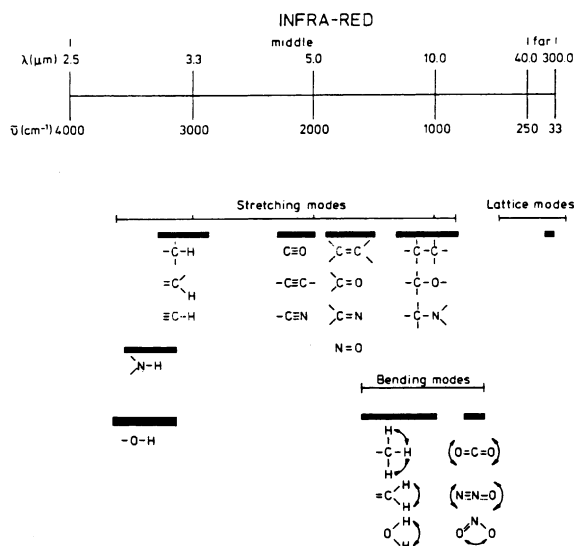


Fig. 4. Schematic of the infrared fingerprint region for vibrations of various molecular groups. Bending and stretching modes are indicated for a variety of molecular groups. The 3  $\mu\text{m}$  region corresponds to stretching modes of C–H, N–H and O–H. For example, solid  $\text{H}_2\text{O}$  has a strong absorption at about 3.1  $\mu\text{m}$ . Solid CO and  $\text{CO}_2$  have strong C–O stretching absorptions at about 4.5  $\mu\text{m}$ .

molecules that have C–H stretch features. By comparisons with laboratory spectra of simulations of the interstellar ices, it has been possible to identify about 15 molecules, radicals and ions. Fig. 5 shows observations made with the Infrared Space Observatory (ISO) of some of these molecules which are to be found in molecular cloud dust. In addition, a silicate absorption is clearly seen. This feature is always observed for the interstellar dust but it is not always accompanied by the ices. Even when we look far towards the center of our Milky Way, and looking mainly through diffuse clouds as early observed by Becklin et al. [18] (see Fig. 6), there is little or no ice (at 3.1  $\mu\text{m}$ ) to be seen [19–21]. What is seen in its place is the relatively insignificant absorption at 3.4  $\mu\text{m}$ . This turns out to be the ‘tip of the iceberg’ indicating the presence of enormous amounts of complex organic molecules in the dust. What is equally interesting is that there is another component of complex organics which absorbs infrared poorly but is an efficient emitter of what are called the ‘unidentified infrared features’. Although we can-

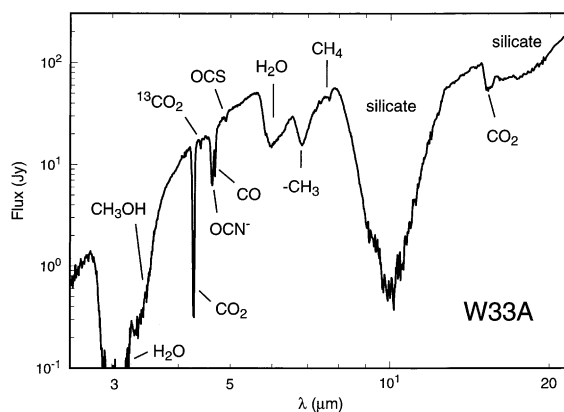


Fig. 5. Spectrum of the dust around the embedded protostar W33A in the wavelength region between about  $\lambda = 2.5$  and 20  $\mu\text{m}$  showing such identified molecules in the ice mantles as  $\text{OCN}^-$  [32,33] and OCS which are photoproduced in interstellar ices. The flux is given in janskys (jy). Note that the  $\text{H}_2\text{O}$  absorption is so large that it is completely saturated (little penetration). Identified absorption features are labeled according to the identified molecule or ion. Note the very broad feature at 10  $\mu\text{m}$  which corresponds to the Si–O stretch of silicates.

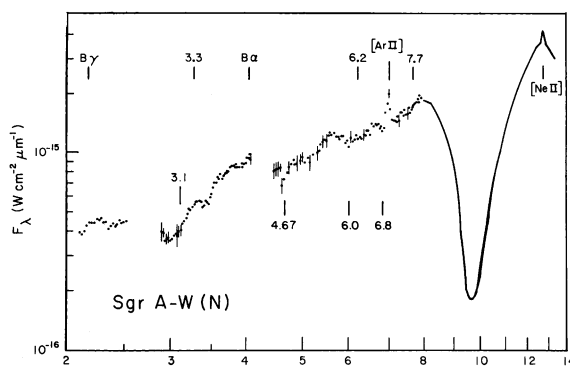


Fig. 6. Infrared spectrum of the galactic center [17,19,20] showing the lack of the ice band at 3.1  $\mu\text{m}$  but the ubiquitous presence of the silicate band at 9.7  $\mu\text{m}$ . The relatively inconspicuous feature at 3.4  $\mu\text{m}$  is the ‘tip of the iceberg’ evidence for the major fraction of organic refractories in the interstellar dust. The abscissa is  $\log \lambda$ . A few gaseous atomic lines such as the hydrogen Brackett  $\gamma$ , Brackett  $\alpha$  and emission lines due to ionized argon and neon are noted. All the other features are due to dust components.

not specify precisely those molecules which emit these features, we are relatively certain that they are of the type called PAHs [22–24] made up of ensembles of benzene rings resembling the exhaust from automobiles. But exactly how they are made

in space is one of the problems being probed by astrophysicists. A suggested source is one resulting from ultraviolet processing of the surface organics of the large dust grains [44]. One thing we do know, is that there are no cars in space.

### 3.3. Amount of dust

The dust is so intimately associated with the gas, it is almost a perfect marriage. The amount of dust and the amount of gas are correlated with each other. In quantitative terms the total blockage of visible starlight (visual extinction) is directly proportional to the number of atoms of hydrogen contained along the line of sight to the star [25]. The extinction is a measure of the total area of particles along the line of sight and the mean size of the particles is determined by the wavelength dependence. We can combine these to give the total volume of the dust and therefore have a measure of the amount of the dust for each hydrogen atom [26]. An important application of this line of reasoning is that we can demonstrate that even though the extinction to the galactic center shows almost exclusively the silicates, there are not enough cosmically available atoms of Si, Mg, and Fe (as silicates) to give the amount of dust needed to provide the amount of blockage of visible light. If the 'insignificant 3.4  $\mu\text{m}$  absorption' corresponds to a volume of material equal to that of the silicates and if this organic material exists as a mantle on silicate cores, the amount and wavelength dependence of extinction can be satisfied.

## 4. Evolution of interstellar dust

The small particles in space have a complex physical and chemical history. This is summarized in Fig. 7. Although all the growth and variability of dust occurs in the space between the stars, the birthplace of the dust is in the atmospheres of stars and in supernovae.

### 4.1. The nuclei of interstellar dust

The nuclei or cores on which the solids can grow in space start out mostly as small silicate particles

which are condensed in the atmospheres of cool, old (evolved) stars that are in their red giant expansion phase—a phase our own sun will go through some 5 billion years from now [26,27]. While there may be other sources of such cores, they are not as identifiable nor as clearly seen as in the emission spectra of red giants. The spectra of red giants and super giants have excess emissions at 10 and 20  $\mu\text{m}$  caused by the heated dust which is formed in and blown out with gas from the stars. Modern space observations have extended the spectrum beyond 20  $\mu\text{m}$  and show even more emissions corresponding to silicates. The sizes of these particles are not limited by the emission and interstellar absorption observations except that they must be no larger than the order of 1  $\mu\text{m}$ , otherwise the ice mantle observations would be distorted. As a matter of fact, even as little as 2 or 3  $\mu\text{m}$  would distort the 10  $\mu\text{m}$  silicate band appreciably. This is a basic electromagnetic scattering phenomenon. The overall evidence convinces us that the silicates emitted by stars are probably in the range of 0.05  $\mu\text{m}$  [28]. This is consistent with a wide range of astrophysical constraints [17].

### 4.2. Ice mantles

While many (more than 100) molecules are seen in the gas phase using mm and cm radio detection and about 15–20 molecules have been detected in the solid phase as mantles on the dust, both in a variety of space regions, the relative proportions of the identified molecules in the gas and solid phase are uncorrelated. A striking feature of this lack of correlation is that while the water molecule is generally the most abundant in the frozen solid ice mantles it is not very abundant in the gas. In fact both the observed and theoretically predicted gas phase abundances of water are generally much less than one hundredth that of carbon monoxide while it is observed that the water content in the solid ice mantles can be as high as 5–10 times as abundant as CO. The overabundance of H<sub>2</sub>O cannot have resulted from accretion from the gas. Surface reactions are obviously needed to account for this seemingly anomalous result. First, an O atom hits the grain and sticks. One of many H atoms can then hit and while it does not remain

## DUST IN SPACE

### A Brief History of a Dust Grain

#### START

- a) Small silicate particles condense in the atmospheres of cool stars and are ejected into space.

