# Astrophysical and Astrochemical Insights into the Origin of Life

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**P. Ehrenfreund (1,2), W. Irvine(3), L. Becker (4), J. Blank (5), J. R. Brucato (6), L. Colangeli (6), S. Derenne (7), D. Despois (8), A. Dutrey (9), H. Fraaije (2), A. Lazcano (10), T. Owen (11), F. Robert (12), an International Space Science Institute ISSI-Team(13)**

**(1) Leiden Observatory, P O Box 9513, 2300 RA Leiden, THE NETHERLANDS**

**(2) Soft Matter / Astrobiology Laboratory, Leiden Institute of Chemistry, PO BOX 9502, 2300 RA Leiden, THE NETHERLANDS**

**(3) Astronomy Department, 619 Lederle Graduate Research Center, University of Massachusetts, Amherst, MA 01003, USA**

**(4) University of California, Institute of Crustal Studies, Dept. of Geological Sciences, 1140 Girvetz Hall, Santa Barbara, CA 93106, USA**

**(5) Lawrence Livermore National Laboratory, H-Division/Shock Physics Group, P.O. Box 808, L-415 Livermore, CA 94551, USA**

**(6) INAF-Osservatorio Astronomico di Capodimonte via Moiariello 16, I-80131, Napoli, ITALY**

**(7) Laboratoire de Chimie Bioorganique et Organique Physique, UMR CNRS 7573, Ecole Nationale Superieure de Chimie de Paris, 11, rue Pierre et Marie Curie,
75231 Paris Cedex 05, FRANCE**

**(8) Observatoire Aquitain des Sciences de l'Univers (OASO), B.P. 89, F-33270 Floirac, FRANCE**

**(9) Laboratoire d'Astrophysique de l'Observatoire de Grenoble (LAOG), BP 53, F-38041 Grenoble Cedex 9, FRANCE**

**(10) Facultad de Ciencias, UNAM, Apdo. Postal 70-407, Cd. Universitaria, 04510 Mexico D.F., MEXICO**

**(11) Institute for Astronomy, 2680 Woodlawn Ave, Honolulu HI 96822, USA**

**(12) Laboratoire de Mineralogie, Museum National d'Histoire Naturelle, 61 rue Buffon 75005 Paris, FRANCE**

**(13) ISSI Team: "Prebiotic matter in space" (all the authors belong to that team)**

## Abstract

Stellar nucleosynthesis of heavy elements such as carbon allowed the formation of organic molecules in space, which appear to be widespread in our Galaxy. The physical and chemical conditions - including density, temperature, ultraviolet radiation and energetic particles - determine reaction pathways and the complexity of organic molecules in different space environments. Dense interstellar clouds are the birth sites of stars of all masses and their planetary systems. During the protostellar collapse, interstellar organic molecules in gaseous and solid phases are integrated into protostellar disks from which planets and smaller solar system bodies form. After the formation of the planets, 4.6 Ga ago, our solar system, including Earth, was subjected to frequent impacts for several hundred million years. Life on Earth may have emerged during or shortly after this heavy bombardment phase, perhaps as early as 3.90-3.85 Ga ago, but the exact timing remains uncertain. A prebiotic reducing atmosphere, if present, predicts that building blocks of biopolymers - such as amino acids, sugars, purines and pyrimidines – would be formed in abundance. Recent modelling of the Earth early atmosphere suggests, in contrast, more neutral conditions (e.g. $H_2O$, $N_2$, $CO_2$), thus, precluding the formation of significant concentrations of prebiotic organic compounds. Moreover, even if the Earth's atmosphere were reducing, the presence of UV (ultraviolet) photons would readily destroy organic compounds unless they were quickly sequestered away in rocks or in the prebiotic ocean. Other possible sources of organic compounds would be high temperature vent chemistry, although the stability of such compounds (bases, amino acids) in these environments remains problematic. Finally, organic compounds may have been delivered to the Earth by asteroids, comets and smaller fragments, such as meteorites and interplanetary dust particles (IDPs).

It is likely that a combination of these sources contributed to the building blocks of life on the early Earth. It may even have taken several starts before life surpassed the less than ideal conditions at the surface. What is certain is that once life emerged, it learned to adapt quickly taking advantage of every available refuge and energy source (e.g. photosynthesis and chemosynthesis), an attribute that eventually led to complex metabolic life and even our own existence.

Current experimental research investigating the origin of life is focused on the spontaneous formation of stable polymers out of monomers. However, understanding the spontaneous formation of structure is not enough to understand the formation of life. The introduction and evolution of information and complexity is essential to our definition of life. The formation of complexity and the means to distribute and store information are currently being investigated in a number of theoretical frameworks, such as evolving algorithms, chaos theory, and modern evolution theory.

In this article we review the physical and chemical processes that form and process organic matter in space. In particular we discuss the chemical pathways of organic matter in the interstellar medium, its evolution in protoplanetary disks and its integration into solar system material. Furthermore, we investigate the role of impacts and the delivery of organic matter to the prebiotic Earth. Processes that may have assembled prebiotic molecules to produce the first genetic material and ideas about the formation of complexity in chemical networks are also discussed.

# 1. Introduction

The story of astrobiology and life in the Universe begins with the synthesis of the elements that play key roles in life as we know it: hydrogen, carbon, oxygen, nitrogen, sulfur and phosphorus. Other elements are required by specific terrestrial life forms, or perhaps by the Earth's biosphere as an interacting whole, but might be replaceable by different chemical elements under somewhat different initial conditions.

Hydrogen is effectively primordial, having been formed from the soup of quarks that filled the Universe in the earliest stages of the Big Bang. All the other chemical elements that are featured in terrestrial biochemistry were formed by nucleosynthesis during the course of stellar evolution. Carbon, the basis of organic chemistry and the lightest of the "biogenic" elements, is produced by the so-called triple-$\alpha$ process ($3 \times {}^{4}\mathrm{He} \rightarrow {}^{12}\mathrm{C}$) in the cores of stars more massive than half a solar mass. Such stars form carbon after they have fused a significant fraction of their core hydrogen into helium and evolved off the Main Sequence (see review by Trimble 1997, and Figure 1). In the same cores, some carbon is further processed to the principal isotope of oxygen by ${}^{12}\mathrm{C} + {}^{4}\mathrm{He} \rightarrow {}^{16}\mathrm{O}$. The fraction of the C and O produced that is delivered to the interstellar medium, from where it can be incorporated into a new generation of stars (such as the Sun), depends on the mass of the synthesizing star and its resulting final fate (e.g., Matteucci 1991).

In the cores of evolving, massive ($M > 10$ solar masses) stars, heavy element nuclear "burning" produces the most abundant isotopes of sulfur (${}^{32}\mathrm{S}$) and phosphorus (${}^{31}\mathrm{P}$). Obviously ${}^{32}\mathrm{S}$ is built from eight ${}^{4}\mathrm{He}$ units, although the detailed process is more complicated than simple successive addition of $\alpha$ particles to C or O, because there are *bottle necks* along the route (Trimble 1997). A primary source of phosphorus in these stars is the reaction ${}^{16}\mathrm{O} + {}^{16}\mathrm{O} \rightarrow {}^{31}\mathrm{P} + {}^{1}\mathrm{H}$ (e.g. Hansen & Kawaler 1994).

In contrast to the "primary" production of C and O, nitrogen is a "secondary" product, in the sense that its synthesis requires the presence of pre-existing C or O from earlier generations of stars. In particular, nitrogen is a by-product of hydrogen fusion to helium through the CN or the CNO cycles in the cores of massive stars and the shells of evolved lower mass stars, where C or O act as catalyst for the hydrogen "burning" (e.g. Shu 1982).

The step from atomic nuclei to molecules begins with the expulsion of nucleosynthetic products into the interstellar medium (ISM) by stellar winds, planetary nebula ejection, and supernova explosions. These events include the local formation of gas phase molecules and dust grains, the latter being predominantly organic or silicate when the progenitor star is either carbon- or oxygen-rich. The molecules, which can include a rich array of organic species (e.g., Guelin *et al* 2000; Cernicharo 2000), are probably mostly dissociated by UV radiation before reaching the shelter of a dense interstellar cloud. In contrast, both silicate and organic dust grains can survive for extended periods of time in the diffuse ISM and may then be incorporated into dense clouds, where they may acquire icy mantles, be processed in various ways, and serve as sites for molecular synthesis.

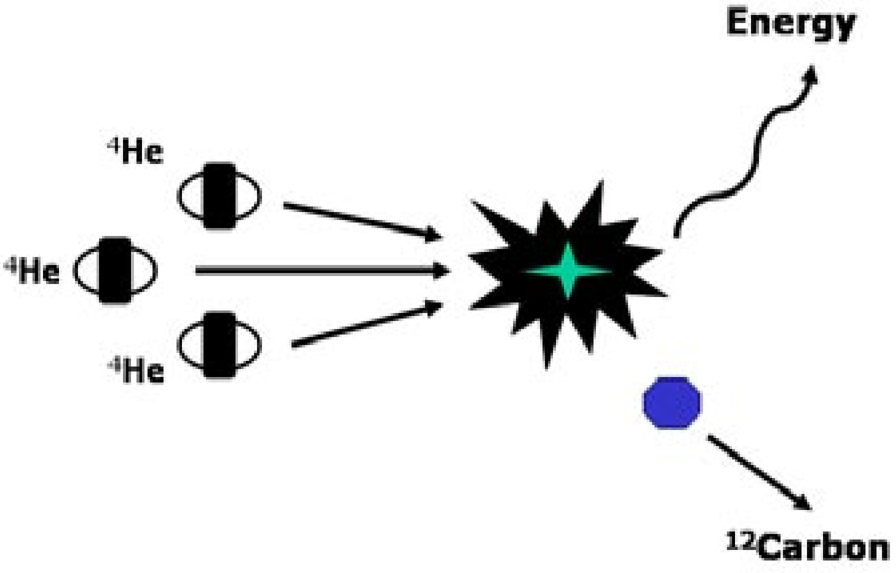


**Figure 1**
Carbon, the 4th most abundant molecule in the Universe and the basis for organic chemistry, is produced via nuclear fusion by the triple-α process (3 x $^4He \rightarrow {}^{12}C$) in the cores of stars via nuclear fusion.

Interstellar clouds are the birthsites of stars of all masses (Mannings *et al* 2000). The gravitational collapse of interstellar dust and gas triggered by cloud instabilities leads to the formation of stars, which may be accompanied by planetary systems. Interstellar species thus provide the raw material from which planets and small solar system bodies formed. The physical and chemical processes that have modified the original material and shaped the structure of our planetary system are partly unknown. However, our knowledge of the composition of interstellar clouds and star-forming processes has strongly increased in recent years due to more sensitive instruments installed on ground based or space borne observatories, as has our understanding of solar system bodies from the successful operation of interplanetary probes. Interplanetary dust and remnant planetesimals delivered material to the early planets and still do in the form of interplanetary dust and meteorites, which represent fragments of small solar system bodies. Part of this material contains organic matter, which may have been crucial for chemical evolution that ultimately led to the origin of life. Spectroscopic analysis of cosmic materials - be they gaseous or solid - remains a vital tool for monitoring their evolution in space and tracing their path from star-forming regions to planetesimals and solar system bodies.

On the other hand it may very well be that life emerged on the early Earth simply due to a combination of the right local conditions, without any "help" from space. The steps from the presence of organic species, such as formaldehyde ($H_2CO$), amino acids or polycyclic aromatic hydrocarbons (PAHs) to a self-replicating protected cell structure are immense and far beyond the field of astrophysics.

This review provides insights into the evolution and distribution of organic material in space, the exogenous delivery of organics to Earth, as well as their possible relevance within the basic hypotheses about the emergence of life on Earth. We have compiled an inventory of organics in interstellar clouds, comets and meteorites, as well as the limited data available for protostellar disks. We also discuss laboratory experiments to aid the identification of compounds in different space environments including isotopic data from the interstellar medium and throughout the solar system. We investigate impact properties and delivery processes as well as the necessary conditions for the origin of life. We conclude with a discussion of future perspectives in astronomy and biochemistry that might help to reveal some of the steps that led to life on Earth and possibly other planets as well.

## 2. The chemistry of dense interstellar clouds

The ISM in our Milky Way and in other galaxies includes regions of differing density, temperature, and radiation intensity. The mass of the interstellar medium comprises a few percent of the baryonic mass of the Galaxy. For the last two decades, debate has continued about the volume fraction of the ISM occupied by

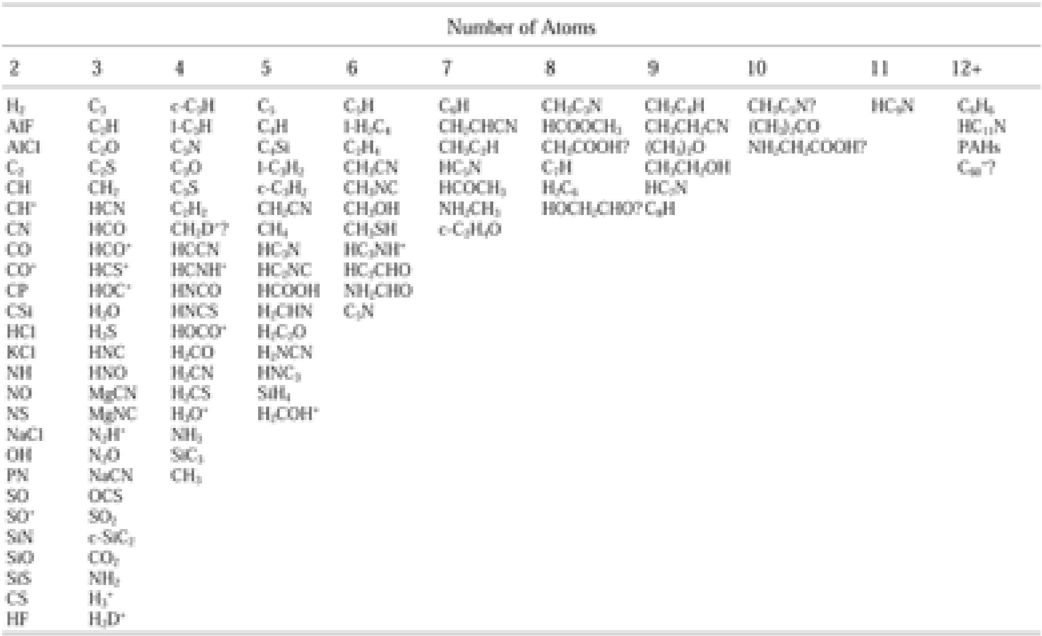
(i) hot (~$10^6$ K), very low density cavities created by supernova remnants
(ii) "warm" (~$10^4$ K) "intercloud" gas that is either mostly ionized or mostly neutral
(iii) interstellar "clouds", identified by specific velocity components observed in absorption or emission (e.g. Shull 1987).

The clouds, which are thought to occupy only a minor volume fraction of the overall ISM, are in turn divisible into the so-called diffuse clouds which are characterized by visual extinctions Av ~ 1 mag, densities of the order of 100 atoms $cm^{-3}$, and temperatures ~ 100 K; dense clouds with Av > 5 mag, densities > $10^3$ $cm^{-3}$, and temperatures as low as 10 K; and the translucent clouds that are intermediate in extinction, density and temperature (e.g. van Dishoeck 1998).

For our purposes the dense clouds are the most interesting, since it is here that a wide variety of organic molecules have been identified. These regions, also referred to as "molecular clouds", may again be subdivided into (i) cold, quiescent clouds; (ii) clouds where low mass stars form and (iii) cores where high-mass star formation is underway (the so-called "hot cores"). In these dense clouds molecular synthesis takes place both in the gas phase and on (or in) the dust grains (cf. reviews by Langer *et al* 2000; Ehrenfreund & Charnley 2000; Herbst 2000; Millar 1997; Hartquist & Williams 1995). The basic, and by far the most abundant constituent, molecular hydrogen ($H_2$), is formed on grain surfaces. Gas phase species that have been identified in molecular clouds and in envelopes expelled by evolved stars are listed in Table 1. The majority of these species were detected at short radio wavelengths, where they have pure rotational transitions. The heterodyne techniques employed allow very high frequency resolution, minimizing the possibility of accidental line coincidences, although the richness of the spectra can still lead to confusion and misidentifications (cf. the careful approach of Dickens *et al* 1997, with the problems identified by Ellder *et al* 1980). The non-polar molecules, such as acetylene ($C_2H_2$), were observed via ro-vibrational transitions in the infrared, typically in absorption against bright background sources such as luminous young stars embedded in the clouds.