#### MOLECULAR CLOUDS

- b) Silicate particles cool to  $T=5-15\text{K}$  and act as condensation nuclei for accretion of gas atoms and molecules as a mantle of frost.
- c) Complex chemical reactions between gas and solids leads to an  $\text{H}_2\text{O}$  and  $\text{CO}$  dominated grain mantle.
- d) Ultraviolet radiation of mantle breaks simple molecules leading to new combinations and to complex organic molecules (photoprocessing).
- e) Star formation occurs leading to dissipation of portions of the collapsed cloud into surrounding low density (diffuse cloud) regions.

#### DIFFUSE CLOUDS

- f) In the low density regions volatile icy mantles are either photoprocessed, evaporated, or destroyed leaving only the complex organic refractory mantles. These mantles are further subjected to photoprocessing and to destructive processes which can break off small pieces.

BACK TO b,c,d,e,f and repeat many times ( $\sim 50$ ) until the grain is consumed by star formation or becomes part of a comet.

Total mean life time of a dust grain =  $5 \times 10^9$  years = Turnover time for the interstellar medium into and out of stars

Fig. 7. Brief history of a dust grain: the basic steps in its evolution from formation to destruction.

indefinitely on the surface it certainly remains long enough to encounter the sitting O and make OH. Another H atom comes along and does the same thing with the OH, thus making water. This is schematically illustrated in Fig. 8. The details of such processes are a subject of intensive laboratory and theoretical study by many groups looking for explanations, not only for the abundance of water but also for the abundance of a molecule such as methyl alcohol (the poisonous kind) in dust mantles. In any case, we have found ourselves coming back to van de Hulst's [8] idea of growing dust in space by surface reactions as well as by accretion. In Fig. 5 the relative over abundance of water relative to carbon monoxide is even more striking

because it occurs in dust which has been heated causing a relative reduction of the CO which evaporates at a much lower temperature than  $\text{H}_2\text{O}$ .

But note that we have only come to the second step in grain evolution and we have only answered some of the questions raised by the observations. There are other molecules in the ices that are either not seen at all or are too under-abundant in the gas to have simply frozen out or even to have been formed by surface reactions. Such molecules as carbon dioxide and the cyanate ion ( $\text{OCN}^-$ ) are candidates that may be created by the effects of ultraviolet on stirring up the ice mantles. This is discussed next.

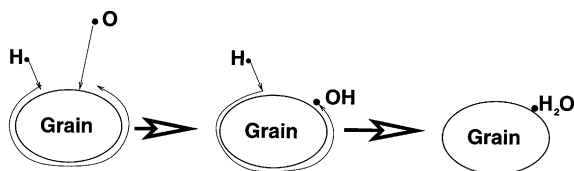


Fig. 8. A schematic illustration of the formation of hydrated molecules, and in particular  $\text{H}_2\text{O}$ , by sequential surface reactions between atoms and radicals with incoming H atoms.

#### 4.3. Photoprocessing of ice mantles

A long standing puzzle is how to account for the presence of gas phase molecules at all, in view of the fact that their freeze out time on the dust is about 10–100 times shorter than the cloud lifetime. The answer to this puzzle and the reason for finding ice mantle molecules which come neither from the gas nor from surface reactions may be found in the effects of energetic processing of grain mantles.

During the lifetime of a molecular cloud the icy mantles are subjected to substantial energetic processing by the prevailing ultraviolet radiation and to the collisions by cosmic ray particles. The former seems to produce the dominant chemical modification while the latter may play an important role in bringing some of the solid molecules back into the gas.

Ultraviolet photons with energy greater than about 4 eV have sufficient energy to break chemical bonds in the ice mantle molecules. This leads to the creation of free (frozen) radicals and to detached hydrogen flying through and sometimes out of the mantle. Since the mantle thickness does not exceed about  $0.02 \mu\text{m}$  all of the photons which impinge penetrate the mantle fully and are therefore effective. The internal chemical processing takes place as adjacent radicals combine and diffusing hydrogen is attached to another radical or molecule. For example, as schematically illustrated in Fig. 9, the breaking of molecules by photons

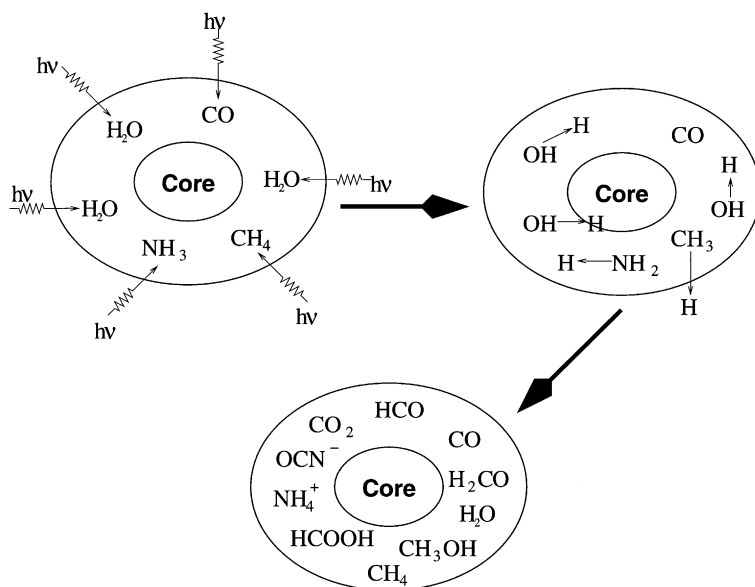


Fig. 9. Schematic of the sequence of bond breaking and recombination of radicals occurring in ultraviolet irradiated interstellar ice mantles. Initially the silicate core accretes (by surface formation or condensation) a mantle of water, methane, ammonia, and carbon monoxide. This mantle is subjected to bombardment by ultraviolet photons whose energy ( $h\nu$ ) is sufficient to break molecular bonds so that, as depicted in the upper right panel, H atoms are detached and leave the radicals OH, etc. frozen (10 K) in the ice matrix. The lower panel depicts how the detached H atoms may combine with CO to produce the HCO radical and the CO may combine with the O from a doubly photoprocessed water to produce carbon dioxide. All the molecules in the lower panel are seen in both laboratory and interstellar spectra.

and subsequent formation of new ones occurs. Therefore, if a water molecule loses an H and an adjacent methane molecule loses an H the OH and CH<sub>3</sub> radicals would instantly combine to form methyl alcohol which is in fact observed in interstellar grains.

The chemistry and the infrared spectroscopy of the evolution of interstellar ice mantles is studied by comparing with results which are created in a laboratory simulation. The basic idea is a simple one and is illustrated by the cartoon (Fig. 10) of the interstellar dust chemical evolution simulator [29,30]. The equipment in current usage by a number of institutes consists of four basic parts: a closed cycle helium refrigerator, a vacuum system, a vacuum ultraviolet source and an infrared spectrometer. One creates a cold (10 K) surface in

a vacuum and allows gas molecules to be accreted and subjected to irradiation by the ultraviolet. The laboratory ultraviolet flux is of course much higher than in space but it has been demonstrated that the laboratory results can be properly scaled to space so that 1 h of irradiation is equivalent to about 500 years in the diffuse interstellar space and about 5 million years in a molecular cloud. This ratio allows us to create changes in reasonable times to compare with the changes occurring in the lifetimes of molecular clouds. These changes can be studied by observing the changes using the infrared spectrometer. Fig. 11 shows the Leiden Lab setup. A typical example of the results of photoprocessing ices is shown in Fig. 12 with a comparison of the spectra of ices before and after ultraviolet. It cannot only be said that astronomical observations confirm the laboratory method but, in fact, that much of what has been discovered has required the data obtained in the laboratory [31]. The identification of molecules when mixed together in a frozen sample is not simply given in terms of the spectra of individual isolated species (for example see Fig. 13 with a comparison of CO in polar and nonpolar ices, [32]). Furthermore such reactive species as the cyanate ion which is observed in space results from ultraviolet radiation of mixtures including carbon monoxide and ammonia so that this provides evidence for the ultraviolet photoprocessing in space [33,34]. Another example is provided by the abundance of carbon dioxide in interstellar grains which is seen to be very efficiently and quickly produced in the laboratory upon irradiation of mixtures containing water and carbon monoxide which are two of the most abundant species in grain mantles. The sample laboratory spectra (Fig. 12) show some of these features. Laboratory studies are underway to test whether CO<sub>2</sub> can also be formed by pure surface reactions.