Chemical processes in the gas phase in cold, quiescent clouds are predominantly ion-molecule reactions, powered primarily by cosmic ray ionization of $H_2$. Calculated abundances of observed molecules match the observations rather well (e.g. Pratap *et al* 1997; Dickens *et al* 2000), although the agreement depends on a limited range of parameters, such as the age of the cloud and the relative abundance of C and O in the gas. Note that physical parameters such as temperature and density may be determined directly from the molecular line emission. By far the most abundant molecule in these clouds is $H_2$, and the most abundant carbon-containing species is CO, with $CO/H_2$ of order $10^{-4}$.

Less abundant by another factor of $10^{-3}$ to $10^{-4}$ are molecules such as formaldehyde ($H_2CO$), hydrogen cyanide (HCN), ammonia ($NH_3$), and methylacetylene ($CH_3CCH$). The chemistry of the cold "molecular clouds" is characterized by the presence of species normally considered to be highly reactive, including radicals, ions, and energetic isomers, as well as by very unsaturated species such as cyanopolyynes and related linear carbon chains (see Table 1).



| Number of Atoms | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12+ |
| $H_2$ | $C_3$ | c-$C_3H$ | $C_5$ | $C_5H$ | $C_6H$ | $CH_3C_3N$ | $CH_3C_4H$ | $CH_3C_5N$? | $HC_9N$ | $C_6H_6$ |
| AlF | $C_2H$ | l-$C_3H$ | $C_4H$ | l-$H_2C_4$ | $CH_2CHCN$ | $HCOOCH_3$ | $CH_3CH_2CN$ | $(CH_3)_2CO$ | | $HC_{11}N$ |
| AlCl | $C_2O$ | $C_3N$ | $C_4Si$ | $C_2H_4$ | $CH_3C_2H$ | $CH_3COOH$? | $(CH_3)_2O$ | $NH_2CH_2COOH$? | | PAHs |
| $C_2$ | $C_2S$ | $C_3O$ | l-$C_3H_2$ | $CH_3CN$ | $HC_5N$ | $C_7H$ | $CH_3CH_2OH$ | | | $C_{60}^+$? |
| CH | $CH_2$ | $C_3S$ | c-$C_3H_2$ | $CH_3NC$ | $HCOCH_3$ | $H_2C_6$ | $HC_7N$ | | | |
| $CH^+$ | HCN | $C_2H_2$ | $CH_2CN$ | $CH_3OH$ | $NH_2CH_3$ | $HOCH_2CHO$? | $C_8H$ | | | |
| CN | HCO | $CH_2D^+$? | $CH_4$ | $CH_3SH$ | c-$C_2H_4O$ | | | | | |
| CO | $HCO^+$ | HCCN | $HC_3N$ | $HC_3NH^+$ | | | | | | |
| $CO^+$ | $HCS^+$ | $HCNH^+$ | $HC_2NC$ | $HC_2CHO$ | | | | | | |
| CP | $HOC^+$ | HNCO | HCOOH | $NH_2CHO$ | | | | | | |
| CSi | $H_2O$ | HNCS | $H_2CHN$ | $C_5N$ | | | | | | |
| HCl | $H_2S$ | $HOCO^+$ | $H_2C_2O$ | | | | | | | |
| KCl | HNC | $H_2CO$ | $H_2NCN$ | | | | | | | |
| NH | HNO | $H_2CN$ | $HNC_3$ | | | | | | | |
| NO | MgCN | $H_2CS$ | $SiH_4$ | | | | | | | |
| NS | MgNC | $H_3O^+$ | $H_2COH^+$ | | | | | | | |
| NaCl | $N_2H^+$ | $NH_3$ | | | | | | | | |
| OH | $N_2O$ | $SiC_3$ | | | | | | | | |
| PN | NaCN | $CH_3$ | | | | | | | | |
| SO | OCS | | | | | | | | | |
| $SO^+$ | $SO_2$ | | | | | | | | | |
| SiN | c-$SiC_2$ | | | | | | | | | |
| SiO | $CO_2$ | | | | | | | | | |
| SiS | $NH_2$ | | | | | | | | | |
| CS | $H_3^+$ | | | | | | | | | |
| HF | $H_2D^+$ | | | | | | | | | |

**Table 1**
Interstellar and circumstellar molecules as compiled by A. Wootten (http://www.cv.nrao.edu/~awootten/allmols.html). Recent detections include benzene by Cernicharo *et al* (2001). Larger molecules have not yet been unambigously identified, but there is no doubt that they are present.

The presence of these de-hydrogenated species in an overall very reducing environment is a result of the kinetics of low temperature, low density reactions in the gas phase; in particular, reactions that add carbon to molecules tend to result in the loss of hydrogen, and many hydrocarbon ions have barriers to re-hydrogenation by reaction with $H_2$ (e.g. Herbst *et al* 1983). The large values for the hydrogen isocyanide/cyanide (HNC/HCN) abundance ratio have also been considered to be a classic indicator of ion-molecule chemistry, making the detection of HNC in comets of special interest (e.g. Irvine *et al* 1998a).

As cold clouds evolve, and particularly as cores collapse as part of star formation, molecules freeze out onto the grains, forming icy mantles over the underlying silicates and organics (Ehrenfreund & Schutte 2000). An active chemistry takes place on grain surfaces and can lead to the formation of complex interstellar molecules. At 10 K only H, D, C, O and N atoms have sufficient mobility to interact on the surfaces of grains. The formation of the simplest mantle molecules (water ($H_2O$), ammonia ($NH_3$), methane ($CH_4$), etc.) can be explained by simple exothermic hydrogen addition reactions.

However, the presence of more complex molecules (e.g. methanol, $CH_3OH$) and various organics requires reaction processes that are acting on and in the icy mantles (Brown & Charnley 1990). Water ice is the most abundant ice component formed in icy grain mantles and abundances of other species are therefore scaled relative to water ice. Highly volatile species such as pure CO, $O_2$ and $N_2$ sublimate around or below 20 K. This implies that successive layers of ice are formed with different ice compositions according to the prevailing temperatures and gas pressures (or absolute densities) in protostellar regions. Hydrogen-rich ices (polar ices), dominated by $H_2O$ ice, are formed when H is abundant in the interstellar gas. They contain besides water ice: CO, $CO_2$, $CH_4$, $NH_3$, $CH_3OH$, and possibly traces of formic acid (HCOOH) and formaldehyde ($H_2CO$). Such polar ices generally evaporate around 100 K under astrophysical conditions and can therefore survive in higher temperature regions closer to the star (Tielens & Whittet 1997). Trace species such as carbonyl sulfide (OCS), formaldehyde ($H_2CO$), formic acid (HCOOH), methane ($CH_4$), and isocyanate ($OCN^-$) have been observed with the Infrared Space Observatory (ISO) near some protostars and are characterized by abundances between less than a percent to a few percent relative to water ice (Ehrenfreund & Charnley 2000, Gibb *et al* 2000a, Keane *et al* 2001). Apolar or hydrogen-poor ices are formed far away from the proto-star and are composed of molecules with high volatility (evaporation temperatures of < 20 K) such as CO, $O_2$ and $N_2$ (Ehrenfreund *et al* 1997).

Currently the largest molecule observed on interstellar grain mantles is methanol ($CH_3OH$). Methanol, together with ammonia ($NH_3$), is a key molecule in reaction pathways leading to further complexity. The abundance of both molecules is strongly varying and/or debated (Dartois *et al* 1999, Lacy *et al* 1998, Dartois & d'Hendecourt 2001, Gibb *et al* 2001). Carbonyl sulfide (OCS) is currently the only sulphur-containing species identified in interstellar ices, and has an abundance of 0.2 % relative to water ice (Palumbo *et al* 1995, 1997, d'Hendecourt *et al* 1996). Among the most important species, whose presence and abundances are difficult to determine, are the infrared inactive molecules $H_2$, $O_2$ and $N_2$. It has been shown that the infrared transitions of those molecules become weakly infrared active in the solid phase (Ehrenfreund *et al* 1992a, Sandford & Allamandola 1993). None of those molecules has up to now been detected in interstellar ices, but upper limits for $O_2$ and $N_2$ (transitions at 6.45 and 4.28 μm, respectively) have been recently reported by Vandenbussche *et al* (1999) and Sandford *et al* (2001).

With the help of recent ISO observations and ground-based data it is clear that the observations sample the spectral signature of many different grain populations in the line of sight through a molecular cloud. Those grain populations are located within regions of different temperature and density conditions. Grain chemistry may become even more complex in high-energy environments. We observe a dynamical system within which the physical conditions are varying and therefore the chemical composition is altered from one region to another.

The energy released in processes related to star formation can cause icy grain mantles to sublimate, releasing to the gas phase both the unprocessed species originally formed in the cold gas, and those molecules formed on the grains. The formation of massive stars produces the largest energy input to the surrounding cloud, and the resulting "hot cores" are the richest sources of complex (by astronomical standards) organic molecules in the ISM.

It is here that reactions of sublimated species with pre-existing gas phase molecules are thought to give rise to molecules such as dimethylether ($(CH_3)_2O$) and methyl formate ($HCOOCH_3$), and potentially to heavier "biogenic" species such as (not yet confirmed) glycine (Charnley *et al* 2001).

The heavier observed species seem to often be confined to regions of small angular size in the hot cores, and abundances are consequently difficult to determine with the limited angular resolution currently available to radio astronomers (Snyder 1997). However, estimates may be made by applying "rotation diagrams" to observations of multiple transitions that cover a range of energies above the ground state (e.g. Nummelin *et al* 2000). The abundances in these regions for interesting organic molecules can be much higher than the abundances found in cold clouds, e.g. (by number relative to $H_2$) as high as $10^{-5}$ for methanol ($CH_3OH$) and $> 10^{-8} - 10^{-7}$ for propanenitrile ($CH_3CH_2CN$) and methyl formate ($HCOOCH_3$) (Gibb *et al* 2000b), see Figure 2.

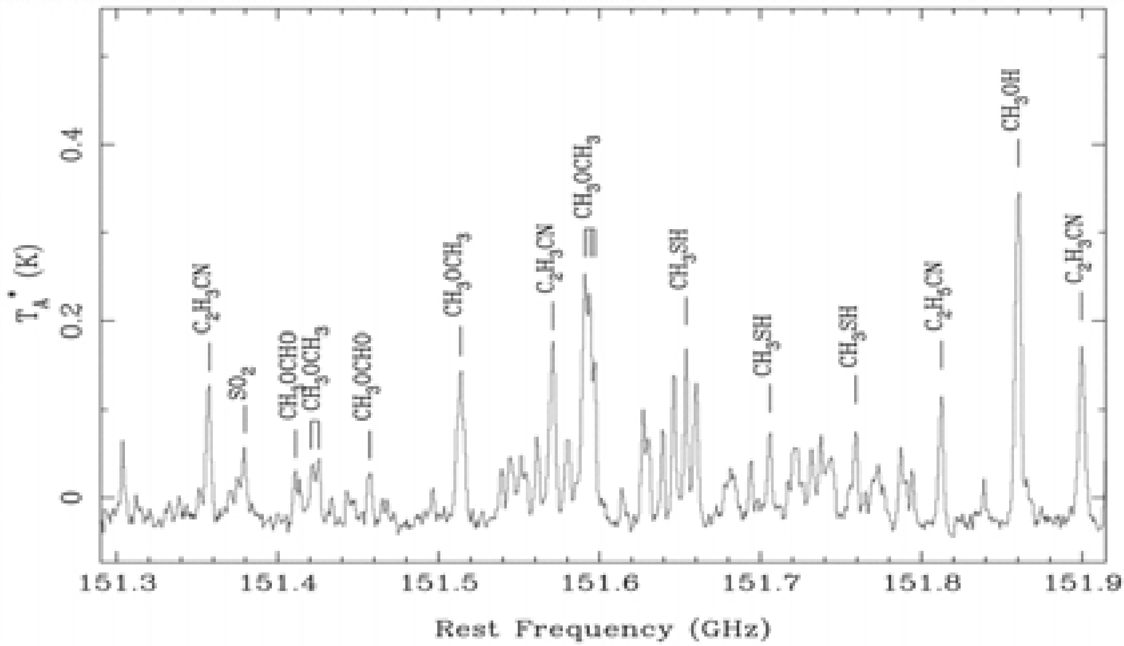


**Figure 2**
Observations of organic molecules toward the hot, molecular cloud core G327 around 151.6 GHz, with suggested line identifications marked. The majority of the emission lines are from organic species such as $CH_3OH$, $CH_3OCHO$, $C_2H_3CN$, $C_2H_5CN$, and $CH_3SH$. Many of the displayed lines are unidentified to date (taken from Gibb *et al* 2000b). Intensity is given in the radio astronomy units of antenna temperature ($T_A$*, in Kelvin).

A key characteristic of the chemistry in quiescent clouds, which is largely preserved in observed hot cores, is a very large isotopic fractionation, particularly for D/H. The kinetics in cold clouds that concentrates deuterium in molecules other than HD is well understood (e.g. van Dishoeck 1998). Enhancements relative to the cosmic D/H abundance ratio ($\sim 2 \times 10^{-5}$) by factors up to $10^4$ for some species (such as cyclopropenylidene, $C_3H_2$) are observed (Irvine & Knacke 1989).

Doubly deuterated species, specifically doubly deuterated formaldehyde ($D_2CO$) and doubly deuterated ammonia ($NHD_2$) and even triply deuterated ammonia ($ND_3$), have been detected (e.g. Turner 1990, Roueff *et al* 2000, Ceccarelli *et al* 2002, Lis *et al* 2002).

The preservation of high isotopic fractionation in the warmer hot core gas is more difficult to understand, but presumably reflects the state of the sublimated gas and the relatively short lifetime of the hot core evolutionary phase (Rodgers & Millar 1996; Roberts & Millar 2000). It is interesting to note that the chemistry of comets, at least as manifested by the composition of the coma, bears a number of close similarities to that of dense interstellar clouds (e.g. Irvine *et al* 2000; Irvine & Bergin 2000). This is the case for the relative abundance of some volatiles, the large isotopic fractionation for D/H, the presence of high energy species such as HNC, and possibly the non-equilibrium values of ortho/para ratios (see section 6).

## 3. Cosmic Dust

Cosmic matter condenses primarily in the extended atmospheres of evolved stars (e.g. red giants), that slowly loose mass, or in dramatic expulsion events from novae and supernovae. The elemental abundance available in the parent stars determines the chemical composition of formed solids: carbon species primarily condense around carbon-rich stars, while silicates dominate in oxygen-rich stellar atmospheres. Here, oxygen, in excess to that locked in CO bearing molecules, forms Si-O networks involving cations, such as Mg and Fe. Once injected into the interstellar medium, materials enter a cycle between diffuse and dense clouds, where various energetic processes contribute to modify the original nature of compounds and new species may condense, despite the low-density conditions. The complex evolution of chemistry, structure and physical properties (e.g., morphology) of materials is driven by interactions with gas and by processes such as heating, UV radiation, ion bombardment and shocks.

The diffuse interstellar medium is less dense (1-100 H atoms $cm^{-3}$) and characterized by higher temperatures (~ 100 K) than the outer regions of stellar envelopes. UV photons can penetrate easily and photochemistry drives the molecular chemistry in these regions. Spectroscopy from the UV to radio wavelengths reveals a diversity of gaseous and solid species. Only diatomic molecules such as CO, CH, CN, and $H_2$ have been securely identified in the diffuse clouds, although there is clearly complex organic matter present in particulate form ("dust" or "grains"), which on the low-mass side probably merges into the large organic molecules referred to generically as polycyclic aromatic hydrocarbons (PAHs) (Tielens *et al* 1999). The latter include both neutral and ionized species, of varying degrees of hydrogenation, depending on the radiation environment, and possibly heterogeneous atoms such as N and O. Simple polyatomic species such as hydrogen cyanide (HCN), formyl cation ($HCO^+$), CO and cyclopropenylidene ($C_3H_2$) appear in the translucent clouds (Turner 2000), which serve as excellent laboratories for testing models of gas phase chemistry in the ISM.