One of the critical consequences of the irradiation of mantles is the creation of a steady state abundance of free radicals. While some recombine to create new molecules there are always new ones being produced. The potential energy stored in the mantle by these radicals is substantial. It has been shown in the laboratory that if the sample can be warmed sufficiently to release these radicals from

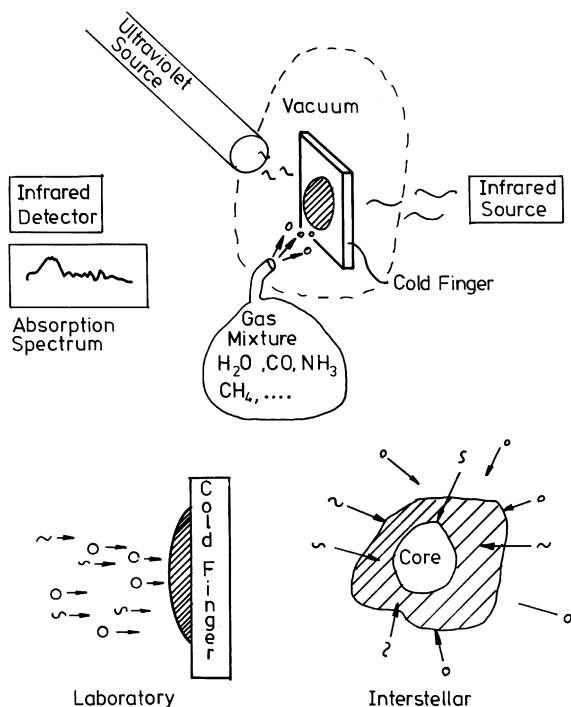


Fig. 10. A schematic of the laboratory analog method simulating the photoprocessing and the infrared spectroscopy of interstellar ice mantles. Gas mixture samples are slowly deposited on the cold finger at 10 K (dust surface analog) in a vacuum chamber (interstellar space). The material is irradiated by a vacuum UV hydrogen lamp (UV in clouds from stars and from cosmic rays) and the changes in infrared spectra are measured with an infrared spectrometer.

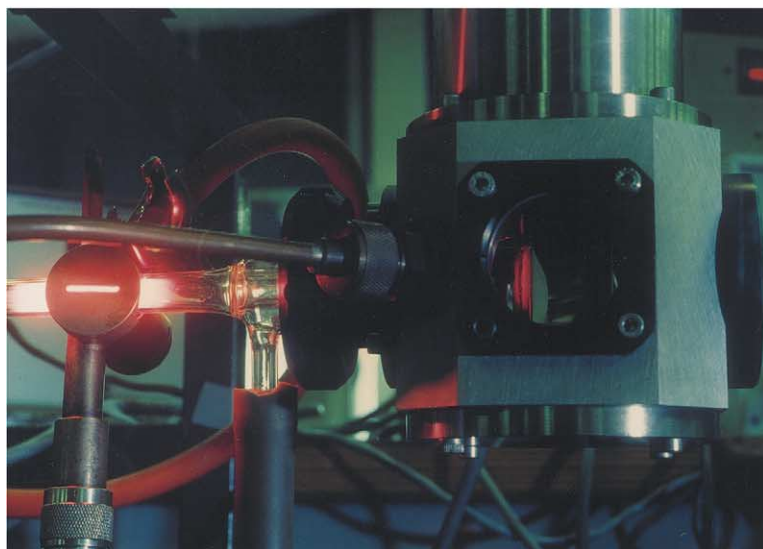
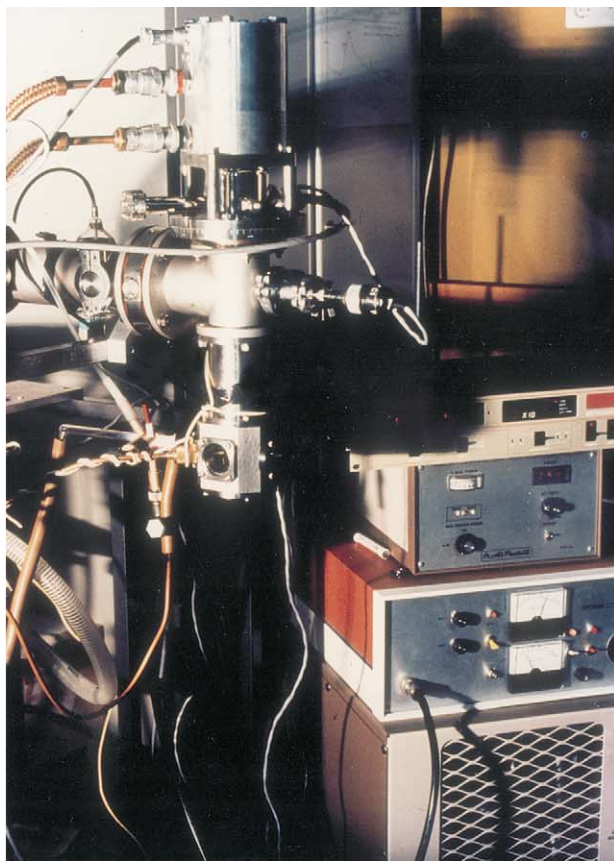


Fig. 11. A photograph of the Leiden Laboratory setup. The vacuum container of the cold finger is at the bottom of the cryocooler and the vacuum UV lamp at its left is seen close up in the other photo. The red color in the vacuum UV lamp is from hydrogen emission.

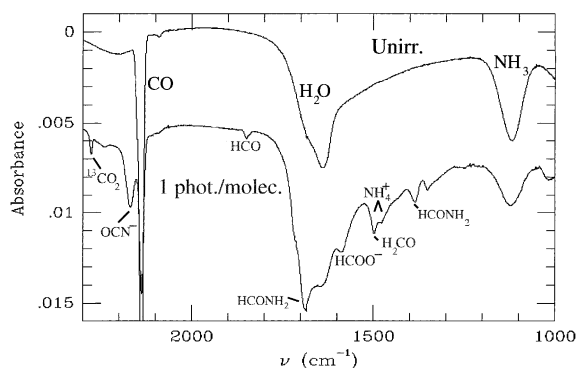


Fig. 12. A laboratory spectrum of a mixture of ices deposited at 10 K before (upper curve, showing the initial spectrum features corresponding to water, ammonia and carbon monoxide) and after irradiation by ultraviolet (lower curve). The presence of new molecules is indicated in the lower spectrum according to their absorptions. Note particularly the  $\text{OCN}^-$  which is observed in both interstellar dust and in comets. The total carbon dioxide produced is very abundant but its absorption is at a shorter wavelength (higher wavenumber  $\nu = 1/\lambda$ ) than is included. But one can see how abundant it is by noting the strength of the isotopic form and multiplying by the relative abundance of about  $^{12}\text{C}/^{13}\text{C} = 80$ .

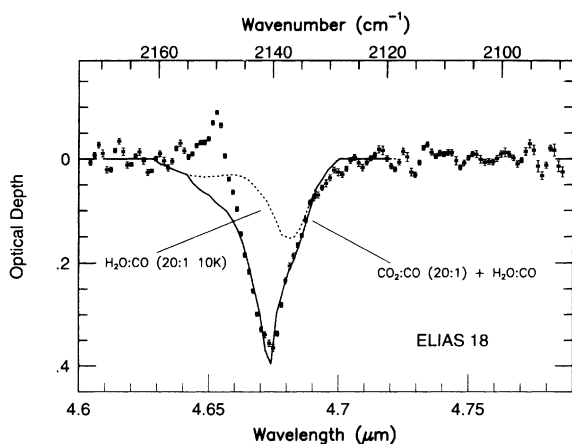


Fig. 13. Spectra showing the shape of the CO absorption and how it varies depending on whether it is totally imbedded in  $\text{H}_2\text{O}$  (···) or partially on the outer surface (—) of the ice mantle [31]. The dots are observations of the absorption spectrum towards a star Elias 16.

their frozen sites enough energy is released by the rapid recombination of the stored radicals to lead to a runaway explosive reaction which desorbs a large amount of material to the gas. It has been

proposed that in space such a trigger is provided by the heat generated when a heavy cosmic ray ion (principally Fe) plows through the mantle. It turns out that protons while relatively more abundant have little heating effect. The explosive desorption of mantle molecules triggered by cosmic ray iron nuclei in mantles with high radical concentrations appears to be the principal mechanism for maintaining a substantial concentration of gas phase molecules against freeze out on the grains. It turns out that a temperature increase of only about 15 K leads to sufficient diffusion of the free radicals in the initially 10 K ice mantle to trigger a chain (explosive) reaction [36]. The desorption problem in the interaction between dust and gas in molecular clouds is a basic one and is currently under intensive study. It plays an important role not only in keeping molecules in the gas but also by injecting different ones back into the gas phase; for example,  $\text{CO}_2$  which is more abundantly made in the dust than in the gas [35–39].

The application of laboratory experiments to the study of evolution of interstellar grains may be one of the most important astrophysical fields at the present time and is a fertile field for many new ideas. There is a burgeoning of experiments using atomic beams as well as molecules on cold surfaces not only to explore how molecules like water, carbon dioxide, and formaldehyde are made but also to study how molecules are desorbed.

#### 4.4. Organic refractory mantles

As noted earlier ice mantles are not to be seen in diffuse clouds. The transition from the molecular cloud to the diffuse cloud is a destructive one associated with the dramatic effects induced when the cloud collapses and forms stars [40]. This is exemplified by the classic photo (Fig. 14) taken with the Hubble telescope showing what look like cumulo nimbus clouds before a thunder storm but are really rapidly expanding interstellar clouds of gas and dust being blown apart by intensive star formation. In such an environment the volatile mantles are destroyed, evaporated or sputtered away. It appears, however, that not all the ‘organics’ in the ices are dissipated. In the laboratory when long term irradiated ices are warmed up they leave a

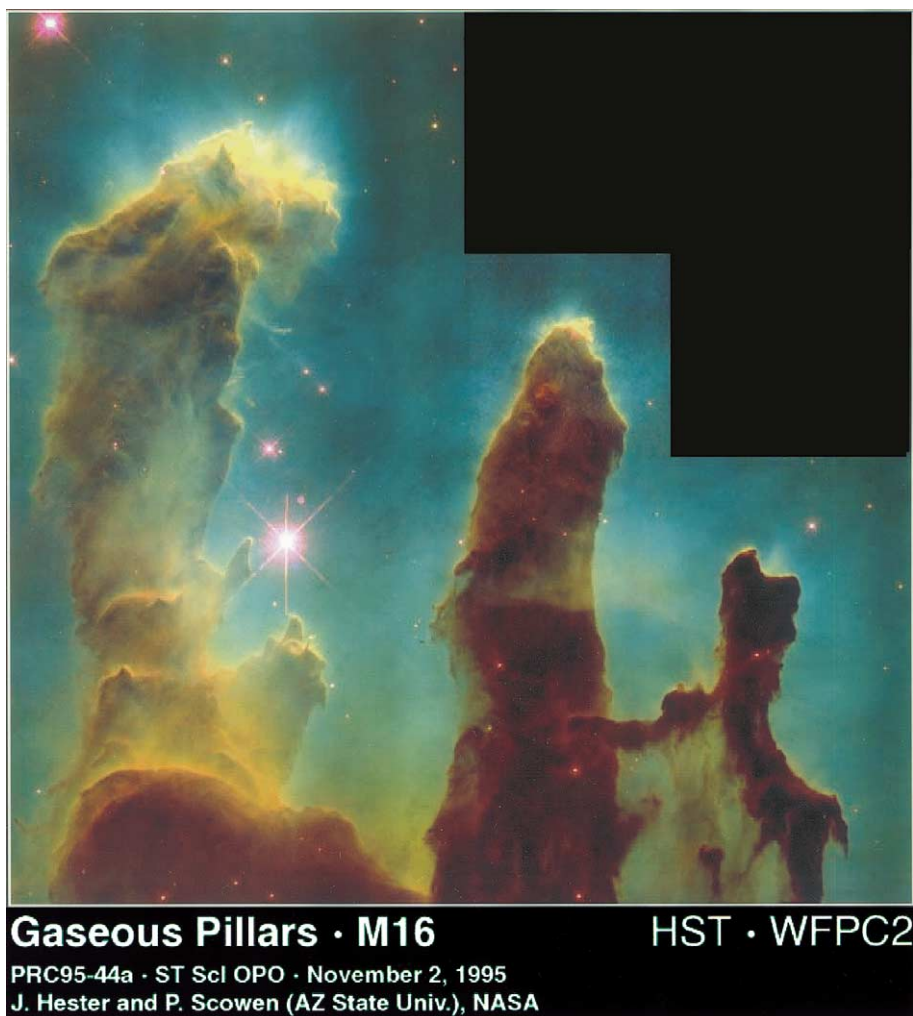


Fig. 14. The Eagle nebula exhibiting the expanding cloud of gas and dust resulting from intensive star formation. The ultraviolet light from hot stars causes the illumination at the colored edges. The pillar at the left is about a light year long.

residue of complex organic molecules which we call ‘yellow stuff’. It had long been conjectured that such material would be created in interstellar space where it would provide the mantles on the silicates needed to account for the extinction (see Section 3.3 and Ref. [41]). When the C–H absorption feature was first observed in the direction of the galactic center (Fig. 6) it was thought to have confirmed this [42]. But what was made in the laboratory could only be what we might call first generation organic refractory mantle material. The ‘yellow stuff’ (see Fig. 15) possessed an infrared

absorption feature similar to the astronomical 3.4  $\mu\text{m}$  feature which was encouraging, but it did not duplicate the astronomical observations. This should not have been surprising because after the dust is ejected from its cocoon in the molecular cloud it finds itself in a much more hostile environment and the first generation yellow stuff material is now exposed to 10,000 times the ultraviolet flux compared with the molecular cloud. It was therefore to be expected that the organics which the actual interstellar dust accumulated were much more highly processed than the laboratory resi-



Fig. 15. A typical residue which remains after an ultraviolet irradiated laboratory ice sample is allowed to warm up to room temperature. Note the characteristic yellow color.

dues. The required amount of photoprocessing was difficult to produce in the lab. However, by placing laboratory samples on a space platform called the exobiology radiation assembly (ERA) which was part of the European EURECA satellite, it was possible to test the effect of long term ultraviolet radiation. A number of laboratory organic residues were put in a sealed sample carrier, and after a year in space (4 months actual solar ultraviolet radiation) they were returned. What went up yellow came back brown (see Fig. 16). The color change indicates that the material has become relatively richer in carbon. When the ‘yellow, now turned brown stuff’ was studied in the infrared, the astronomical  $3.4\ \mu\text{m}$  feature was exactly duplicated as shown in Fig. 17 [43]. This is an indication that the extra radiation leads to a closer representation of the interstellar organic refractory mantles which exist in space.

#### 4.5. *The interstellar dust evolution cycle*

A theoretical study of the principal constituents of interstellar dust must take into account all the

observational constraints. Not all astronomers agree on the same model of dust. One thing which is now generally accepted is that the solid particles are sequentially and repeatedly being cycled into and out of diffuse and molecular clouds. In consequence one can start with how the dust appears in, say diffuse clouds, and try to follow what happens to it when it is swept up into a molecular cloud and finally how, after ejection it recovers its diffuse cloud character. This is what is schematically followed in Fig. 18. The processing which occurs in the molecular cloud phase consists of both accretion and photoprocessing [45,46] while that which occurs in the diffuse cloud phase is discussed in Ref. [44]. Fig. 19 depicts an average diffuse cloud core–mantle grain and an average precometary dust grain; i.e. a grain which is at its final stage in the collapsing cloud having accreted all condensable gases and small particles before the star forms. The elongated shape is needed to account for the interstellar polarization produced by aligned dust grains.

A single cycle lasts about  $10^8$  years and as many as 50 may occur before the dust is consumed in

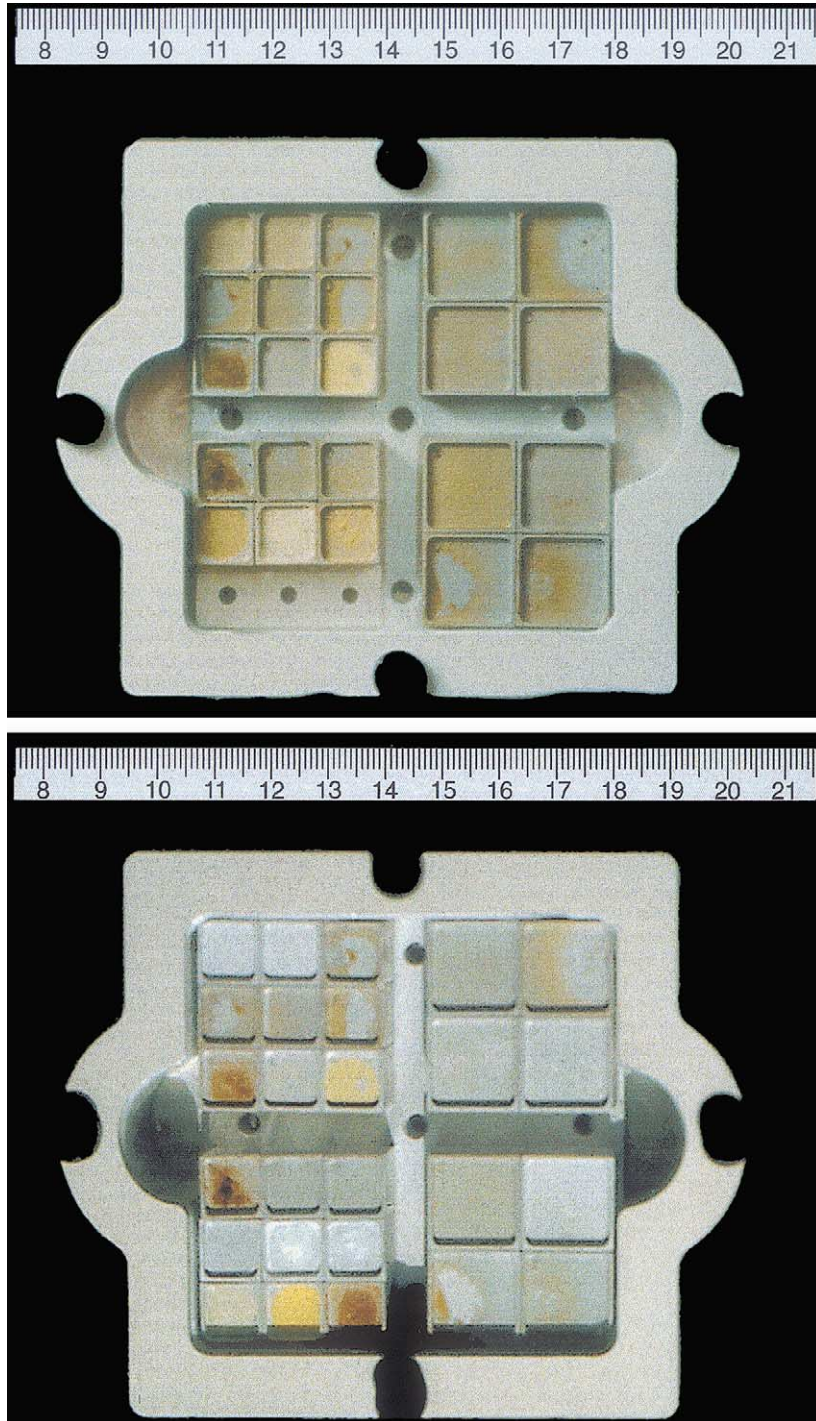


Fig. 16. Photos of the samples of various organic materials before and after ultraviolet radiation by the sun while on the ERA platform of the EURECA satellite above the earth's atmosphere. Note particularly the four (large) samples in the upper right of the sample carrier which went up as yellow organic residues and were returned brown. They are called A, B, C, D in clockwise sequence.