The cosmic carbon abundance is an important criterion when considering the inventory of organics in the Universe. Measurements of solar carbon values give 355 ± 50 carbon atoms per $10^6$ H atoms (ppm). Recent measurements using the Goddard High Resolution Spectrograph (GHRS) on the Hubble Space Telescope indicate in the local interstellar medium carbon abundances that are only two-thirds of the solar values (Cardelli *et al* 1996). Snow & Witt (1995) constrain the total carbon abundance to 225 ± 50 ppm with a mean gas phase abundance of ~140 ± 20 ppm. Approximately 20 % of this cosmic carbon is incorporated in gaseous CO (the most abundant molecule in space after $H_2$) and a few % in ices prevalent in dense clouds (see section 1). It is unclear where the remaining cosmic carbon is hidden. Astronomical observations suggest that a dominant fraction might be present in large carbonaceous species, namely up to 15 % in PAHs and up to 50 % in the form of macromolecular carbon in grains, such as amorphous carbon and complex kerogen-type material. Other organic compounds (in minor abundances) observed or suspected in diffuse clouds are carbon-chains, diamonds and fullerenes (Ehrenfreund & Charnley 2000).

## 3.1 Tracing cosmic materials: Astronomical observations and related laboratory studies

Ground-based and space-born (e.g., Hubble Space Telescope, HST, and Infrared Space Observatory, ISO) observations over the widest spectral range represent the primary source of information about the properties and evolution of materials in space. Identification of typical spectral signatures in the most relevant space environments (e.g., star formation regions, evolved stars, circumstellar and interstellar medium) tells us that carbon components and silicates are key components of cosmic dust.

It is then instructive to perform laboratory experiments aimed at producing "analogues" of these cosmic compounds. Several techniques are used to obtain materials whose chemical and physical properties can simulate species present in space. The study is focused on the analysis of the optical properties versus intrinsic (e.g. chemistry, structure, morphology) characteristics of samples. Different complementary analytical techniques are combined with the aim of investigating the products of synthesis. Another primary goal of laboratory studies is to simulate material processing active in space. The study of the reactivity of materials and of the efficiency of treatments provides quantitative information on how modifications, at the chemical and structural levels, occur both in organic and in refractory materials. This goal is, therefore, achieved by iterative sequences in which samples, produced by different techniques, are analysed both as produced and after processing.

According to indications coming from astronomical observations, materials of primary interest are:

1) carbon compounds, in different forms (pure or hydrogenated, crystalline or amorphous);
2) silicates (crystalline or amorphous) of two main classes
    - olivines $[(Mg_x,Fe_{1-x})_2SiO_4]$, where forsterite has $x = 1$ and fayalite $x = 0$,
    - pyroxenes $[(Mg_x,Fe_{1-x})SiO_3]$, where enstatite has $x = 1$ and ferrosilite $x = 0$.

Several production techniques are used in the laboratory to synthesise samples useful to simulate cosmic compounds. Arc discharge between carbon/graphite electrodes in an inert (Ar, He) or $H_2$ atmosphere (e.g. Colangeli *et al* 1995), resistive heating of graphite rods coupled with molecular beam extraction (e.g. Schnaiter *et al* 1996, 1998), IR laser pyrolysis of gas phase molecular species (e.g. Herlin *et al* 1998) and quenching of hydrocarbon plasmas in vacuum (e.g. Sakata *et al* 1984) are typical condensation techniques used for production of carbon-based material. High power laser bombardment of pure mineral targets in an $O_2$ atmosphere (e.g. Brucato *et al* 1999), as well as chemical reactions in gas phase (e.g. Nuth *et al* 2000a), can be applied to obtain amorphous silicon-based materials of the desired chemical composition. Crystalline grains can be obtained by grinding pure terrestrial minerals.

To test the sensitivity of laboratory analogues to cosmically relevant processes, several methods are used. When possible, laboratory experiments are performed by applying doses and rates comparable to those typical of different space environments.

The summary in Table 2 reports a synthesis of experiments performed so far and a comparison of doses/rates achieved in the laboratory and estimated in space.
All the examined mechanisms are expected to be effective in modifying most of the chemical and structural properties of materials.

**Table 2**
Relevant processes active on grains in space and doses/rates in space and in the laboratory (Colangeli *et al* 1999).

| **Process** | **Space** | **Laboratory (max.)** | **Units** |
|---|---|---|---|
| UV irradiation | $3 \times 10^{25}$ – diffuse ISM ($10^9$ yr)<br>$4 \times 10^{20}$ – dense ISM ($10^9$ yr) | $4 \times 10^{22}$ | eV cm$^{-2}$ |
| Ion bombardment | $3 \times 10^3$ – diffuse ISM ($10^9$ yr)<br>$3 \times 10^2$ – dense ISM ($10^9$ yr)<br>$1 \times 10^6$ – pre-comet<br>$6 \times 10^2$ – comet | 660 | eV mol$^{-1}$ |
| H atoms | $8 \times 10^{21}$ | $6.9 \times 10^{19}$ | cm$^{-2}$ |
| Thermal | 1000 – stellar outflows<br>100 – pre-solar nebula | 1300 | K |

The full characterisation of samples is obtained by a complement of techniques capable of demonstrating the relationship between the nature of materials and their optical characteristics. Morphology and structure (shape, size and crystalline degree) are characterised by scanning electron microscopy (SEM), while the elemental composition can be identified by energy dispersive X-ray (EDX) analysis. Further information on structure comes from X-ray diffraction and Raman spectroscopy. Spectroscopy is a diagnostic method to explore different properties of materials depending on the wavelength range used. Features in the UV (ultraviolet)-VIS (visible) and far-IR (infrared) ranges are generally associated with structural properties, while near-medium IR bands are diagnostic of molecular bond resonances. The detailed shapes and positions of bands are sensitive to morphology, chemical composition and crystalline degree. Moreover, different spectroscopic methods of analysis, such as extinction, absorption, scattering, reflectance and emission, allow us to examine different manifestations of the intrinsic natures of the considered samples.

## 3.2 Carbonaceous Dust

Carbonaceous dust in the interstellar medium may show considerable diversity and may include amorphous carbon (AC), hydrogenated amorphous carbon (HAC), coal, soot, quenched-carbonaceous condensates (QCC), diamonds, fullerenes and other compounds (e.g. Papoular *et al* 1996, Henning & Salama 1998, Ehrenfreund & Charnley 2000 and reference therein). Figure 3 displays a hypothetical model of the basic chemical structure of carbonaceous interstellar dust in the diffuse interstellar medium (modified from Pendleton & Allamandola 2002). Observations indicate that a major fraction of the cosmic carbon in space is present in such a form.

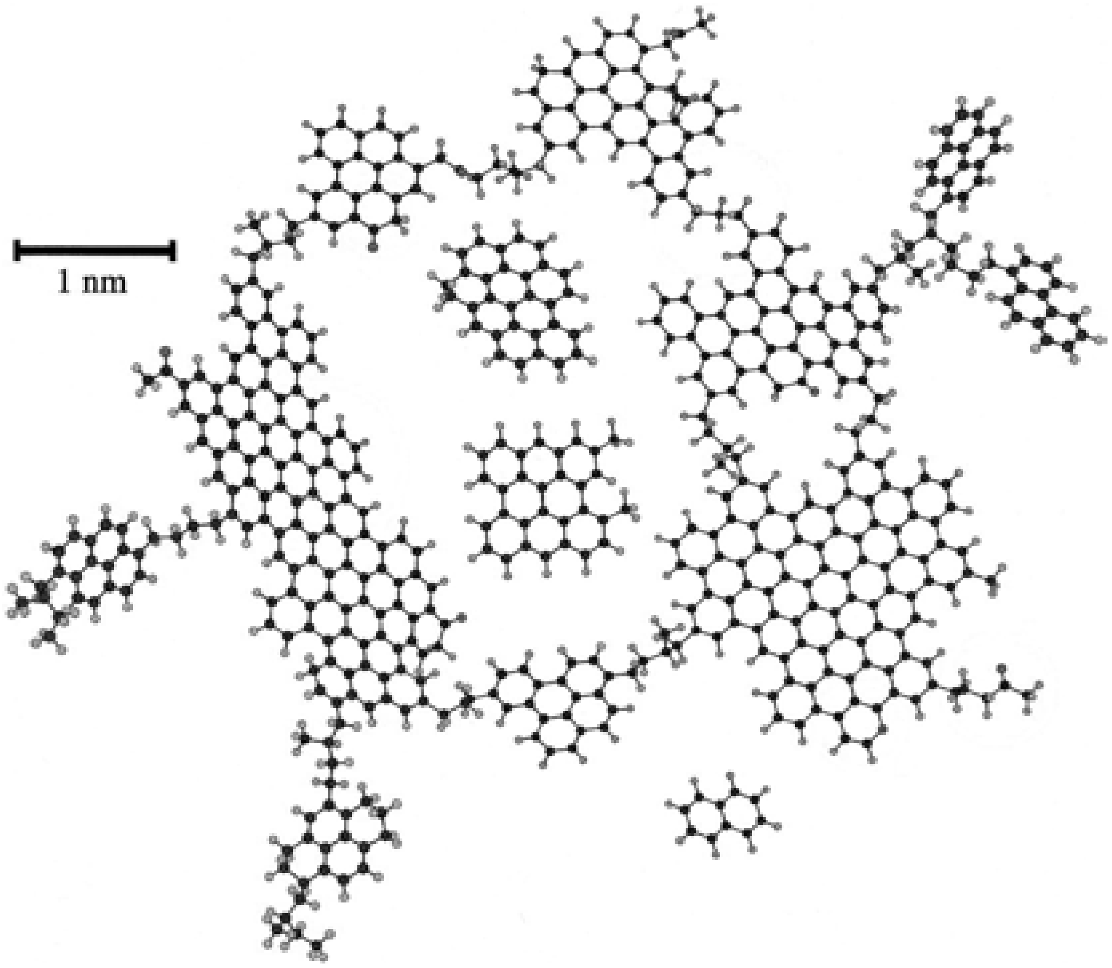


**Figure 3**
The hypothesized basic structural and molecular character of carbonaceous, interstellar dust in the diffuse interstellar medium. The structure is a kerogen-type aromatic network bridged by aliphatic chains, including side-groups and heteroatoms. The specific geometries of the aromatic plates and aliphatic components are inferred. A typical 0.1 μm carbonaceous dust grain contains ~ $10^4$ fragments (modified from Pendleton & Allamandola 2002).

One of the most relevant signatures of interstellar dust is detected by observing the "extinction" of starlight caused by ISM material towards different sources in our Galaxy. The so-called "ultraviolet extinction bump" at 217.5 nm (e.g. Fitzpatrick & Massa 1990) has an unambiguous attribution to carbon-bearing materials, but several candidate carriers (e.g., graphite, PAH's, amorphous carbon) fail to match the observational constraints and to account for the carbon budget, locked in solid form, available in space (Snow & Witt 1995, 1996).

Intense laboratory activity has focussed on the evolution of hydrogenated and hydrogen-free carbon materials subjected to different processes: thermal annealing (Mennella *et al* 1995), UV irradiation (Mennella *et al* 1996) and ion bombardment (Mennella *et al* 1997). These experiments have demonstrated that carbon-based grains are extremely sensitive to processing and the efficiency of mechanisms in modifying organic material in space has been measured. For an example, the processing of hydrogen-rich carbon dust by UV photons produces the release of hydrogen and the progressive formation of small aromatic units (1-2 nm in size) forming the inner grain network. The optical manifestation of such change is the evolution from a featureless UV spectrum towards the appearance of a well defined band around 220 nm, whose intensity grows as a function of applied UV photon doses (Menella *et al* 1998).

The direct application of such a result to the astronomical context allows the possibility of simulating the "UV extinction band" observed in the ISM with a combination of UV processed carbon grain populations (see Figure 4, Mennella *et al* 1998). The approach based on such laboratory results provides a successful fit to observations and gives, for the first time, the opportunity to interpret the UV spectral characteristics in terms of carbon grain structural changes, perfectly compatible with the conditions actually expected in space. Moreover, the approach seems viable also in terms of elemental budget requirements, as about 50 ppm of carbon (relative to hydrogen) are needed (in the worst case) to match observations. Laboratory experiments confirm that carbon grains (also in space) may occur in two main forms: aliphatic structures are dominant in the presence of hydrogen, while processes such as thermal, UV, electron and ion reactions remove hydrogen and favour the formation of aromatic domains inside the particles (Mennella *et al* 2001).

The signature of polycyclic aromatic hydrocarbons is observed through their vibrational frequencies in the infrared between 3-15 μm (Tielens *et al* 1999, Allamandola *et al* 1999). Two decades of research show strong evidence that PAHs are present in the interstellar gas in many galactic and extragalactic regions. Up to 15 % of the carbon might be hidden in such aromatic species in the gas (Dwek *et al* 1997). Free individual PAH molecules, PAH clusters and particles comprised of aromatic (PAH) subunits are believed to be responsible for the overall interstellar emission spectrum (Allamandola *et al* 1999). Figure 5 shows a comparison of an emission spectrum of a protoplanetary nebula and the Orion ionization ridge with different PAH mixtures. Nevertheless, it must be stated that no single PAH has yet been identified in the ISM.

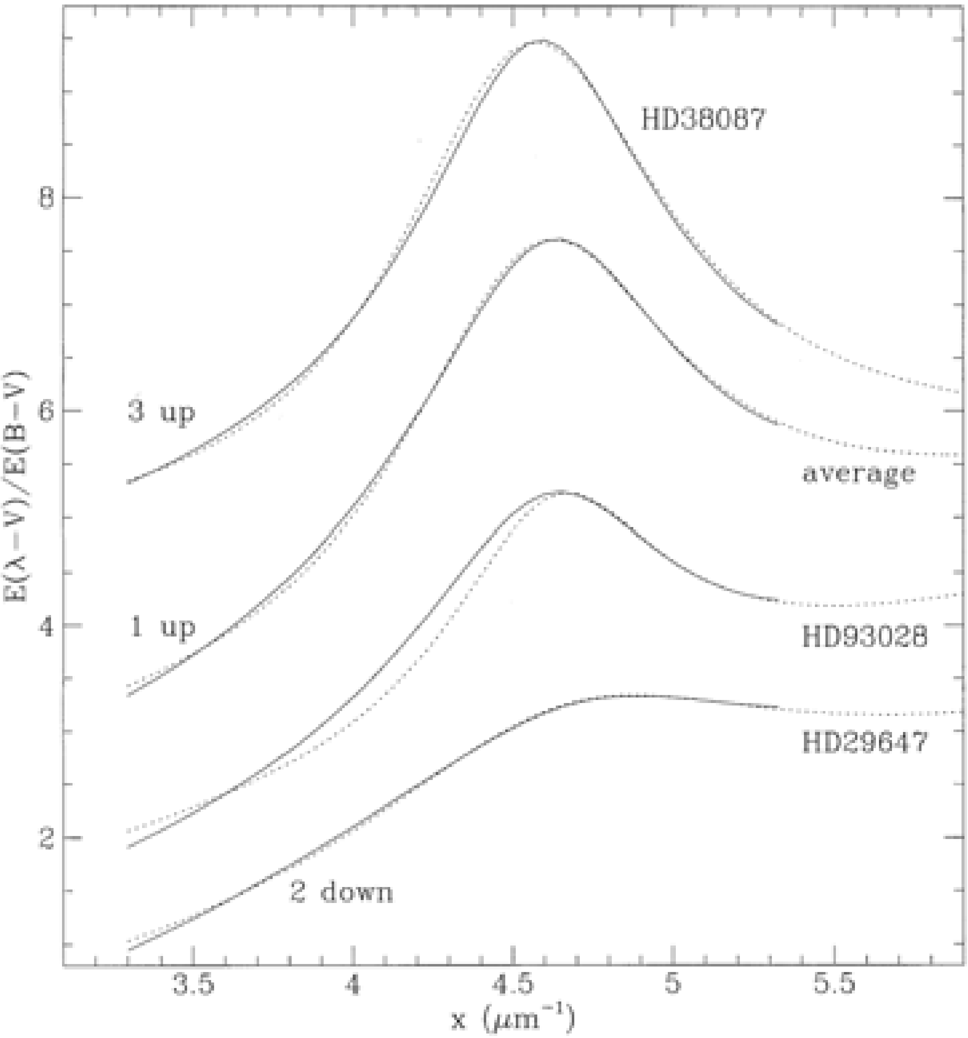


**Figure 4**
Fit to interstellar extinction curves from Cardelli & Savage (1988) and Fitzpatrick & Massa (1990) (dotted lines) by means of blends of the optical properties of UV processed carbon grains (solid lines). The average bump and the profiles with the extreme deviations observed in peak position and bandwidth of the interstellar extinction bump are considered (HD38087, minimum peak position; HD93028 minimum width; and HD29647, maximum peak position and width). Curves are shifted up and down by 1, 2, or 3 extinction scale units for the sake of clarity (Mennella *et al* 1998).