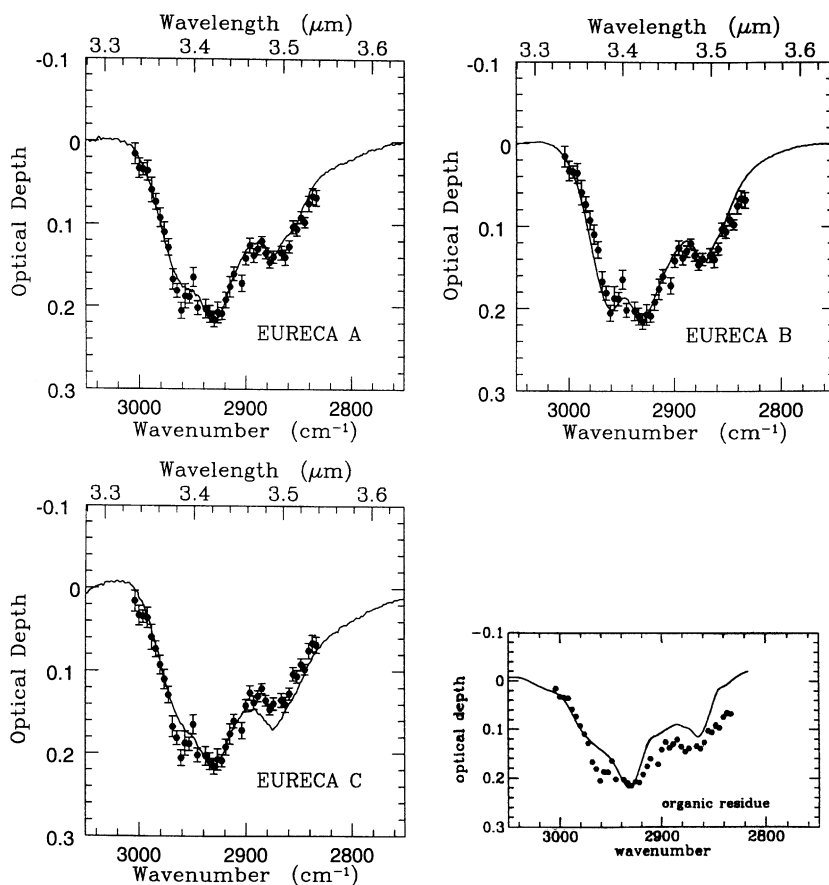


Fig. 17. Infrared absorption spectra of samples A, B, C compared with the 3.4  $\mu\text{m}$  absorption towards the galactic center. For comparison is shown the same region of the spectra for a sample of the yellow stuff (lower right).

star formation as noted in Fig. 7. An interesting consequence of this concept is that if one assumes a mean lifetime of a large dust grain to be 5 billion years then those which aggregated to form the solar system comets 4.5 billion years ago carry a chemical history back almost 10 billion years—close to the beginning of the universe. What the first dust looked like is still open to conjecture but it is unlikely to have been the result of the evolutionary picture above because in the earliest galaxies seen at high red shift the energetics of the large hot stars and the high rates of formation of supernovae would not have permitted the growth of mantles and the concomitant production of PAH and hump particles [47,48].

## 5. What is a comet?

Comets have long been thought to be the most pristine bodies in the solar system. They are relics of the collapsing cloud which went into making the sun and the planets. They may appear as spectacular bright objects spanning distances of hundreds of thousands of kilometers and covering large parts of the sky as shown in the color photo of Hale–Bopp (Fig. 20). But the source of this display is a rather small object—the nucleus—which is only kilometers across as was first seen in the photographs of Halley taken by GIOTTO (Fig. 21). The peacock-like display of a feathery tail and coma is made up of the gas and dust which boils off as the nucleus comes close to the sun. It

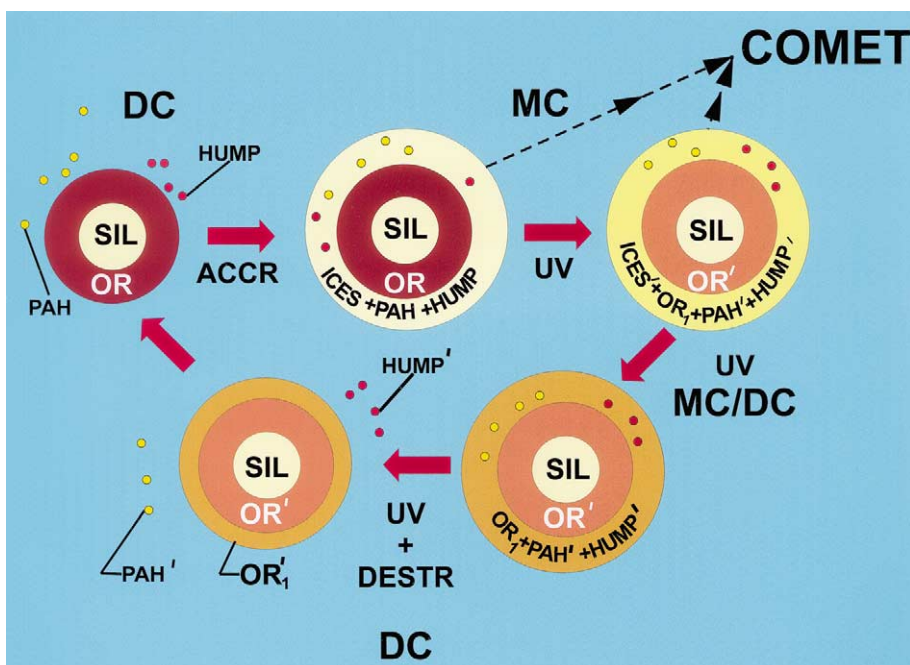


Fig. 18. Cyclic evolution of interstellar grains. One starts with diffuse cloud dust. Upper left is an average tenth micron radius silicate core–organic refractory mantle grain in the diffuse interstellar medium (DC). The mantle is heavily processed organic materials—even more heavily processed than the brown stuff in Fig. 14. Schematically illustrated are the hundreds of thousands to millions of very small carbonaceous hump particles (denoting their effect on the interstellar extinction) and even smaller PAH particles as described in Fig. 2. Following clockwise, the next phase depicts what happens after entering a molecular cloud (MC) showing the accretion of a complex ice mantle along with the very small particles and, simultaneously with accretion, the ultraviolet photoprocessing of the outer mantle and the organic inner mantle as well as the PAH and small carbonaceous particles (primes denote modified material). The next phase corresponds to the emergence out of the molecular cloud (MC/DC) after star formation when the ices are evaporated/destroyed leaving first generation organics ( $OR_1$ ). And finally, the ultraviolet processing and partial destruction of the newly added first generation organic material ( $OR_1 \rightarrow OR'_1$ ) as well as re-emergence and reforming of PAH and hump particles leading back to the ‘original’ diffuse cloud (DC) dust. The arrows leading upward depict the kinds of dust, which would make up the protostellar material (material in the collapsing cloud in which the star and planets were born) aggregating to form comets. In this representation it is assumed that this occurs with little or no evaporation and reforming of ices. A single cycle lasts about  $10^8$  years and as many as 50 may occur before the dust is consumed in star formation.

was the pioneering work of Whipple [49,50] which suggested that a comet should be an icy aggregate containing meteoritic type rocky materials. The more recent theories which provide a fundamental basis for this will be discussed in Section 6. The source of comets as having been made in the early solar system and thrown out to distances of 50,000 times the distance from the earth to the sun (astronomical unit (AU)  $1.5 \times 10^{13}$  cm) there to reside for 4.5 billion years along with hundreds of billions of companions in what is called the Oort cloud (of comets) was the contribution of Oort [51]. These ‘nascent’ comets which are too distant

to be seen are almost in interstellar space and remain very cold. It is not until such a comet which has been in cold storage in the Oort cloud since the birth of the solar system receives a small gravitational perturbation from some object far removed from our solar system that it leaves its home to join with the planets closer to the sun. As it approaches the sun it is heated and the frozen gases (mostly water ice and carbon monoxide) evaporate and like a wind carry the dust along with them. The illumination of the dust by sunlight and the fluorescent emission of the outflowing emitted gases induced by the solar ultraviolet which lead to