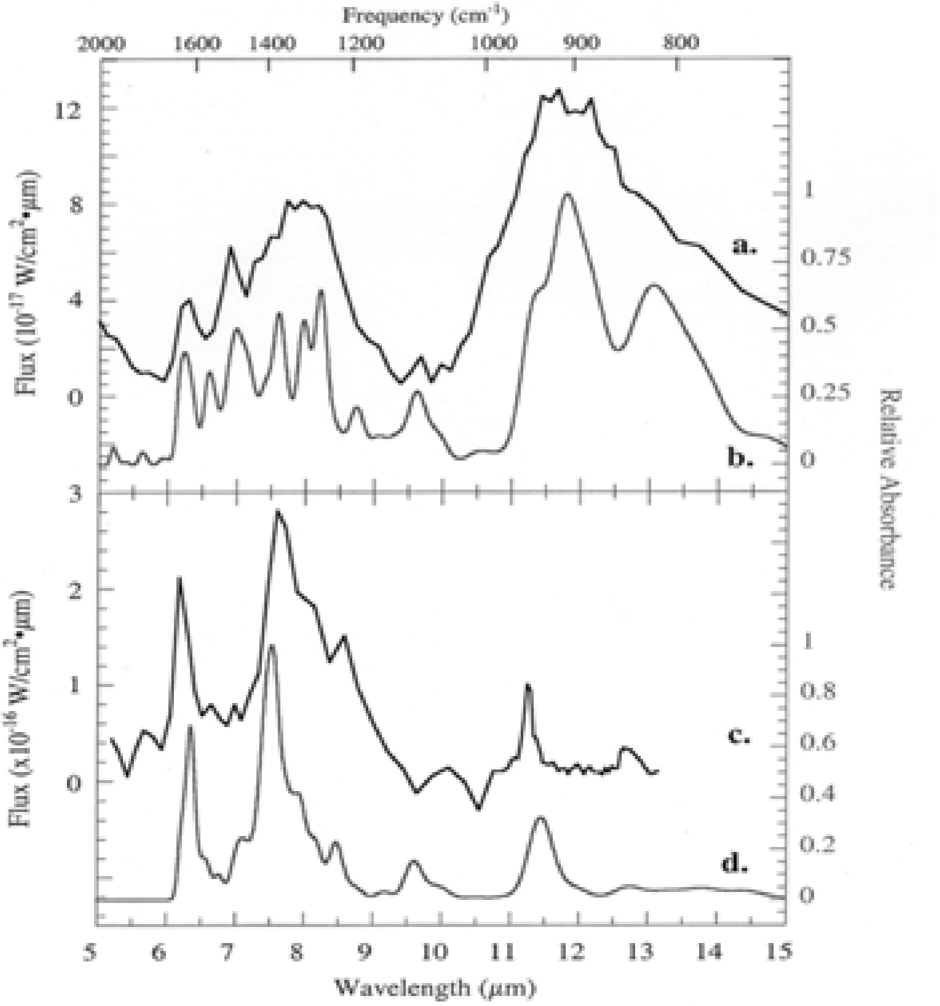


**Figure 5**
Comparison of (a) emission spectrum from the protoplanetary nebula IRAS 22272+5435 with (b) the absorption spectrum from a mixture of neutral and cationic PAHs. Comparison of (c) emission spectrum from the Orion ionization ridge (d) the absorption spectrum from a mixture of fully ionized PAHs (from Allamandola *et al* 1999).

### 3.3 Silicates

The scenario suggested by the spectral observations of silicates is complex. Silicates are predominantly present in an amorphous state, as indicated by the broad bands at 10 and 20 μm (due to Si-O stretching and O-Si-O bending modes) observed in the diffuse ISM (Whittet *et al* 1997) and in dense clouds (Whittet *et al* 1996). The presence of a smaller fraction of crystalline Mg-rich silicates is required to explain the sharp emission bands detected by ISO both in circumstellar environments (Malfait *et al* 1998, Molster *et al* 1999) and in comets (Crovisier *et al* 1997). Overall, spectral characteristics of silicates reflect modifications induced in space by the local environment.

Silicate particles condense in the circumstellar environment of oxygen-rich evolved stars; their structures (crystalline or amorphous) reflect condensation rates, which are composition dependent. Astronomical observations suggest that crystalline silicates are predominantly Mg-rich. In contrast, laboratory experiments show that Fe-rich olivine crystallizes faster. Given the similar cosmic abundances of Fe and Mg, the absence of Fe-bearing crystalline silicates in the astronomical context is puzzling. Condensation models for a gas with solar chemical composition show that almost all the Fe condenses as pure metal or alloy at temperatures above 600 K (Grossman 1972; Ebel 2000). Mg partitions to a much greater extent in the silicate rather than metal phase. In the ISM, the temperature is too low for crystallisation to occur, so that the segregation between Mg-rich silicates and pure metallic Fe should remain unchanged. During the formation of the solar system, coagulation processes in larger bodies and thermal diffusion are required to produce iron in silicates.

The production of silicates with various relative Mg and Fe concentrations has been the focus of numerous laboratory experiments. Studies on their thermal processing have shown that the synthetic materials are generally similar to interstellar particles, with significant differences when analysed in detail (e.g. Hallenbeck *et al* 1998; Brucato *et al* 1999; 2002; Fabian *et al* 2000; Koike *et al* 2001). The two most relevant results of these experiments are: a) the combination of time and temperature conditions required for the amorphous-to-crystalline transition occur seldom in space environments, and b) crystallisation of Fe-rich olivine proceeds faster than for Mg-rich olivine, see Figure 6.

Concerning the presence of signatures due to crystalline silicates in the spectra of comets, laboratory results pose a rough requirement of about $10^6$ yr at 1000 K for the transition to occur. These conditions could not be achieved in the outer regions of the early solar system. Mixing of materials from the inner solar system region with the outer, unevolved compounds might be invoked to justify the presence of crystalline silicates in comets, formed at the border of the protosolar nebula (Nuth *et al* 2000b, Bockelee-Morvan *et al* 2002). More recently, annealing of silicates by nebular shocks around 10 AU (Astronomical Unit) has been suggested to explain the presence of crystalline silicates in the solar system (Harker & Desch 2002). Alternatively, mechanisms other than pure thermal annealing, could be invoked to produce crystalline silicates in the presence of peculiar metastable conditions of the original materials (Molster *et al* 1999). In this field much work still remains to be done in the laboratory to adequately support the interpretation of observations.

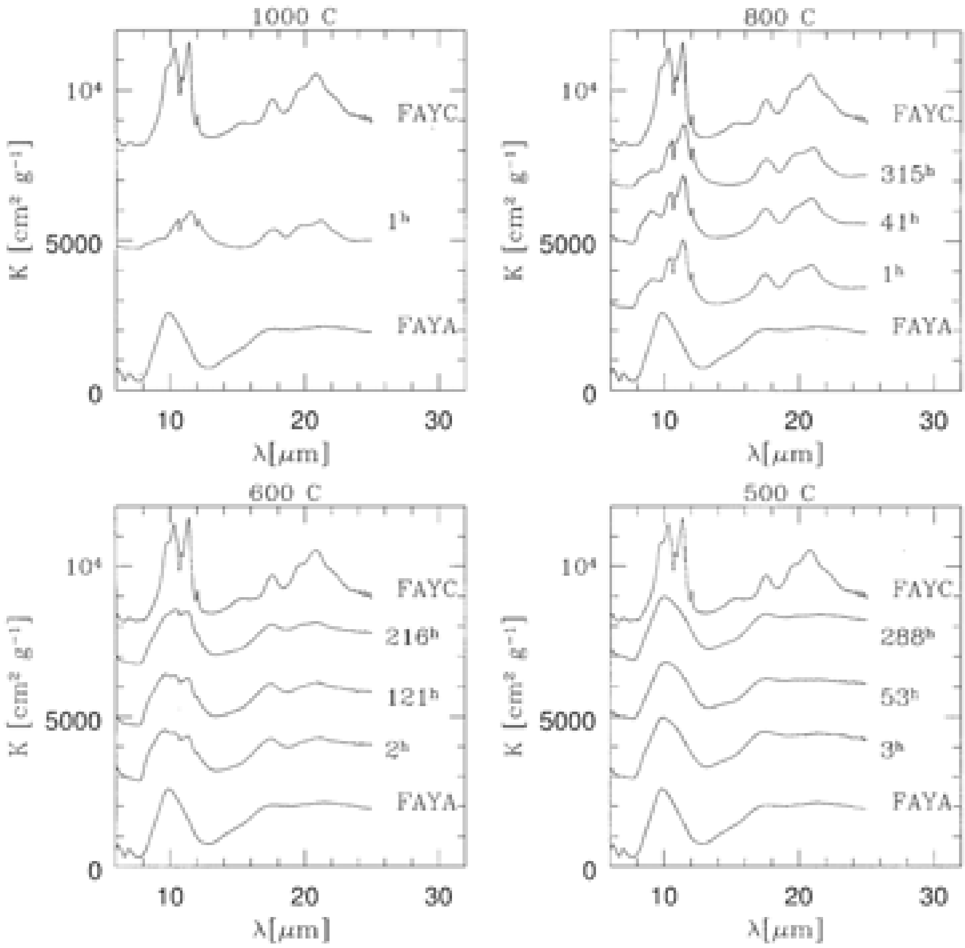


**Figure 6**
Mass absorption coefficients of natural Fe-rich olivine (FAYC – crystalline fayalite) and the same material after laser ablation (FAYA – amorphous fayalite). The other spectra refer to FAYA after thermal annealing at various temperatures (see top of each panel) and times (reported aside each plot). The spectra are shifted in ordinate for the sake of clarity (Brucato *et al*, 2002).

Finally we must hold open the possibility that the apparent absence of crystalline silicates in the diffuse interstellar medium might be caused by an unknown observational bias. This possibility emerges from observations of crystalline silicates in spectra of planetary nebulae, HII regions, and evolved stars (see Lequeux 2000 for review), and the absence of other indications of high temperature chemistry in cometary material.

# 4. Prebiotic molecules in protoplanetary disks

## 4.1 Overview of low-mass star formation

Low mass ($\leq$ 2 solar mass) stars have an important temporal advantage for the long-term development of life compared to the more massive ones which evolve much more rapidly and remain stable for less than 1 billion years (e.g. Shu 1982). Therefore, though high-mass stars are fundamental to the nucleosynthesis of heavy elements, we will concentrate in this section on the low-mass stars, which comprise the bulk of the stellar population.

A significant fraction of all stars in the Galaxy are members of binary or higher order multiple systems. One of the basic unsolved questions concerning the Sun is whether it formed as part of a cluster or in a more isolated event within a molecular cloud. Although some isotopic anomalies in meteorites may suggest formation in a cluster, which might have involved close physical and chemical interaction with supernova debris, is more likely, theories of solar type star formation have predominantly assumed the isolated scenario described below.

The formation of isolated stars occurs through the gravitational collapse of individual galactic molecular cloud cores within the dense clouds such as described in section 2. Following the onset of collapse, there are two main phases. In the protostellar phase, the central protostar, strongly embedded in its parent cloud, is accreting surrounding material while ejecting a powerful bipolar outflow which regulates the angular momentum resulting from the original contraction of the rotating parent cloud. After about one million years, the surrounding cloud has dissipated sufficiently and the young stellar object becomes visible; this is the T-Tauri phase (from the name of the first discovered object). The star has a mass very close to its final value, and is surrounded by a disk of dust and gas. T-Tauri stars are precursors of solar-type stars. After about 50 million years more, these objects finally begin their life as “adult" stars by reaching the Main Sequence of the temperature-luminosity diagram (starting nuclear burning). In the meantime, the surrounding protoplanetary disk has dissipated and planets may have formed in orbit around the star. The surrounding dust disk, called a ``debris disk", is now optically thin in the near-infrared (NIR). In such disks, the lifetime of dust particles is very short compared to the disk lifetime and the small grains originate from the collisions of larger bodies such as planetesimals (Lagrange *et al* 2000). The prototype of such an object is the famous β-Pic disk (Vidal-Madjar *et al* 1998).

Figure 7 (from van Dishoeck & Blake 1998) summarizes the important steps leading to planetary formation with emphasis given to the chemical evolution of the gas phase during the formation of a low-mass star. This figure describes the observed molecules depending on the physical conditions that evolve with time. For a more complete review of stellar formation, the reader can refer to Dutrey (1999).

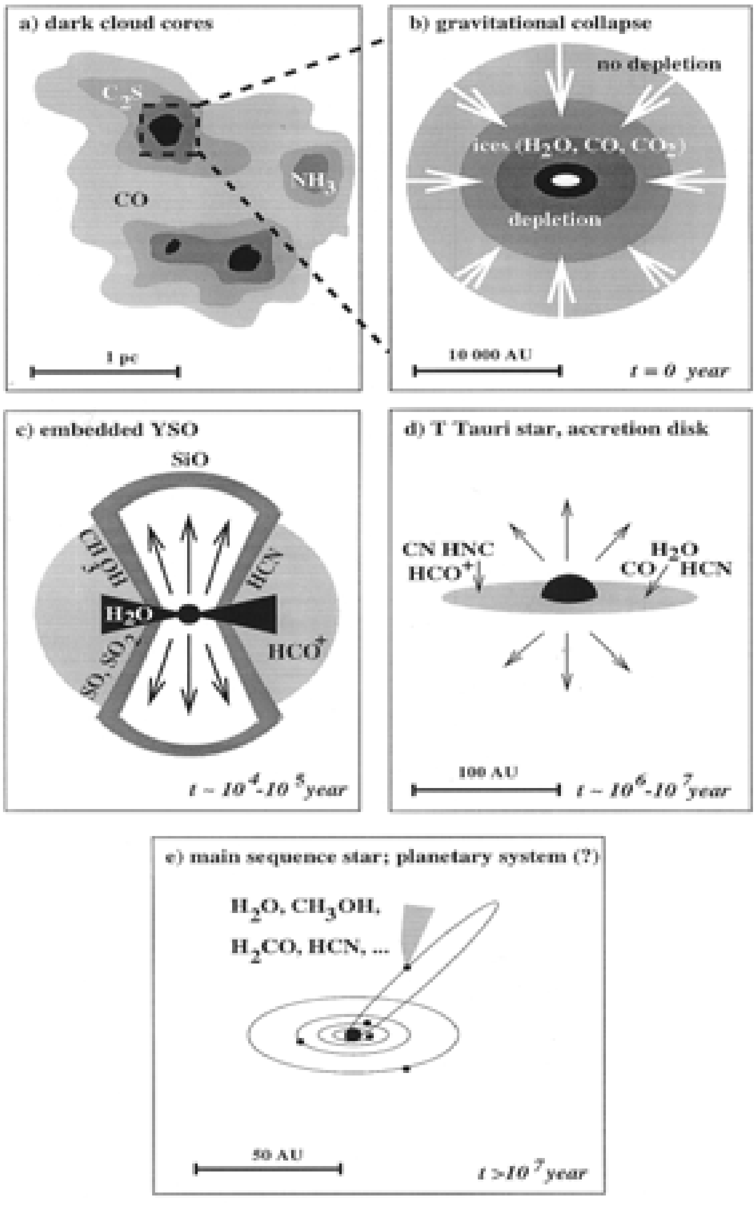


**Figure 7**
This figure summarizes the main stages in star formation, showing the molecular species observed in the gas phase of a low-mass star: a) the pre-stellar phase (also known as molecular cloud core); b) and c) the proto-stellar phases (YSO for Young Stellar Object); d) the T-Tauri phase (pre-Main Sequence star) where a large disk of gas and dust surrounds the young star; and e), the star has reached the Main-Sequence stage (starting its nuclear ``burning") and may be surrounded by a planetary system (taken from van Dishoeck & Blake 1998, adapted from M. Hogerhejde).

### 4.2 From protoplanetary disks to planets

Planetary formation is thought to begin during the protoplanetary disk phase. Many of these disks are massive enough (0.1- 0.001 solar mass) to provide the reservoir of matter necessary to form planets. Heated by the central T-Tauri star, these disks are cold, with typical temperatures within the range ~ 10-100 K, and they therefore radiate at millimeter and submillimeter wavelengths. Only the central 30 AU, additionally heated by viscous accretion ($\alpha$-disk model, e.g. D'Alessio *et al* 1999), are significantly hotter. Millimeter spectroscopic interferometric observations (CO rotational lines) confirm that these objects are in Keplerian rotation around their central star (Koerner *et al* 1993, Dutrey *et al* 1994). Both millimeter interferometric CO maps and optical images of dust disks scattering light from their central star revealed that many disks are large, with radii of ~ 100-1000 AU. The gas and dust are remnant material from the molecular cloud, and most of the mass is still in the gas phase (a gas-to-dust ratio of 100 is usually assumed). The molecular content is poorly known; $H_2$ is, however, the most abundant molecule, while CO remains the most abundant species containing carbon. The chemical conditions change with the disk radius. Studying the molecular disk content close to the star is, however, out of the scope of current telescopes due to lack of adequate angular resolution. Recent models of disks irradiated by stellar X-ray emission also show that X-rays can significantly affect the disk surface and can even penetrate deep inside the disk (Najita *et al* 2001), with important chemical implications.

Dutrey *et al* (1997, 2000) summarize the molecules detected in the protoplanetary disk surrounding DM Tau, a T-Tauri star of 0.5 solar mass (Table 3). This corresponds to the deepest survey performed so far. Because of sensitivity limitations, the observed molecules only trace the outer disk chemistry (radius > 50 AU). Simple organic molecules like $H_2CO$ or HCN have been detected, suggesting that even more complex molecules may exist. The molecules that are currently detected correspond to the most abundant species found in dark clouds (abundances in TMC-1 are given in Table 3, col.2), but all the molecules appear depleted with respect to TMC-1 abundances (Table 3, col.5). The outer regions of these disks are very cold and dense, and molecules are expected to condense on dust grains. Note that such molecular depletions do not bring any direct constraint on the possible depletion of $H_2$ with respect to the dust.

Overall, due to a lack of sensitivity and angular resolution, the evolution of disks toward planetary formation is poorly constrained today, and only a few organic molecules are observed in protoplanetary disks.

**Table 3**

Molecules observed in the protoplanetary disk surrounding the TTauri star DM Tau. Both detections and upper limits at 3 σ are shown. Sν is given in Jy.km s$^{-1}$. "f" is the depletion factor in the gas phase with respect to X, the abundance in TMC1 by comparison to $H_2$. Abundances, measured in TMC-1, come from Ohishi *et al* (1992) and Cernicharo & Guelin (1987). For details, see Dutrey *et al* (1997, 2000).

| **Species** | **X** | **Transition** | ***Sν*** | ***f*** |
|---|---|---|---|---|
| $^{12}CO$ | 8(-5) | 2-1 | 13.95(0.43) | |
| $^{13}CO$ | 4(-6) | 2-1 | 5.40(0.13) | 3 |
| $C^{18}O$ | 4(-7) | 2-1 | 0.68(0.07) | 5 |
| HCN | 2(-8) | 1-0 | 0.38(0.05) | 40 |
| | | 3-2 | <1.9 | |
| HNC | 2(-8) | 1-0 | 0.16(0.03) | 90 |
| CN | 3(-8) | 1-0 | 1.38(0.24) | 10 |
| | | 2-1 | 8.7(0.40) | |
| CS | 1(-8) | 3-2 | 0.47(0.07) | 30 |
| | | 5.4 | 0.67(0.11) | |
| $H_2CO$ | 2(-8) | $2_{12}$-$1_{11}$-o | 0.30(0.04) | 50 |
| | | $2_{02}$-$1_{01}$-p | 0.11(0.04) | 100 |
| | | $3_{13}$-$2_{12-}$o | 0.48(0.40) | 100 |
| $C_2H$ | 8(-8) | 1-0 | 0.55(0.08) | 7 |
| $HCO^+$ | 8(-9) | 1-0 | 0.82(0.04) | 11 |
| | | 3-2 | 4.1(0.50) | |
| $C^{34}S$ | 5(-10) | 5-4 | 0.38(0.11) | ≥ 6 |
| Undetected | | | | |
| $H^{13}CO^+$ | 1.1(-10) | 1-0 | <0.06 | ≥ 3 |
| $N_2H^+$ | 5(-10) | 1-0 | <0.45 | ≥ 2 |
| SiO | ≤ (-12) | 2-1 | <0.13 | |
| | | 5-4 | <0.36 | |
| SiS | 1(-11) | 5-4 | <0.09 | |
| | | 8-7 | <0.09 | |
| $H_2S$ | ≤5(-10) | $1_{10}$–$1_{01}$ | <0.50 | |
| $C_3H_2$ | ≤4(-10) | $1_{10}$–$1_{01}$ | <0.14 | |
| $HC_3N$ | 6(-9) | 10-9 | <0.07 | |
| | | 16-15 | <0.15 | |
| $CH_3OH$ | 2(-9) | $3_0$–$2_0$ | <0.24 | |
| $CO^+$ | ≤1(-11) | 2-1 | <0.54 | |
| SO | | $6_5$–$5_4$ | <0.28 | |
| $SO_2$ | | $25_{323}$–$24_{420}$ | <0.16 | |
| $SiC_2$ | | $4_{04}$–$3_{03}$ | <0.15 | |
| HNCS | | $12_{012}$–$11_{011}$ | <0.23 | |
| HCO | | $1_{10}$–$0_{00}$ | <0.12 | |
| $HCOOCH_3$ | | $20_{020}$–$19_{019}$ | <0.40 | |
| $HOHCS^+$ | | 2-1 | <0.14 | |

## 5. Exoplanets and habitable zones

When we had only our own system to study, the widely accepted model for its formation began with the collapse of a fragment of an interstellar cloud into a disk (see section 4) called the solar nebula, dominated by a central condensation that became the Sun. Accretion of dust grains in the disk led to the formation of planetesimals that ultimately collided with one another to form the planets. In the inner, warmer zone of the solar nebula, "rocky" planetesimals aggregated to form Moon-sized planetary embryos and, eventually, the terrestrial planets. Beyond the distance from the Sun at which ice could first condense, often referred to as the "snowline", this plentiful raw material allowed the formation of solid objects with masses ten times the Earth's or more, sufficient to enable the gravitational collapse of surrounding solar nebula gas. The existence of a snowline thus explained the location of the giant planets in the outer part of the solar system. The remaining populations of rocky planetesimals formed in the inner nebula exist today as asteroids and meteoroids, while in the outer solar system icy planetesimals occur as comets, Centaurs, and Kuiper Belt objects.

This brief outline omits an extremely complex series of interactions that are still poorly understood in detail. But the greatest challenge to the current model comes from the planets that have been discovered around other stars over the last seven years. These new planets are all giants, most of them are more massive than Jupiter. Except for uncertainties due to the unknown inclination of the orbits, also Saturn mass planets have now been found. The most surprising characteristic of those newly detected planets is the proximity to their parent stars: instead of orbiting outside the "snowline", almost all of the giant planets discovered to date circle their stars at distances less than 4.5 AU (Marcy *et al* 2000, http://exoplanets.org, http://cfa-www.harvard.edu/planets/encycl.html, Queloz 2000). Nearly 30 of them have orbits smaller than Mercury's! Within 0.07 AU, the orbits are nearly circular, but at greater distances, another major surprise occurs: their eccentricities increase to values as high as 0.7. Such highly elliptical orbits are only occupied by comets in our solar system.

What are we to make of these glaring contrasts to our own planetary system? Could it be that our configuration of planets is extremely rare, perhaps even unique? Models that explain the configurations of these newly-discovered systems invoke tidal interactions between the giant planets and the surrounding disk of gas and dust that could cause the planets to migrate inwards toward their stars from their original, distant positions (Lin & Papaloizou 1986, Lin & Ida 1997). Such migrations follow the inward movement of the disks themselves, suggesting that any Earth-like planets in such systems would be swept into the central stars by the migrating giants.

There is still a possibility that small planets could be captured into stable positions in the giant planets' orbits, much as Jupiter has captured the Trojan asteroids. One could also invoke the change in scale appropriate to such giant planets to suggest the presence of giant satellites that might possess Earth-like characteristics (Owen 2000). Note that Jupiter's satellite Europa has been proposed as a potential carrier of life, because of evidence suggesting the presence of a subsurface liquid water ocean heated by tidal interaction with Jupiter.

In either of these extreme cases, one must assume that the giant planet ceases its migration when the semi-major axis of its orbit is about 1 AU, and indeed a few such planets have been discovered among the dozens now known to exist.

But it is premature to invoke such speculative scenarios when the data on these new planetary systems are so incomplete. It is important to note that giant planets close to their stars are by far the easiest planets to discover with presently available methods, and consequently the sample of planetary systems from which we are trying to glean insight is distorted by observational bias. The first extra solar planet was discovered in 1995 (Mayor & Queloz 1995), so we must expect to wait several more years to have reliable statistics of planets in orbits with 12-year periods and low eccentricities. Systems with such a planet will resemble our own. The detection of Earth size planets in such systems will have to await the launch of dedicated orbiting telescopes.

The ultimate detection of life "as we know it" will presumably require the identification of Earth-like planets. What is an Earth-like planet? The basic criteria are straightfoward. We want a rocky planet with liquid water on or below its surface. To achieve this requires a nearly circular orbit about a Sun-like star, so the planet experiences a uniform temperature throughout its year. Obviously some deviations from this state are acceptable, barring an orbital eccentricity that would freeze the planet's water in one part of its orbit or boil it in another. A planet's distance from the Sun is critical – Venus is 25% closer and this is too close for comfort – liquid water is not stable on the planet's surface. A runaway greenhouse effect may have developed that led to boiling of the oceans; loss of water through photo-dissociation in the planet's upper atmosphere, results in jeans escape of hydrogen. A distance much beyond that of Mars would lead to permanent freezing of the oceans. Mass and distance from the parent star are essential criteria, but are they sufficient? For life to begin and evolve, we need a supply of biogenic elements, specifically C, H, N, O and various minor species such as Ca, P, S, etc. The latter are provided by the rocks and may be assumed to be present on any rocky planet, although it is clearly advantageous (again!) to have a planet sufficiently massive to have undergone differentiation and produced a crust that concentrates some of these important elements. But it is the first four elements that merit major concern.

HOCN are the four most abundant, chemically active elements in the Universe, see section 1. They are also the most abundant elements in all forms of life known to us. Yet, with the exception of O, these elements are relatively rare on Earth. Relative to silicon, the common rock-forming element, hydrogen, nitrogen, carbon and oxygen are depleted by factors of $10^7$, $10^5$, $10^3$ and 10 respectively, compared with abundances in the Sun. Oxygen is the least depleted as it is an essential component of silicates, the most common type of rock on the planet.

The hydrogen and oxygen essential to life are found in their greatest abundance in $H_2O$, as life does not extract O from silicates. But what about C and N? Life without carbon (and complex life without oxygen) is unimaginable to us, yet the origin of this element on the Earth is somewhat mysterious. It is relatively rare in rocks; without biological assistance it occurs most abundantly as graphite. The great deposits of carbon on Earth are either carbonates – consisting of $CO_2$ that was once in the atmosphere – or biogenic compounds such as coal and petroleum.

Nitrogen is even more absent from geology, with no major minerals and nitrate deposits that are overwhelmingly biogenic. Comparative planetology is a crucial research field which will help us in the near future to understand how C and N have reached the planets, thus revealing more about the evolution of life and our existence.

# 6. Comets

Cometary nuclei consist of ices, organic compounds, and silicates. The ratio of refractory components to ice varies considerably from comet to comet, prompting the description of the nucleus to range from an “icy dirtball” to a “dirty iceball”. Traditionally, comet nuclei have been thought of as the building blocks of the ~ 10 Earth mass solid cores that initiated the formation of the giant planets. Recently, however, it has been suggested that, at least in the case of Jupiter, those building blocks were solar composition icy planetesimals (SCIPs) (Owen *et al* 1999). The high volatile content of SCIPs would make these objects considerably more primitive than the nitrogen-deficient comets observed. The origin of the SCIPs is still under discussion (Owen *et al* 1999, Owen 2000, Gauthier *et al* 2001a,b). In contrast, it is widely accepted that the comets were formed in the outer solar nebula, at the orbit of Jupiter and beyond.

Early in the history of the solar system, Jupiter and the other giant planets perturbed the orbits of the comets in their vicinities. Some of these comets then collided with the Sun, some with the terrestrial or giant planets, some were ejected out of the solar system. A fraction coming from the whole Jupiter-Neptune zone built the Oort cloud, whereas Kuiper-Belt objects were probably formed in the belt itself (Weissman 1999). Recent reviews have focused on the composition of comets (Altwegg *et al* 1999, Crovisier & Bockelee-Morvan 1999, Irvine *et al* 2000, Ehrenfreund & Charnley 2000, Charnley *et al* 2002), as well as various aspects of their possible role in the origin and evolution of life (Thomas *et al* 1997). A general presentation on comets can be found in Crovisier & Encrenaz (2000), and a detailed account of many aspects in Festou (1993a,b) and in Newburn *et al* (1991).

Most cometary nuclei reside in two reservoirs, the Oort cloud (at $10^4$-$10^5$ AU from the Sun), and the Kuiper Belt (beyond Neptune, 30-100 AU). The estimated total mass of these reservoirs is 1-250 Earth masses and 0.1-1 Earth mass, respectively, for bodies 0.5-500 km in size (the Halley nucleus, for example, was 8 x 8 x 16 km). More than 100 new comets are discovered each year, when the highly elliptic orbits of the Oort cloud comets bring them into the zone of the planets. When closer than ~10 AU to the Sun, comets become active and release volatiles, first mainly CO and then, within 4 AU, mainly $H_2O$, which drag other species and dust grains into the coma (the comet’s atmosphere). The largest grains spread along the orbit and contribute to the interplanetary dust responsible for meteor showers. We use the popular names Halley, Hyakutake and Hale-Bopp in the paragraphs below, though the full astronomical names of these comets are 1P/Halley, C/1996 B2 Hyakutake and C/1995 O1 Hale-Bopp.

## 6.1 Composition of cometary matter

Comets contain, within an order of magnitude, roughly the same mass of ices and of dust. Some comets appear richer or poorer in dust, which seems to be due to an initial composition difference (A'Hearn *et al* 1995). Note that the dust mass is difficult to evaluate precisely, due to the large range of particle sizes and the possible differences in particle size distribution from one comet to another.

The knowledge of the chemical composition of cometary ices is now mainly based on measurements by millimeter wave or infrared spectroscopy of the molecules in the coma, which sublimated from the nucleus (e.g. Irvine *et al* 2000, Bockelée-Morvan *et al* 1997, 1998, Despois 1997/99, Crovisier 1997/99). The derivation of the abundances in the nucleus from these observations normally assumes that the molecules come directly from the nucleus (no carrier), and any chemical processes in the coma other than photochemistry are usually neglected; this has been questioned for some of the species (CO, $H_2CO$, HNC; see below). In the future cometary observations may have to be interpreted in the context of a nucleus whose ices are stratified in density, temperature and porosity (Prialnik & Podolak 1999).