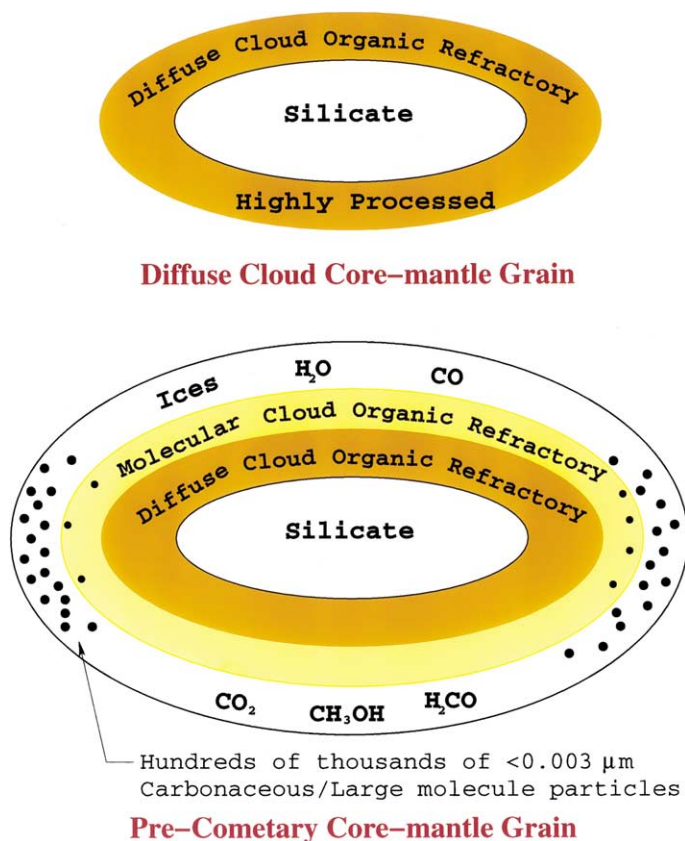


Fig. 19. Upper figure depicts a diffuse cloud silicate core–organic refractory mantle particle. It has to be nonspherical (here elongated) in order to provide for interstellar optical polarization. Lower figure depicts a fully accreted grain in the protosolar nebula; i.e. an average large grain on which all available gas phase molecules have accreted along with all the hundreds of thousands of very small grains/large molecules remaining in the dense collapsing cloud out of which the sun and planets were born.

the extended region of visible light extending over thousands of kilometers in the coma and over hundreds of thousands of kilometers in the tail make the appearance of the comet so dramatic. The source of all this is the small dark nucleus shown in Fig. 21. We are now aware of another system of comets which is much closer (perhaps only hundreds of AU from the sun) known as the Kuiper belt although it was likely to have originally formed even farther out than the Oort cloud comets. These comets started from the same or similar material in the protosolar nebula (the dense cloud of gas and dust out of which the sun and planets formed) as the Oort cloud variety. Comets are the best probe we have of the origin of the solar system.

## 6. The composition of comets

A matter of common belief is that comets have preserved the elemental composition of the protosolar nebula with the exception of helium which could not condense and hydrogen which have remained, as in the collapsing cloud, in almost totally gaseous form. Whatever hydrogen was maintained would have been in molecular combinations with other elements. The major question is the degree to which all the volatiles might have frozen onto the dust in the final cloud collapse phase and maintained their identity during aggregation into comets. Did some of the icy mantles of interstellar dust evaporate and recondense after partaking of chemical processing in the presolar



Fig. 20. A photo of the large comet Hale–Bopp showing the fluorescent gas tail (fluorescing from solar UV) and the dust tail scattering the sun light.

nebula or was the dust preserved totally? This is the subject of many hot arguments and the final agreed on answer is not yet in. Some suggestions of particle evaporation have been made [52,53]. It is however well documented by many modern observations that most if not all of the interstellar dust icy mantles are preserved.

Classically, the composition of comet nuclei was derived primarily from the coma (the cloud of gas and dust closest to the nucleus) volatile molecules dominated by water or OH. The dust was considered mostly in terms of its scattering properties. The discovery of silicates in comets as an infrared emission feature [54] confirmed the existence of refractory material in comets along with the ices (volatiles). The idea of organic refractories as a major comet nucleus constituent was first introduced in the interstellar dust model of comets by Greenberg [55]. In fact it was predicted to be as important as the silicates. But it was the mass spectrometric evidence of the GIOTTO/VEGA space probes which provided the first proof that the refractory material in comet dust consisted of both the organic elements (O, C, N) as well as the rocky elements (Mg, Si, Fe) [56–59] in approximately equal mass proportions. While the visual

and ultraviolet emission of coma molecules excited, photolyzed, and ionized by the solar radiation is used to deduce the volatile components, the infrared radiation by the heated dust tells us about the refractory components.

### 6.1. Interstellar ices and comet coma volatiles

A recent compilation of the molecules observed in a variety of comet comae and in interstellar dust mantles reveals a remarkable similarity (see Ref. [60]). Water is of course always the dominant volatile species with CO next and CO<sub>2</sub> and CH<sub>3</sub>OH running a close third and even such relatively exotic species as OCS and the cyanate ion OCN<sup>−</sup> being represented. It is interesting that as more and more comet molecules are identified the similarity in the comparison between interstellar dust and comet molecules is enhanced. The remarkably bright comet Hale–Bopp provided the vehicle to observe many new molecules [60]. These new results prompted the remark that “It supports models (of comet nuclei) in which cometary volatiles formed in the interstellar medium and suffered little processing in the solar nebula” [61]. Similar statements have been made by a number of comet



Fig. 21. A composite photo of the nucleus of comet Halley taken with the camera on board the GIOTTO space vehicle. The sun is  $30^\circ$  above the horizontal on the left and between  $15^\circ$  and  $12^\circ$  below the image plane. Note that the nucleus is very dark and that the emission of dust and gas occurs locally on those parts facing the sun while those in the shadow do not emit. The small hill is lit only on one side where it is evaporating (image courtesy Max-Planck-Institute für Aeronomy).

specialists [60,62,63]. How cold the water was when it originally condensed (or formed) was inferred from the state in which the water molecule is observed in the coma; i.e. whether the two symmetric H atoms exist with their nuclear spins parallel (ortho) or anti-parallel (para). Because the ortho state has spin 1 it can exist in three projections while the para state with spin 0 has only the one, so that they are normally (in thermodynamic equilibrium) found to be in the ratio 3:1. But, in comet Halley this ratio was found to be substantially smaller, corresponding to a temperature of condensation of 23 K (interstellar) thus excluding formation in a warm solar nebula [64] and any long time heating in the solid thereafter. It is worth noting that such molecules as  $S_2$ ,  $SO_2$ ,  $H_2S$  and OCS and  $OCN^-$  owe their consideration and identification in comets as of interstellar dust origin (see Table 2) largely if not exclusively because of experiments done with photoprocessing of ice mixtures in the laboratory [65–68] at temperatures

Table 2

Comparison of the abundances of ices in the interstellar medium (towards IRS9, a high mass protostar) and of cometary volatiles (at  $-1$  AU)

Species	Interstellar ices	Cometary volatiles
$H_2O$	100	100
CO	15	2–20
$CH_3OH$	6.3	1–7
$CO_2$	12	2–6
$H_2CO$	<3	0.05–4
HCOOH	3	–0.1
$CH_4$	1.6	0.7
Other hydro-carbons	?	–1 ( $C_2H_2$ , $C_2H_6$ )
$NH_3$	<6	0.5
$O_3$	#2	?
$OCN^-$	0.5	0.2
		(nitriles + HNCO)
OCS	0.2	0.4 (OCS + CS)
$SO_2$	?	–0.1
$H_2$	$\geq 1$	?
$N_2$	?	?
$O_2$	?	?

Cometary abundances are from Table 7 in Ref. [60]. ISM ice abundances are adopted largely from a compilation of Schutte [31] from various sources. The values are numbers of molecules relative to  $H_2O$  taken as 100. Although they generally follow the cometary distribution it must be noted that the sun was a low mass protostar when comets formed and the interstellar ices were probably somewhat different in detail.

corresponding to the interstellar dust. Comets appear to have been born cold and remained cold and relatively unmodified since they were born along with the earth and other planets.

### 6.2. Amorphous versus crystalline ice: further evidence for interstellar dust in comets

An important and useful example of the surface physics of ice is the study of the conditions of water molecule condensation which determine whether the resulting ice is to be found in an amorphous or crystalline state in comets and elsewhere. The conditions for formation and preservation of amorphous ice have been studied both theoretically and experimentally [69]. When a water molecule hits a surface it may diffuse to neighboring sites. If the diffusion rate is slow compared with the rate of deposition the molecule is essentially frozen in the vicinity of its adsorption site and does not have

time to find and settle in a crystalline site before the next molecule hits; i.e. if the flux of impinging molecules is lower than a critical amount the crystalline form is deposited. Thus amorphous ice may be formed under the condition that the diffusion distance during the time of coverage of the surface by adatoms (molecules) is smaller than the lattice constant of the substrate ice. It may be shown that on the interstellar dust in the parent molecular cloud the ice is both deposited and preserved in its amorphous form. If the interstellar ice is evaporated and recondensed in the solar nebula the only region where ice could reform is limited to the region beyond the asteroid belt which is where comets may have formed. The temperature in this region is such that diffusion rate is high enough and the flux of molecules is low enough (lower than the critical flux) that the ice is formed crystalline. Thus whether comets formed directly from interstellar dust or from dust from which the ice was evaporated and recondensed determines whether the ice in comets was initially amorphous or crystalline respectively. Furthermore, since the ice condensation region of the solar nebula encompasses temperatures significantly higher than that corresponding to the condensation temperature derived from the ortho/para ratio observed in the water evaporated from comets we may conclude that the ice in comets is indeed amorphous. This has been a classical assumption which we can now claim is justified by the solution of a problem in surface physics.

### 6.3. Interstellar and comet organic refractories

When pieces of the comet are ejected and blown away by the expanding heated gas the volatile constituents are removed leaving only the more refractory components called comet dust. One of the remarkable results established by the space missions GIOTTO and VEGA to Comet Halley (see Introduction) was that its dust was not, as some people expected, just of rocky composition (Mg, Si, Fe) but consisted of about equal amounts of the organics (O, C, N) as indicated in Fig. 22. This was one of the principal predictions of the interstellar dust model. The mass spectroscopic results not only confirmed the presence of an or-

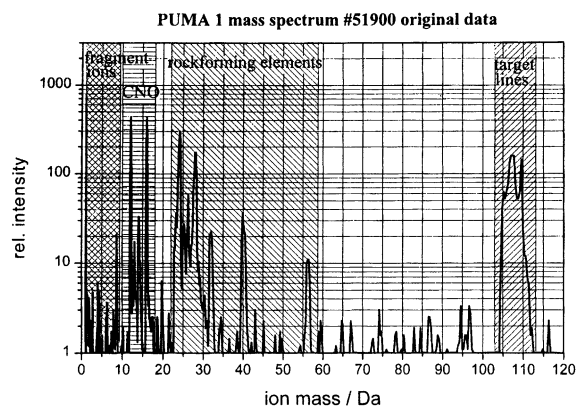


Fig. 22. An example of the kinds of mass spectra typical of comet Halley dust. The dust hit at  $\sim 70$  km s<sup>-1</sup> and was reduced to its ionized elemental components. Note that all particles had a mixture of the organic elements along with the rockies but the ratio varies. The peaks labelled O, C, and N primarily come from the organic mantles of the interstellar dust in the comet dust while 'rock forming elements' beyond mass 24 correspond to the elements Mg, Si, Fe, etc.

ganic refractory component of the dust but gave indication that it occurs as a mantle on the silicates [58] further substantiating the interstellar dust concept [17]. The organic part of comet dust revealed a large abundance of molecular species that are recognized to be of relevance to prebiotic chemistry; i.e. molecules which are believed to have been building blocks of the first living organisms. Mass spectroscopy and gas chromatography of laboratory analogue organics—the yellow stuff and brown stuff discussed in Section 4.4—also reveal the presence of a number of important prebiotic species. Amino acids are present in significant amounts but also molecules like hexamethylene tetramine which can also be sources of amino acids in the right environment [45,87,88]. The brown stuff is rich in PAHs [44] and one of the molecules observed in comets was phenanthrene—an intermediate sized PAH [89].

## 7. The structure of comets

Even if we know that presolar interstellar dust maintains its composition when aggregated to form a comet nucleus there would still be ques-

tions remaining about the end product of the way it aggregated. And furthermore what does the interior of a nucleus look like after 4.5 billion years? A good deal of theoretical work is going into looking for a solution to this problem (thermal processing, collisions etc.). We cannot hope to have the final answer to these questions until we can sample a comet directly or, better yet, bring back a piece. But in the meanwhile we have been able to use what comes off the comet to arrive at some pretty clear notions about the density of comets.

### 7.1. Comet dust density

One of the pieces needed to solve the puzzle of how a comet nucleus is constructed is to look at the pieces of a comet—its dust. GIOTTO and VEGA provided a major clue in establishing the mass (size) distribution of the dust fragments of the Halley nucleus [70,71] shown in Fig. 23. These are the only real (direct) data on comet dust masses less than  $10^{-6}$  g. Because of the concerted effort between space and ground based observers a great deal of additional information was made

available. Among these was the infrared observation of the comet dust. As had been observed in other comets before, there was the presence of a  $10\ \mu\text{m}$  emission feature produced by heated silicates. Now it is well known that only silicate particles much smaller than  $10\ \mu\text{m}$  in size (those indicated in Fig. 23 with a mass of  $\sim 10^{-11}$  g) can emit such a feature, and when one looked at the Halley dust mass distribution there just were not enough particles small enough to be the source of the emission if they were compact. The answer to this question already existed in the prediction that the dust consists not only of aggregates but these aggregates are not compact [72,73]. Simply stated, if one considers a compact particle as a collection of fine pieces and separates them, the ensemble acts like a sum of the small particles. As indicated in Fig. 23 a  $10^{-9}$  g fluffy ensemble (porosity  $P = 0.99$ ) of 100 particles of  $10^{-11}$  g acts like a sum of the small units so that by considering the Halley mass distribution as for very porous particles there are enough because we can include all those with masses  $\sim 100$  times larger than the maximum if compact. It is beyond the scope of this article to go into the details of the calculations or the arguments but the end result is that one can show that the constraint imposed by the observed Halley dust mass distribution is that the dust consists of very fluffy aggregates of silicate core–organic refractory particles whose individual mean masses correspond to the hashed region of masses ( $\sim 10^{-14}$  g) indicated in Fig. 23. The porosity had to be about 95% [74] corresponding to 95% vacuum.

### 7.2. Comet nucleus

As seen in the photograph of comet Halley (Fig. 21) the comet nucleus is a relatively small solar system body and even the largest one seen recently (Hale–Bopp) is only the order of 20 km in size, while they may be as small as or smaller than 1 km in size. Within the framework of the interstellar dust model one may reconstruct the comet nucleus from its dust if one assumes that the ejected pieces of the nucleus, heated by the sun, maintain their basic structure while evaporating all volatiles and leave only the skeletal remains (Fig. 24). This amounts to reconstructing each of the interstellar

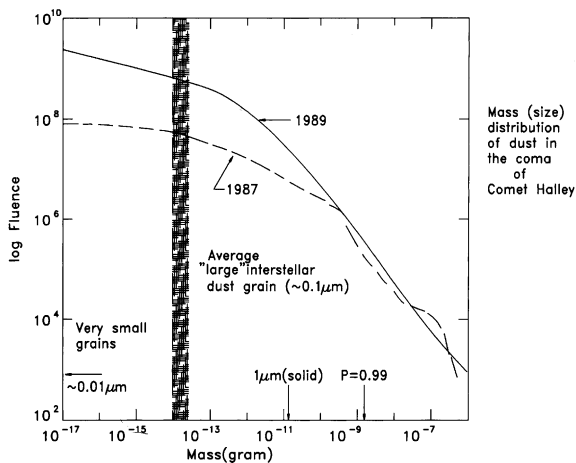


Fig. 23. The measured distribution of dust masses coming off of comet Halley [70,71]. The mean mass corresponding to the core–mantle interstellar dust distribution is indicated by the hatched region. Note that there are particles whose sizes are much smaller which may correspond to the hump and for ultraviolet particles in the unified dust model size spectrum. The larger dust grains are aggregates of the core–mantle grains.

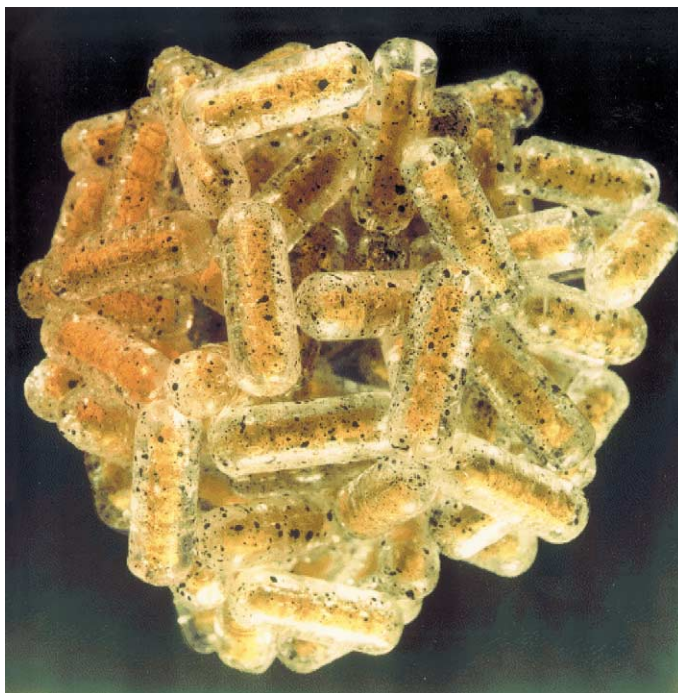


Fig. 24. A schematic model of a piece of a comet consisting of an aggregate of 100 average interstellar grains. Each grain consists of a silicate-core organic refractory mantle particle with an outer mantle of ices in which are imbedded the very finely divided carbonaceous and PAH particles as accreted in the final stages of cloud contraction to the protosolar nebula. The model is designed to be  $3\ \mu\text{m}$  in diameter and to have a porosity of  $P = 0.8$ . The corresponding density of a comet made of such material would be  $\rho = 0.28\ \text{g cm}^{-3}$ .

grains in the aggregate by putting the less refractory organics (those that evaporate at temperatures of  $>450\ \text{K}$  and are not seen by the GIOTTO/VEGA mass spectrometer in the dust) back on each core along with the icy mantle molecules. The result of this is pictured as a model of 'A Piece of a Comet' which was actually constructed in 1986 [75]. The model consists of 100 average core-mantle interstellar grains which have fully accreted all condensibles in the presolar cloud along with the hundreds of thousands of very small carbonaceous particles and PAH particles. The overall dimension is about  $3\ \mu\text{m}$ . The porosity as shown is about 80% meaning that a comet made this way would be 80% empty space. It is now generally accepted that comets are indeed low density objects but exactly how low is still an open question. The model would predict a comet nucleus density of about three tenths that of ice but recall that a large part of the stuff in comets has a much higher

density. In fact the amount of actual water ice in a comet is only about 30% (by mass) and, with the organics and rockies constituting about 45%, it may be more appropriate to call a comet a frozen mudball rather than a dirty snowball [76].