Cometary ices are predominantly (more than 50 %) water ice; but more than 25 other small molecules have been identified. Their abundances in percent relative to water molecules are listed in Table 4, and range from 20-30 % (for CO in some comets) down to 0.01 %, which is at present the lowest abundance detected. The inventory of cometary species is certainly not yet complete in the range 0.01-1%. Many small reactive molecules important in prebiotic aqueous chemistry are detected: $H_2O$, $CO_2$, formaldehyde ($H_2CO$), ammonia ($NH_3$), hydrogen cyanide (HCN), acetonitrile ($CH_3CN$), isocyanic acid (HNCO) and hydrogen sulfide ($H_2S$). But other species, less often considered as components of the "primitive soup", are also present in noticeable amounts, and may play a role in aqueous or anhydrous synthesis of more complex species, e.g. methanol ($CH_3OH$,1-5%), acetylene ($C_2H_2$, 1 %) and CO (up to 30 %). The most complex species identified to date are: acetaldehyde ($CH_3CHO$), methyl formate ($HCOOCH_3$), and formamide ($NH_2CHO$); this last compound bears some resemblance to glycine ($NH_2CH_2COOH$). Glycine, the simplest amino acid, has not yet been detected, and the present upper detection limit of 0.5 % is not very significant compared to other species.

All comets are expected to contain more or less the same compounds, but relative abundances may differ: from 1 to 5 % for methanol ($CH_3OH$), from less than 1 % up to 30 % for CO. The variation in methanol ($CH_3OH$) may reflect formation in different zones of the protosolar nebula (Mumma *et al* 2001). On the other hand, the high volatility of CO is probably the main reason for its variation from comet to comet. That may be linked again to the comet formation zone, but also to the aging of comets and to the distance from the Sun at which the active comet is observed.

Such a differential sublimation does not seem to affect the relative production rate of other, less volatile, species, with two exceptions (in addition to CO): formaldehyde ($H_2CO$) and isocyanide (HNC) (Biver 1997/99). Release of formaldehyde ($H_2CO$) from grains, and especially those containing its polymer (polyoxymethylene, POM), has been proposed (Huebner 1987, Cottin *et al* 2001). For HNC, interconversion between HNC and HCN through chemical reactions has been proposed, as well as the possible release of HNC from organic grains in the coma (Irvine *et al* 1998b, Rodgers & Charnley 1998, 2001).

The chemical composition of cometary grains has been analyzed in situ in comet 1P/Halley by mass spectrometers on board the Vega 1 and 2 and Giotto spacecraft (Fomenkova 1999, Kissel & Krueger 1987). Approximately 5000 grains have been collected, with masses from $5.10^{-17}$ to $5.10^{-12}$ g (and sizes from a few hundreds of μm to a few μm); the total analyzed mass was thus only a few nanograms. About 70 % of the dust grains were composed of a mixture of organics and refractory material, whereas the rest of the grains was devoid of organic material. The so called "CHON grains", containing mainly C,H,O,N atoms, have been one of the major discoveries and have been found to be interspersed with silicates on the sub-micron scale (Jessberger *et al* 1988).

The carbon rich grains are apparently components of various types: i) pure carbon particles; ii) PAHs; iii) branched aliphatic hydrocarbons iv) carbon-oxygen or carbon-nitrogen polymers and v) more complex compounds containing all four C,H,O and N atoms (heteropolymers or complex organic molecules have been proposed). A more specific list of organic compounds in the grains has been proposed by Kissel *et al* (1997), but it remains very speculative due to the limited resolution of the mass spectrometers, that flew through Halley's coma.

The detection of a PAH, phenantrene ($C_{14}H_{10}$) has also been suggested in Halley based on UV spectroscopic data (Moreels *et al* 1994). However, no PAHs have been detected in the ISO IR spectra of C/1995 O1 Hale-Bopp (Crovisier 1997/99), which may be due to a larger heliocentric distance at the time of observation.

The nature of the silicate particles has been partly revealed also by infrared observations. Laboratory spectra of olivines, pyroxenes, and carbonaceous particles are combined to match cometary spectra (see section 3). ISO observations (Crovisier 1997/99) led to the identification of forsterite. The pyroxene/olivine ratio appears to be ten times higher than in carbonaceous chondrites (see section 7), those meteorites whose composition is the closest to comets. The presence of crystalline silicates is a major puzzle when trying to link cometary and interstellar matter (see section 3.3).

## 6.2 Comets and the origin of life

Comets are rich in water and carbon, two key constituents of terrestrial life. Moreover, as realized by Oro (1961) 40 years ago, they could bring to the Earth reactive C-bearing molecules which might assemble to form amino-acids, purine and pyrimidine bases and sugars, i.e., the basic building blocks of nucleic acids and proteins. The importance of this suggestion has grown as models for the early Earth's atmosphere have changed.

The presently postulated $CO_2$-$H_2O$-$N_2$ atmosphere would be much less likely to produce complex organic molecules than the mixtures of reducing gases ($CH_4$-$H_2$-$NH_3$) used in the original Miller-Urey experiments. Under these more oxidizing conditions, extraterrestrial delivery of complex molecules would be a more important source of organic matter, as shown in the pioneering work of Chyba & Sagan (1992, 1997), see section 8.

The importance of comets for the origin of life on Earth has also been strongly advocated by other authors (e.g. Delsemme 1992, 2000, Greenberg 1982, 1996). Could comets deliver organic molecules made in the ISM to the surfaces of rocky planets? This is a contentious subject at the moment, with advocates of preservation of pristine interstellar material arrayed against those who think considerable reprocessing and mixing occurred in the solar nebula. The most common argument for the preservation of interstellar material in comets comes from a comparison of their molecular composition, as revealed by studies of their comae, and the list of molecules found in interstellar clouds (e.g., Crovisier & Bockelee-Morvan 1999, Bockeleé-Morvan *et al* 2000, Ehrenfreund & Charnley 2000, Irvine & Bergin 2000). Additional support can be derived from measurements of D/H, see section 9. In the one comet where it was measured (Hale-Bopp, by Meier *et al* 1998) D/H in HCN is 7 times higher than the value found in $H_2O$. This is the factor expected for deuterium exchange via ion-molecule reactions at a temperature of 30 ± 5 K (Millar *et al* 1989). Measurements of the ratio of ortho to para hydrogen in cometary $H_2O$ and $NH_2$ yield temperatures of 23 ± 5 and 28 ± 3 respectively (Crovisier 1998, Kawakita *et al* 2001). This agreement suggests that interstellar chemistry has been preserved during the cometary formation process. Another indicator of such preservation is provided by the high value of D/H and $^{15}N/^{14}N$ found in cluster IDPs (Messenger 2001). These are the most fragile of the IDPs and thus the ones most commonly assumed to originate from comets. These anomalous high isotope ratios are usually assumed to require an interstellar source, and they clearly have not been allowed to re-equilibrate with hydrogen gas in the solar nebula.

High isotope ratios found in organic material surrounding crystalline silicates in IDPs suggest that these silicates were also brought in from the ISM (Keller *et al* 2000). The existence of crystalline silicates in comets- as revealed by cometary IR spectra – and their apparent absence in the ISM, has been invoked as an argument for mixing of inner nebula material to the outer nebula (e.g. Mousis *et al* 2002). The argument is that crystalline silicates can only be formed near stars where temperatures above 1000 K exist, see section 3.3. Since they are not seen in the ISM, their presence in comets requires formation near the Sun followed by transport to the outer nebula and incorporation in forming comets.

**Table 4**

Molecular abundances of ices for comets Hyakutake and Hale-Bopp (in % with respect to water ice) as deduced from observations of the gas phase coma. After Bockelée-Morvan *et al* (2000) and Crovisier *et al* (2002).

The limits on NaCl and NaOH are still uncertain.

*Notes*

a) extended source - the abundance is model dependent
b) abundance deduced from CS
c) was measured 20 % at 2.9 AU by the ISO satellite

| **Molecule** | **Hyakutake** | **Hale-Bopp** | **Notes** |
|---|---|---|---|
| $H_2O$ | 100 | 100 | |
| $H_{2O2}$ | < 0,04 | - | |
| CO | 6-30 | 20 | a) |
| $CO_2$ | <7 | 6 | c) |
| $CH_4$ | 0.7 | 0.6 | |
| $C_2H_2$ | 0.5 | 0.1 | |
| $C_2H_6$ | 0.4 | 0.1 | |
| $CH_3C_2H$ | - | <0.045 | |
| $CH_3OH$ | 2 | 2.4 | |
| $H_2CO$ | 0.2-1 | 1.1 | a) |
| HCOOH | - | 0.08 | |
| $HCOOCH_3$ | - | 0.08 | |
| $CH_3CHO$ | - | 0.02 | |
| $H_2CCO$ | - | <0.032 | |
| $C_2H_5OH$ | - | <0.05 | |
| $CH_3OCH_3$ | - | <0.45 | |
| $NH_3$ | 0.5 | 0.7 | |
| HCN | 0.1 | 0.25 | |
| HNCO | 0.07 | 0.06 | |
| HNC | 0.01 | 0.04 | a) |
| $CH_3CN$ | 0.01 | 0.02 | |
| $HC_3N$ | - | 0.02 | |
| $NH_2CHO$ | - | 0.01 | |
| Glycine | - | <0.5 | |
| $CH_2NH$ | - | <0.032 | |
| $HC_5N$ | - | <0.003 | |
| $H_2S$ | 0.8 | 1.5 | |
| OCS | 0.1 | 0.3 | a) |
| SO | - | 0.2-0.8 | a) |
| $CS_2$ | 0.1 | 0.2 | b) |
| $SO_2$ | - | 0.1 | |
| $H_2CS$ | - | 0.02 | |
| $S_2$ | 0.005 | - | |
| | | | |
| NaCl | - | <0.0008 | |
| NaOH | - | <0.0003 | |

However, as stated in section 3.3, the apparent absence of crystalline silicates from the ISM is a puzzle, in that they are evidently delivered there (Lequeux 2000). Furthermore, the observed chemical composition of comets – retaining the mix of fully oxidized and fully reduced carbon compounds in rougly interstellar proportions - argues against extensive mixing with material exposed to high temperatures. Nevertheless, we still miss an unequivocal connection between the composition of comets and the composition found in interstellar clouds, so that testing the link between comets and the ISM remains an important research topic. The determination of D/H in other cometary molecules besides $H_2O$ and HCN may provide a definitive result (cf Irvine *et al* 2000).

## 7. Chemical composition and classification of the meteorites

Meteorites are usually divided into three main groups, the iron meteorites, the stony irons and the stones. The iron meteorites are composed of at least 90 % metal, mainly iron and nickel. The stony iron meteorites are further divided into pallasites, which mainly comprise olivine crystals embedded in a metallic matrix, and mesosiderites, also made up of silicates and metal but more finely grained and thus intimately mixed. The stony meteorites consist predominantly of silicates and are divided into chondrites and achondrites, due to the presence or absence of infra-millimeter-sized spheres termed chondrules. Chondrites are divided into three groups based on chemical composition: ordinary, enstatite, and carbonaceous. Ordinary chondrites are the most abundant group and are further divided into three sub-groups on the basis of total iron content and iron content in the olivines and pyroxenes (H-chondrites for high total iron, L- for low total iron and LL- for low total iron and low metal). Enstatite chondrites are characterized by a high iron content but contain virtually no silicates.

Carbonaceous chondrites include several groups designated according to the initial of the type specimen (e.g., CI after Ivuna, CM after Mighei) and are all characterized by a black color. CI chondrites have the same elemental composition as the Sun with the exception of the most volatile elements such as He, H, O, N and C, and are thus considered as the most primitive rocky bodies of the solar system apart from comets. Carbonaceous chondrites have been shown to contain organic compounds, which will be described below in more detail. The best studied of these meteorites (Orgueil, Murchison, Allende, Tagish Lake) exhibit a range of thermal and aqueous alteration believed to have occurred on their parent bodies.

Achondrites show a magmatic texture and are considered to derive from more primitive material by a melting process, in contrast to the chondrites, which have retained their original composition. The most abundant achondrites (eucrites, howardites and diogenites) resemble terrestrial basalts. Aubrites are also referred to as enstatite achondrites and are supposed to be derived from enstatite chondrites through melting and differentiation processes. Ureilites are characterized by a high carbon content (~ 2 %) and by the occurrence of diamonds and are thus assumed to have originated from carbonaceous chondrites. SNC meteorites, namely shergottites, nakhlites and chassignites, contain sodium-rich feldspar and in some cases minerals with water-bearing inclusions indicative of formation under more oxidizing conditions. Their young age (0.8 - 1.8 Ga ($10^9$ years) for most compared to 4.6 Ga for chondrites) suggests that their hydrothermal alteration took place in a parent body after its formation. Elemental and isotopic ratios of volatile species trapped in these rocks revealed a Martian origin for the SNC meteorites.

### 7.1 Macromolecular organic matter in meteorites

Carbonaceous chondrites are known to contain a substantial amount of C, up to 3 % by weight. The major part of this carbon corresponds to a macromolecular organic fraction (Hayes 1967). This insoluble organic matter (IOM) is usually isolated from the bulk meteorite as the insoluble residue that is left after solvent extractions and drastic acid treatments using HF and HCl, which aim at removing the soluble organic compounds and the bulk of the minerals, respectively.

A number of analytical tools can be considered for the study of such refractory organic material, including spectroscopic methods such as FTIR (Fourier Transform Infrared) (Hayatsu *et al* 1977, Khare *et al* 1990, Ehrenfreund *et al* 1991, 1992b, Salisbury *et al* 1991, Murae 1994), Raman (Strazzulla *et al* 2001), solid state $^{13}$C NMR (Nuclear Magnetic Resonance) (Cronin *et al* 1987, Gardinier *et al* 2000, Pizzarello *et al* 2001), XANES (X-ray Absorption Near-Edge Structure) (Cody *et al* 1999, Flynn *et al* 1999) and EPR (Electron Paramagnetic Resonance) (Duchesne *et al* 1964, Schulz & Elofson 1965, Binet *et al* 2002). IR spectroscopy pointed to pronounced similarities between interstellar carbonaceous grains and IOM in carbonaceous chondrites. The main two characteristic features are (1) an equivalent intensity of the asymmetric stretching mode absorptions for $CH_3$ (2960 cm$^{-1}$) and $CH_2$ (2920 cm$^{-1}$) and (2) a lack of aromatic CH-stretching mode (3040 cm$^{-1}$). Micro-Raman investigation in the Orgueil meteorite revealed that the amorphous carbon is homogenous and suggested that this material has not been exposed to significant irradiation (Strazzulla *et al* 2001).

Solid state $^{13}$C NMR is a powerful technique to determine the nature and environment of carbon atoms in macromolecular materials, see Figure 8. Since the pioneering study carried out by Cronin *et al* (1987), it has been recently applied to the IOM of the meteorites of Orgueil, Murchison and Tagish Lake showing their highly aromatic character (Gardinier *et al* 2000, Pizzarello *et al* 2001). This method revealed a high level of branching of the aliphatic chains and showed that the aromatic units are highly substituted, especially in Murchison. These results imply that the IOM of these meteorites did not suffer a marked thermal maturation during the late aqueous alteration on the parent body. Its synthesis involved a statistical combination of all the possible bonds between $–CH_3$, $-CH_2$ and $–CH$ radicals, producing both the aliphatic and aromatic moieties. This model explains not only the chemical features of the chondritic IOM but also the typical FTIR signature of the interstellar medium (Gardinier *et al* 2000).