## 8. Comets and the origin of life

The search for extraterrestrial sources of life is an old one. There is of course the concept of Panspermia which is defined as the case where life is transported throughout the universe having originated on one planet and is then transported to another. While this theory may not be excluded because of the evidence of its possibility in Martian meteorites being transported to the earth (for a recent review see Ref. [77]) and vice versa we shall not discuss this because it begs the question of how life started in the first place. The concept

that prebiotic molecules might be created right here on earth was the incentive for the Miller–Urey experiment [78] and was probably inspired by Oparin’s theories of life’s origins from basic chemical processes. By passing an electrical discharge through a vapor mixture including water, methane and ammonia as a simulation of lightning in an early earth atmosphere, Miller showed with careful chemical analysis that many molecules such as amino acids, which are building blocks of life, were produced. However we now know that the earliest atmosphere which existed at the time when life emerged was almost totally carbon dioxide and in such a gas the production of prebiotic building blocks by such a process is extremely limited. This has led to the search for initiating prebiotic chemistry by extraterrestrial sources.

There are many objects hitting the earth which contain complex organic matter—interplanetary dust particles, micrometeorites, etc. as well as comets. In fact, the overall input from comets is not even the predominant source being outweighed by IDPs and meteorites. It appears most likely that all the objects which bring organics have started with interstellar dust at some stage so that one could say that the principal source of extraterrestrial organics is the interstellar dust. There are a number of cogent reasons to believe that comets are (were) the chosen vehicle to bring interstellar created building blocks to initiate life on earth—the right stuff at the right time.

### 8.1. *Timeliness*

There is an interesting coincidence between when life first appeared and the massive bombardment of the earth by comets and other objects was just beginning to tail off. It can be seen from the cratering record on other solar system objects, where the record has not been erased by weathering and crustal evolution (see Ref. [79] for a review), that during the first 700 million years after the earth formed it had undergone about 20 million impacts by comets—at least one 5 km comet every 10 years and that it was not until 3.8 billion years ago that this rate dropped quickly. It appears from the fossil evidence that life was already extensive 3.6 billion years ago and possibly even 200 million years be-

fore that based on carbon isotopic evidence [97]. We may even speculate that the evidence for the earliest living organisms could be extended further back in time by noting that the lack of evidence is possibly because the amount of datable rocks decreases with time similarly to the amount of identifiable fossils so that the percentage of fossil material may not be zero 3.8 billion years ago. In any case if we assume that all that heavy bombardment was delivering millions of death dealing blows to the earth similar to the single one which took care of the dinosaurs 65 million years ago there was not a great window in time for life to have emerged. The question is whether comets were the source of life as well as death.

### 8.2. *The right stuff*

The question is what constitutes the ‘right stuff’ for most rapidly initiating the prebiotic chemical evolution. There is certainly a great abundance of complex organics in each comet Halley equal in mass to about 1% of the current ‘living mass’ on the earth. Not only that but if we can believe that comets have preserved the interstellar dust better than meteorites then these organics already resemble those of living organisms in that they have a specific mirror symmetry—the amino acids are left handed [80,81]. However the packaging may be even more important than the contents as has been emphasized by Krueger and Kissel [82,83]. It involves the physical structure of comet dust as well as its chemistry. If comets are indeed very fluffy aggregates of the interstellar dust as postulated by Greenberg [84], the early bombardment of the earth by comets brought an enormous amount of complex organics to the earth in the form of very low density comet dust particles. Small fluffy aggregates of interstellar dust would have not been heated sufficiently to modify the organics [85] and could have floated to the earth preserving their character except for the evaporation of the volatile components which actually could cool the remaining material. Favorable factors provided by comet dust to the initiation of life involve three factors: (1) high porosity, (2) inorganic (mineral) surfaces for significant catalysis, and of course, (3) the presence of preformed chiral organics. We

envisage that these comet dust fragments may fulfill the requirements for chemical thermodynamics to start molecular self-organization [82]. Each comet dust particle, consisting of a porous aggregate of submicron silicate cores with organic refractory mantles sitting within a water bath (the local “ocean” containing nutrients much of which were also brought by comets), satisfies the conditions for non-equilibrium thermodynamics [86]. A very porous comet dust grain pictured as a piece of a comet minus the volatiles may be thought of as having an inside and an outside in the sense that the diffusion of small nutrient molecules into it from the bath occurs more readily than the diffusion of large molecules outward. There is already a substantial concentration gradient of preformed complex organic molecules in the initial structure. Therefore reactions within are unidirectional towards higher complexity and organization. An optimum size of the porous structure depends on the combined diffusion-reaction equations. If the aggregate is too small the small molecules pass through without interacting and the large ones may even diffuse out. If it is too large the small molecules interact only on the outside and do not penetrate fully. For example an aggregate of 100 particles as pictured in Fig. 24 with a diameter of 3  $\mu\text{m}$  (but with the ices gone) may allow many small molecules to pass through without a collision. A rather simple calculation suggests the order of 5–10  $\mu\text{m}$  diameter as an optimal aggregate size. The first discussion of this mechanism by Krueger and Kissel [82] pointed out particularly to the chemical composition of the organics predicted by Greenberg [87,88] provide excellent precursors for the making of biological molecules. An additional advantage of the comet dust is that if one tenth of a percent of the comet is shed as 5  $\mu\text{m}$  dust particles there would be available  $10^{25}$  (!) of them as possible seeds. Laid end to end they would stretch 100 times the distance to the nearest star. One can always argue that if the chance of any one being a life precursor is zero then the vast multiplying factor is not significant. But the value of large numbers of concentrated ‘cell-like’ chemical factories compared with a dilute soup of prebiotic molecules is difficult to counter. Kissel and Krueger estimate that 1 in  $10^4$  could make it [83]!

### 8.3. Delivery

The safe delivery of these dust particles with their organics is not a trivial problem when one considers the energy released in an impact occurring at say  $20 \text{ km s}^{-1}$ . However there are very special characteristics of the comet nucleus which could have provided the conditions needed for bringing a significant fraction of its organics unheated (or unpyrolyzed) to the earth’s surface. First of all one should bear in mind that not every collision will be head-on. Secondly, comets are rather fragile objects and may break up on approaching the earth and shed a great deal of dust [90,91] as was recently demonstrated by the break up of comet Shoemaker–Levy in the vicinity of Jupiter. Thirdly the earth’s early atmosphere was as much as 10 times denser than now providing a much thicker cushion for small particles to be slowed down [92]. Fourthly, comet dust is very underdense and, being made up of tenth micron units, may (according to Basiuk et al. [85]) undergo insufficient heating to pyrolyze the organics. The fluffiness of comet dust and the tenth micron size of its elementary units is therefore highly favorable to its low entry heating and survival to float ‘gently’ to the earth. Another possibility for controlling the overheating is the cooling by evaporation of volatiles initially contained in the dust [93–96]. Small fluffy particles have a great chance of surviving with their organics intact.

## 9. Space missions to comets

The future prospects in our understanding of interstellar dust, comets and our origins are exciting. Already from the first space missions to comet Halley we became aware of their complex chemistry. Both the US NASA and the European ESA have planned missions to comets and asteroids which will reveal even more details about their composition. It is the goal of the ESA Rosetta mission to explore the nucleus of a comet (P/Wirtanen) in detail from close distance over an extended period of time not only remotely from the Orbiter, but also by means of a Lander on the surface of the nucleus. Laboratory analog samples

in Leiden will be used to test the validity of the origins of prebiotic organics in interstellar space. The molecular composition of the organic phase of the solid cometary particles will be used to establish its exobiological relevance as possible organic precursors to the origin of life.

The Rosetta orbiter will both see (photograph) the comet and will measure its mass from its orbit just as the mass of the moon is determined by its orbit around the earth. Thus by knowing simultaneously the size and mass, we will for the first time know the density of a comet—how fluffy it really is! What might we anticipate being accomplished in the next hundred years? When we retrieve bulk material from a comet intact and bring it back to earth one thing to try is to distribute 5–10  $\mu\text{m}$  pieces in appropriate nutrient water baths and follow their chemical evolution. We can expect that new experimental techniques will have developed to the point at which this will be possible. In conclusion, it is fascinating to think that ongoing research may well reveal more information about the directed processes of chemical evolution and a greater insight into the mechanisms by which these life-forming processes reached the earth. And in any case we may have in our hands the interstellar dust out of which the solar system was born.

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