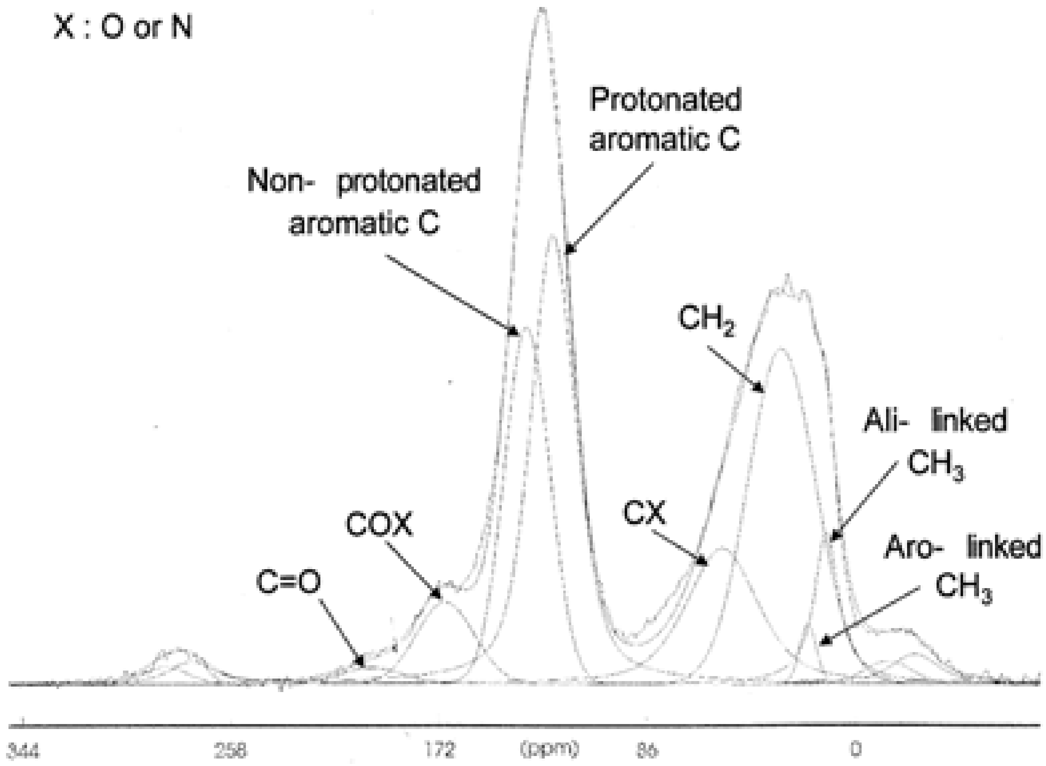


**Figure 8**
Solid state $^{13}$C-NMR spectrum of the insoluble organic matter from the Orgueil meteorite. Eight types of carbon were identified using variable contact time and inversion recovery cross polarization along with magic angle spinning; their relative abundances were determined through spectral deconvolution (Gardinier *et al* 2000).

C-XANES spectra of the IOMs of Murchison, ALH 84001 and Nakhla show intense absorptions assigned to aromatic organic compounds (Cody *et al*, 1999, Flynn *et al* 1999). N-XANES showed similar spectra for Orgueil and Murchison IOMs, with strong absorptions due to pyridine, pyridone and pyrrole rings whereas significant differences are observed between these two meteorites when the S-XANES spectra are considered (Derenne *et al* 2002).

Indeed, firstly a peak is observed at low-energy in Murchison due to the persistance of pentlandite (an iron-nickel mineral sulfide) upon IOM isolation. Moreover, when the organic sulfur species are considered, their relative abundances calculated after deconvolution of the spectra are different in Orgueil and Murchison. (i) A significant contribution of oxidized species (sulfoxides, sulfones) is observed in Orgueil, whereas they are virtually absent in Murchison and (ii) the aliphatic sulfides to thiophenes ratio is much higher in Murchison than in Orgueil (Derenne *et al* 2002).

These differences may be related to different intensities in the hydrothermal processes undergone on the parent body. Based on detailed mineralogical studies, it is generally accepted that carbonaceous chondrites underwent aqueous alteration on the parent body (Bunch & Chang 1980).

The nature of the organic free radicals in chondritic IOM has been revisited recently using EPR and ENDOR (Electron Nuclear Double Resonance) (Binet *et al* 2002). This study confirmed the occurrence of a relatively high concentration of radicals (> $10^{18}$ spin $g^{-1}$, number of free radicals per gram of sample) in Orgueil and Murchison and showed that these radicals (i) exhibit a moderate level of oxygenation and (ii) are not randomly distributed in the IOM. Radical-rich regions (3-4 $10^{19}$ spin $g^{-1}$) can be viewed as pristine parts of the OM which would have survived the hydrothermal process on the parent body.

Chemical and thermal degradation provide information at the molecular level. Ozonolysis of Orgueil IOM released a number of benzenepolycarboxylic acids, suggesting that the aromatic units have a limited number of aromatic rings (Bitz & Nagy 1966). Such products were also detected in the alkali soluble fraction of Murchison IOM along with alkylbenzenes and phenolic compounds (Studier *et al* 1972) and, following oxidation with nitric acid, various other aromatic acids such as naphthalene acids and pyridine acids (Hayatsu *et al* 1977). Chemical degradation of Murchison IOM using trifluoroacetic acid ($CF_3COOH$), copper oxide ($Cr_2O_7$) and alkaline CuO oxidation also yielded a number of aromatic compounds including naphthalene, phenanthrene, anthracene, indane, pyrrole and benzothiophene, but some aliphatic hydrocarbons and acids were also shown to be released (Hayatsu *et al*, 1977, 1980). The first pyrolysis of Murchison IOM, performed as a direct heating in the mass spectrometer source, released aromatic hydrocarbons containing up to three rings (Studier *et al* 1972). Pyrolysis at various temperatures, ranging between 150 °C and 600 °C, showed that most of the pyrolysis products are generated from Murchison and Orgueil between 300 and 450 °C (Levy *et al* 1973, Bandurski & Nagy 1976). Alkylthiophenes and benzothiophenes were also reported in these pyrolysates, but it has been noted that they may be formed through cyclisation and aromatisation of other compounds upon pyrolysis. Aliphatic compounds, i. e. alkanes and alkenes up to $C_8$, have been shown to be present in these pyrolysates (Bandurski & Nagy, 1976, Hayatsu *et al* 1977). Acetonitrile and acrylonitrile were identified and considered as possibly derived from proteins or amino acids (Bandurski & Nagy 1976). High temperature pyrolysis (600 °C) of Murchison IOM was performed as an attempt to release fullerenes and led to the detection of numerous high molecular weight PAHs including coronene (de Vries *et al* 1993). A follow-up study using sublimation (200, 450 and 600 C) to extract intact kerogen from an acid residue of Murchison revealed an even more complex high molecular weight component including PAHs up to $C_{50}$ (Becker *et al* 1999).

Interestingly, no $C_{60}$ was detected in these sublimates, however, some higher fullerenes were detected when extracting the acid residue with higher boiling solvents (Becker *et al* 2000). Examination of the IOM from several CM2 chondrites from Antarctica by pyrolysis/gas chromatography/mass spectrometry (pyrolysis-GC/MS) showed that these chondrites were more or less affected by aqueous alteration and thermal metamorphism (Komiya *et al* 1993).

Similar products as those obtained from the above mentioned carbonaceous chondrites were released upon pyrolysis-GC/MS of the IOM of Nakhla, a Martian meteorite (Jull *et al* 1999). Hydrous pyrolysis, i. e. pyrolysis in the presence of water, has been performed on Murchison, Cold Bokkeveld (two CM chondrites) and Orgueil (a CI chondrite) IOM (Sephton *et al* 1998, 1999).

The samples have been heated at 320°C for 72 h in a sealed vessel. In addition to aromatic hydrocarbons, phenolics have been detected pointing to the occurrence of ether bridges between the aromatic units (Sephton *et al* 1998). Moreover, these results suggest a higher extent of condensation of the aromatic units along with a higher contribution of ether linkages in the CM chondrites than in the CI one, which may be related to the more extensive aqueous alteration undergone by Orgueil (Sephton *et al* 1999, 2000).

Stepwise combustion of the IOM of Murchison and Orgueil revealed isotopic heterogeneities in C, N and H (Halbout *et al* 1990, Kerridge *et al* 1987). This has been recently confirmed in an extensive study on one CI chondrite (Orgueil), three CM chondrites (Murchison, Murray and Cold Bokkeveld), one CR chondrite (Renazzo), five ordinary chondrites including Semarkona and three enstatite chondrites (Alexander *et al* 1998). Based on the N isotope release profile, it appears that all the chondrites have accreted similar organic material, which can still be observed in Renazzo and Semarkona (Alexander *et al* 1998).

Isotope composition can now also be obtained at a molecular level using pyrolysis-GC-irMS, which allows the determination of the C-isotope composition of the individual pyrolysis products. This technique was applied to the Martian meteorite Nakhla to distinguish indigenous OM from terrestrial contamination (Jull *et al* 1999). It also allows determination of the isotopic and chemical features of the IOM isolated from small amounts of meteorites (Sephton & Gilmour 2001).

In summary, the origin of the chondritic IOM is not yet well understood and no model is so far able to explain its observed structural and isotopic diversity.

### 7.2. Volatile Organic Compounds in meteorites

The classes of soluble meteoritic organic compounds that have familiar biochemical counterparts include amino acids, fatty acids, purines, pyrimidines and sugars (see Botta & Bada 2002 for a recent review). Moreover, alcohols, aldehydes, amides, amines, mono- and di-carboxylic acids, aliphatic and aromatic hydrocarbons, heterocyclic aromatics, hydroxy acids, ketones, phosphonic and sulfonic acids, sulfides, ethers as well as fullerenes have been reported (Cronin & Chang 1993, Cooper *et al* 1992, Becker *et al* 2000). Concentrations vary widely from less than ten ppm (amines) to tens of ppm (amino acids) to hundreds of ppm (carboxylic acids) (Botta & Bada 2002), Table 5.

Cooper *et al* (2001) reported recently a variety of sugar polyols that are present in the CM meteorites Murchison and Murray in amounts comparable to amino acids. Chromatographic analyses of virtually all classes of acyclic compounds reveal complex molecular assemblages containing homologous series of compounds up to $C_{12}$ in some cases (carboxylic acids).

**Table 5**

Abundances of soluble organic compounds in the Murchison meteorite (taken from Botta & Bada 2002) and PAHs and fullerenes (taken from Becker *et al* 2000). Amino acid concentrations for several CI chondrites are also listed.

a) average of the abundances in the CI carbonaceous chondrites Orgueil and Ivuna (Ehrenfreund *et al* 2001a);

b) for the Yamato-791198 carbonaceous chondrite (Naraoka *et al* 1988);

c) 0.1 ppm estimated for $C_{60}$ in Allende (Becker *et al* 1994); d) Cooper & Cronin 1995.

| **Compound Class** | | **Concentration (ppm)** |
|---|---|---|
| Amino Acids | | |
| | CM meteorites | 17-60 |
| | CI meteorites | ~5[a)] |
| Aliphatic hydrocarbons | | >35 |
| Aromatic hydrocarbons | | 3319[b)] |
| Fullerenes | | > 100[c)] |
| Carboxylic acids | | > 300 |
| Hydroxycarboxylic acids | | 15 |
| Dicarboxylic acids & Hydroxydicarboxylic acids | | 14 |
| Purines & Pyrimidines | | 1.3 |
| Basic N-heterocycles | | 7 |
| Amines | | 8 |
| Amides | linear | > 70 |
| | cyclic | > 2[d)] |
| Alcohols | | 11 |
| Aldehydes & Ketones | | 27 |
| Sulphonic acids | | 68 |
| Phosphonic acids | | 2 |

Complete structural diversity also occurs among cyclic meteoritic compounds such as PAHs, along with a variety of $C_{15}$ to $C_{30}$ branched alkyl-substituted mono-, di- and tri-cyclic alkanes (Botta & Bada 2002, Cronin & Chang 1993). Polycyclic compounds together with the alkyl phosphonic and sulfonic acids comprise the most thermally stable species in the Murchison inventory (Cooper *et al* 1992).

Distinctive patterns of structural diversity have emerged from several studies of molecular assemblages, none of which are exhibited by the classes of compounds used in living systems. Studies of carbonaceous chondrites like Murchison have revealed the following structural characteristics (taken from Cronin & Chang 1993):

(1) The abundances of compounds decrease with increasing carbon number (e.g. α -methyl branched and straight chain series of α-amino acids)

(2) The abundances of branched chain isomers far exceed those of the straight chain isomers (e.g. α-methyl and α-methyl branched isomers vs. straight chain α-isomer)

(3) Structural diversity dominates at the lower carbon numbers (e.g. acyclic monoamino acids).

Overall, ~70 amino acids have been identified to date among the 159 possible $C_2$ to $C_7$ isomers (Cronin & Chang 1993, Botta *et al* 2001, Botta & Bada 2002); eight of these are used in terrestrial proteins. Presently, life is known to encode only 20 protein α-amino acids, all of which have an α-H group. Living systems use a ubiquitous but restricted number of isomers from a few classes of organic compounds to fulfill requirements for structure and function.

The observed patterns of variation in molecular structure and abundance with increasing carbon number in carbonaceous chondrites suggest synthesis routes involving small free radical initiators and intermediates (Cronin & Chang 1993, Curl 1993). Such pathways tend to produce all possible structural isomers at lower carbon numbers by more or less random synthesis. Primary reactions in interstellar clouds could have produced mixtures of nitriles and other compounds. When exposed to liquid water on the meteorite parent body, the nitriles would have been converted to various substituted and unsubstituted carboxylic acids, including the amino acids. Other classes of compounds were likely to have formed in secondary reactions. For example, the Strecker synthesis of cyanohydrins and aminonitriles from HCN, aldehydes/ketones and ammonia/amines, followed by hydrolysis, could account for the synthesis of some of the α-amino- and α -hydroxy acids. Amino acids substituted at more distant positions from the carboxyl group require other synthetic pathways. These pathways have not been identified and are an important research topic for the future.

The Tagish Lake meteorite, a very recent fall showed a s of soluble organic compounds including mono- and dicarboxylic acids, dicarboximines, pyridine carboxylic acids, sulphonic acid and aliphatic and aromatic hydrocarbons in contrast to carbonaceous chondrites such as Murchison, Orgueil and Ivuna (Pizzarello *et al* 2001, Ehrenfreund *et al* 2001a). There are practically no amino acids found in Tagish Lake, but the meteorite shows evidence of substantial aqueous alteration yet no Strecker-type products. Almost all research on organic molecules in meteorites has focussed on the Murchison meteorite. Tagish Lake shows that it is important to investigate other carbonaceous chondrites, in particular recent finds (in Antarctica) and falls.

‘Prebiotic’ evolution appears to have occurred early on some parent bodies of carbonaceous meteorites, and yet despite the abundance and diversity of organic compounds identified, the chemistry falls short of creating life. Nevertheless, samples from these objects offer a rich and accessible source of information for identifying model characteristics for organic matter and their environments.

Becker *et al* (2000) have identified an extensive suite of high molecular weight carbon molecules ($C_{60}$ to $C_{400}$) or fullerenes in the Murchison and Allende carbonaceous chondrites. These caged carbon molecules contain trapped noble gases that are "planetary' in composition. Fullerenes are now accepted as the third form of pure carbon besides diamond and graphite. Previous investigations of the nature of noble gases in meteorites centered on the isolation of the carrier phase. After much debate, it was determined that these gases are trapped in carbon including diamond, graphite and amorphous phases. It is difficult to reconcile how noble gases may be trapped or retained in amorphous carbon or even graphite grains since these carbon forms have no closed structure (diamond is tetrahedral and fullerenes are closed cage molecules that can easily trap noble gases). The abundance of noble gases measured in isolated fullerenes and diamonds, however, does not explain the amount of planetary gas measured in the bulk carbon-rich acid residue. More work is needed to resolve these differences and to better characterize the amorphous carbon phase in carbonaceous chondrites.

A search for fullerenes in sedimentary deposits associated with severe mass extinctions on the Earth (e.g. the Cretaceous/Tertiary, Permian/Triassic) has also resulted in the isolation and identification of fullerenes with this unique planetary signature (Becker *et al* 2001). Based on these findings, fullerenes appear to form in an extraterrestrial environment, are exogenously delivered to the Earth in some meteorites or comets and contribute to the inventory of volatiles identified in terrestrial planetary atmospheres. Thus, the notion that large impact events lead to complete devolatilization and destruction of most of their organic inventory needs to be re-examined (see section 8).

### 7.3 Interplanetary Dust Particles IDPs

Finally, IDPs are considered to be small fragments of objects stored at very low temperature (Sandford & Walker 1985, MacKinnon & Rietmeijer 1987, Bradley & Keller 1999, Keller *et al* 2000, Messenger 2000, Rietmeijer 2002). Among these objects are carbon-rich icy asteroids, comet nuclei from the Oort cloud, and comets from the Kuiper belt. Except for the most volatile compounds, IDPs may preserve unchanged the nature of the materials present in these bodies. As such, they would be among the most important indicators of silicate and organic materials present in the early phases of formation and evolution of our solar system. IDPs are composed of mixtures of many minerals, such as anhydrous pyroxene and olivine and hydrated layer silicates or mixtures of sulfides, carbonates, sulfates as well as organic compounds. A systematic study of carbon compounds has been conducted by Flynn (2000) and showed that organic carbon, including aliphatic hydrocarbon, are common in IDPs. Models, which are assuming an organic carbon content of ~2 % in such particles, indicate that the accretion of IDPs currently contributes more than 10,000 kg/year of unpyrolyzed organic matter to Earth (Flynn 2000).

Preliminary studies have suggested that grain surfaces could have an important role in chemical processes related to the prebiotic formation of molecules relevant to the origin of life on Earth. In particular, adsorption and catalysis on mineral surfaces have been shown to facilitate chemical reactions such as the polymerization of amino acids and nucleotides or the synthesis of complex molecules. IDPs are very porous, showing a high surface/volume ratio. Unlike large objects with the same porosity, IDPs survive during the entry into the Earth atmosphere. The presence in such grains of inorganic components with layered or porous cavity structure could provide large surface areas which represents a favorable local microenvironment where a high content of energy can be stored and utilized for prebiotic chemical reactions.

## 8. Delivery to Earth and prebiotic consequences

Having inventoried the classes of identified organic molecules and mechanisms for their production in space, we turn now to the question of delivery of these materials to the terrestrial planets. Of particular interest are those mechanisms that may have been in play early in the Earth's history, when infalling organic compounds could have contributed to the chemical evolution leading to the origin of life.

The notion of extraterrestrial delivery of organic matter to the early Earth has gained wide recognition because of the indisputable evidence that biomolecules, such as amino acids, have reached the Earth's surface associated with meteorites (e.g. Botta & Bada 2002). Extraterrestrial organic material reaches the Earth in one of three ways: (1) As a component of dust grains and other particulates (< 1 mm) that rain perpetually down to the planet and is ultimately of asteroidal and cometary origin, (2) as part of a cometary payload, and (3) incorporated in asteroid fragments (meteorites) that hit the planet. The proportion of material that survives these delivery processes without modification is unknown. The fraction that is altered on its way to the Earth's surface to form new compounds (e.g. McKay & Borucki, 1997; Sugita & Schultz 2001) is usually counted in the terrestrial prebiotic inventory. The overall contribution of larger objects, such as comets and asteroid, to the early Earth's inventory of organic matter has generally been considered to be insubstantial, however, because of the significant heating associated with passing through the Earth's atmosphere and the impact itself.

### 8.1 Numerical simulations of impact events

Although the contribution to the extraterrestrial inventory of carbon to the early Earth from IDPs and micrometeorites may have been significant (e.g. Maurette 1998, Maurette *et al* 2000), models of delivery of extraterrestrial material to the surface of the planet have focused on large (>1 km) body impact events. The principal argument against direct delivery of organic material to the Earth by these larger objects focuses on the very high temperatures expected in a high-velocity impact. Any impactor must have a minimum relative velocity of 11.2 km $s^{-1}$ (the escape velocity for the Earth), and this value constrains the possible temperature ranges a comet might experience. Most of the hydrodynamical models for impacts have simplified the nature of the impacting comet by treating it as a sphere of water ice. Because the pressures and temperatures generated in impacts scale proportionally with the density of both the projectile and the impacted material, it follows that the conditions generated in a cometary impact will be less extreme than those generated by an asteroid impacting the Earth at a given speed and trajectory.

Chyba *et al* (1990) calculated that maximum peak temperatures of 40,000 K would be reached if all the kinetic energy of an 18 km $s^{-1}$ comet were converted to heat. They suggested that this temperature multiplied by Boltzmann's constant is much higher than the activation energies typical for pyrolysis reactions of organic compounds (i.e., $k_BT >> E_a$) and that an impact should induce complete breakdown of any organic molecules present. Subsequent modeling (Blank & Miller 1998, Pierazzo & Chyba 1999) suggests that special conditions such as oblique impacts would generate lower peak temperatures.

When temperature alone is taken as a measure of chemical stability, the possible impact delivery flux would appear insignificant in comparison to terrestrial production mechanisms. Blank & Miller (1998) reevaluated this kinetic argument using canonical activation volumes for bond breaking which, when positive, favor slower reaction kinetics associated with bond cleavage (e.g. pyrolysis) as pressure increases. On the basis of simple Arrhenius-like behavior, the rate of pyrolysis at 7,000K and 100 GPa, conditions corresponding to planar impact of a water ice comet against a basaltic crust at escape velocity, should be comparable to that at 900K and 1 atm. Given the short time scale of an impact event, on the order of a second, organic compounds present in comets might survive brief exposure to high temperature and simultaneous high pressure, and their flux to the surface of the planet might therefore be significant. These authors considered the joint effect of pressure and temperature together and cautioned that intuition based on observations of material behavior at ambient pressure and high temperatures are likely to mislead.

A thermodynamic argument can also be made for the stability of organic compounds in impacts. If the Clapeyron slope for pyrolysis reactions is steeper than the slope of loci of states achieved by a shocked material, then the thermodynamic path of the shocked material will favor the stability of reactants versus that of pyrolysis products to a higher temperature, than predicted by a breakdown reaction boundary. Similarly, the pressures achieved in impacts also favor the combination of organic monomers to form polymers, including the combination of amino acids to form polypeptides.

Finally, the temperatures incurred in oblique collisions can be more moderate than might be assumed. Shock temperatures scale with the normal component of the impact velocity, which can be made arbitrarily small as the impact vector approaches the horizontal (Blank & Miller 1998). Obliquity reduces the vertical component of the impact velocity but increases the horizontal component. The kinetic energy of the horizontal (tangential) velocity component must be dissipated as heat, which could result in temperatures as high as ~ 40,000 K. However, hydrodynamic phenomena such as jetting (e.g. Miller 1998) produce heterogeneous energy distribution. In fact, parts of the jetted material ejected in the opposite direction of the impact vector may experience very low peak temperatures (owing to the obliquity of the impact) and very low residual horizontal velocity (owing to the speed and orientation of the outflow jets). Blank & Miller (1998) examined impact jets formed from a comet made of water ice hitting a rocky Earth and considered the possibility of landing part of a comet as liquid water (an idea proposed by Clark 1988) which could be a localized reservoir of exogeneous organic matter at elevated concentration levels in aqueous solution.

Although the fraction of a given object that could be "soft landed" as a liquid pool may be small (in particular because the jetted material represents only a few percent of the total impactor mass), it may be a small fraction of an arbitrarly large impactor.

Most numerical models of large-scale impacts applied to the question of extraterrestrial delivery of organic material have invoked a comet collision with an ocean. While this impact scenario will allow a minimum of heating associated with impact, cometary organic material delivered in this fashion would merely add to the repository of organic material in the ocean rather than create an aqueous environment rich in organics. Blank & Miller (1998) focused on the alternative impact scenario of a comet colliding at a low angle with a rocky Earth surface in order to identify those regions of the impactor most likely to bring a source of concentrated organic material to the surface of the planet. They noted that material jetted in the direction opposite to the impact would have a) the lowest temperatures and b) the lowest kinetic energy (and hence velocity) among the impacted cometary materials. The low temperatures would increase the likelihood for delivery of cometary water-ice in the form of liquid water. The low relative velocities would maximize possibilities for the delivery of material, in the form of water and associated organic compounds, without its being dispersed and diluted. In other words, the reverse-directed portion of the impacted comet offers the greatest potential for the extraterrestrial delivery of a concentrated aqueous pool rich in organic matter. If such a low-angle impacting comet were to deliver even a few percent of its material in this manner, the contribution to the overall organic flux would be significant, if not overwhelming (see Table 6).

## 8.2 Laboratory Experiments

Hypervelocity shock experiments have been conducted to characterize the survivability of organic compounds in carbonaceous chondrites and water or water ice (to represent comets). These experiments typically involve a stationary sample in a metal container that is impacted by a high-speed metal bullet accelerated down a flight tube, or gun barrel, to velocities of several km $s^{-1}$. Pressures, generated by the metal-metal collision, are higher than would be produced by a direct impact of the sample materials alone. Sample impact pressures are therefore higher for a given impact velocity due to the reverberation, or "ringing up", of shock waves through the sample material as they reflect off the metal surfaces of the container. In general, though the pressures achieved in these experiments correspond to those of a low-angle impact, the temperatures are lower than would be expected in a natural scenario. The duration of the impact is substantially shorter because it scales with the thickness of the impactor, which in the laboratory is on the order of millimeters.

There have been few impact studies on the shock chemistry of the organic materials associated with carbonaceous meteorites. Tingle *et al* (1992) reported results from three shock experiments on cored pieces of the Murchison meteorite encapsulated in stainless steel capsules. The samples experienced peak pressures as high as 19, 20, and 36 GPa, respectively, through a sequence of shock reverberations (e.g. Gibbons & Ahrens 1971), and recovered samples were analyzed by thermal desorption photo-ionization mass spectrometry.

While there was negligible change in the organic constituents of samples shocked to peak pressures less than 20 GPa, approximately 70% of the original organic matter degraded in the sample exposed to a 36 GPa impact. The residual organic compounds appeared to have a lower C/H ratio than the starting material, suggesting that the bulk composition had changed. As neither peak temperatures nor time-temperature-pressure histories of the samples are reported, the connection to chemical thermodynamics and kinetics cannot be made. Nonetheless, it is significant that organic material survived the extreme conditions of an impact to some degree. Peterson *et a*l (1997) conducted a series of similar shock experiments over a pressure range of 3.5-32 GPa using powdered Murchison and Allende meteorite samples stripped of their original organic carbon and subsequently doped with well-characterized amino acids whose breakdown and reaction products were readily measured and distinguished. In these experiments, the abundance of residual amino acids was found to diminish substantially with high pressures, with typically 50% loss by 30 GPa. The formation of new daughter amino acids was inferred, in particular the decarboxylation of aspartic acid to form β-alanine.

Cooper *et al* (2000) considered the survivability of four classes of organic compounds known to be indigenous to carbonaceous meteorites, by embedding them in a matrix of Murchison meteorite and subjecting them to laboratory shock pressures of up to 40 Gpa. They observed generally that survival of the compounds studied was inversely proportional to shock pressure (organic sulfur survived best, followed by organic phosphorus, PAHs and amino acids).

Blank *et al* (2001) simulated cometary impacts using water and/or ice doped with five amino acids (LD-2-Aminobutyric acid (AMB) and L-Norvaline (NOR), L-Lysine (LYS), L-Phenylalanine (PHE), and D-Proline (PRO)) and subjecting their aqueous samples to impact conditions ranging over 5-21 GPa and 412-870 K lasting several microseconds. Post-experiment analysis demonstrated survival of >40-75% of the original amino acids; the cyclic amino acid, Phe, was the most reactive while the aliphatic amino acids, LYS and NOR, were the least. They also observed the persistence of the original population of amino acids to a greater extent in those capsules shocked to a higher peak pressure and temperature, contrary to the trend associated with the solid or powder samples mentioned above. The reason for this is uncertain, though it may be due to the higher-temperature thermal histories of the organic materials associated with the silicates host materials. Of possibly greater significance is the fact that the dominant reaction products identified by Blank and co-workers consisted of dipeptides formed from all possible combinations of the initial amino acids, with lesser amounts of higher-order peptides also present. A peptide bond forms via a dehydration synthesis reaction between the carboxy group of the first amino acid with the amino group of the second amino acid. Cyclic dipeptides (diketopiperazines), formed by two amino acids linked together following loss of two water molecules, were also abundant among reaction products. These experiments demonstrated a mechanism by which impacts might actually increase the complexity of biologically relevant molecules from an initial starting pool.

### 8.3 Relevance to the prebiotic inventory of the Earth

Dynamical considerations and experimental results thus support the possibility of organic carbon delivery via large impacts – both in its pristine form and evolved in the impact to longer polymers. The flux of organic matter to the Earth via comets and asteroids, averaged over the period of heavy bombardment prior to 3.8 Ga ($10^9$ yr), may have been as high as $10^{11}$ kg $yr^{-1}$ (calculated from data in Chyba *et al* 1990, see also Zahnle & Sleep 1997, Table 6). This estimate is larger than the value of $10^{8-10}$ kg $yr^{-1}$, the best estimate of the terrestrial contribution during that time, assuming that the atmosphere was moderately oxidizing (Chyba and Sagan 1997). As an example, consider the contribution of HCN. Assuming that cometary nuclei have a 1 g $cm^{-3}$ density, a comet 1 km in diameter would contain 2 x $10^{11}$ M HCN, equivalent to 40 nmoles $cm^{-2}$ on the Earth's surface, or more than the estimate for the annual production of HCN in the atmosphere (Miller & Lazcano, 2002). Note that this calculation assumes a complete survival of the HCN on impact (Miller & Lazcano 2002), and therefore represents an upper limit on such a cometary contribution.

Cometary flux of organic material may overshadow the possible contribution via IDPs, which until recently was perceived as the most efficient mechanism for extraterrestrial delivery (Anders 1989) (see Table 6). Thus even a small fraction of organic material, delivered intact in a cometary body, could have a significant influence on the global budget. In addition, impact delivery may potentially localize this flux in space and time, leading naturally to concentrations of organic material significantly above levels easily achieved by endogenous production mechanisms. However, geological approaches are limited in their ability to probe this period of interest because of the fragility of organic compounds and the paucity of the ancient sedimentary record. While a better preserved record of early planetary history may exist on Mars, the controversy raised from the recent appraisal of the ALH84001 Martian meteorite (McKay *et al* 1996) illustrates that the question of early organic environments and life on Mars will likely remain unanswered until samples can be returned to Earth.

**Table 6**

Modified from Chyba & Sagan (1997).

* Assumes intermediate atmosphere, defined as $[H_2] / [CO_2] = 0.1$

[1] Synthesis of the Miller-Urey type

[2] Such as that caused by lightning interacting with a volcanic discharge

[3] An estimate for compounds created from the interaction between infalling objects and the Earth's atmosphere

[4] Based on present-day estimates for total organic matter in hydrothermal vent effluent as reported by Kadko *et al* (1994); cf., Elderfield & Schultz (1996)

[5] Conservative estimate based on possible cumulative input calculated assuming flux of $10^{22}$ kg of cometary material during first Ga ($10^9$ years) of Earth's history. If comets contain on the order of 15 wt% organic material (e.g., Delsemme, 1992), and if ≈ 10% of this material survives, it will comprise approximately $10^{11}$ kg $yr^{-1}$ average flux via comets during the first $10^9$ Ga.

**Major Sources (in kg/yr) of Prebiotic Organic Compounds in the Early Earth**

| Terrestrial Sources | kg/yr* |
|---|---|
| UV Photolysis[1] | $3 \times 10^8$ |
| Electric Discharge [2] | $3 \times 10^7$ |
| Shocks from impacts[3] | $4 \times 10^2$ |
| Hydrotheraml Vents[4] | $1 \times 10^8$ |
| Extraterrestrial Sources[5] | |
| IDP's | $2 \times 10^8$ |
| Comets | $1 \times 10^{11}$ |
| Total | $10^{11}$ |

# 9. The hydrogen isotopic composition (D/H) in solar system organic matter and water

## 9.1 The synthesis of organic matter and water in the primitive solar system as recorded by the deuterium to hydrogen isotope ratio (D/H)

The hydrogen isotopic composition (referred to as the deuterium-hydrogen ratio, D/H) of water and organic matter is, in principle, an efficient tool to reconstruct the chemical synthesis of H-bearing volatile components in the early solar system. From an "astrobiological" perspective, it is interesting to note that water and organic molecules are often associated in primitive planetary bodies such as meteorites, comets and IDPs. Accordingly, if water and organic matter, the essential components of life, originated in space, they may have originated in similar conditions.

This point of view is reinforced by the fact that, throughout the solar system, water and organic matter are systematically enriched in deuterium ($125 \times 10^{-6} < D/H < 2000 \times 10^{-6}$) relative to the "protosolar" D/H, i.e. to $D/H = 26 \pm 5 \times 10^{-6}$ (Geiss & Gloecker 1998). No stellar (nuclear) process can yield such an isotopic enrichment, which is thus ascribed to chemical isotopic exchange reactions (on planets from which hydrogen can escape, enrichment can also occur as H escapes more readily than D). During these reactions, the deuterium of the protosolar hydrogen reservoir, which is in the form of the neutral atomic D or of molecular hydrogen HD, is transferred to water and to organic matter. It is now generally accepted that such a large enrichment in deuterium can only be achieved at low temperature ($T < 200$ K), in media dominated by hot atom (ions or radicals) chemistry. In that respect, the deuterium enrichment suggests that solar system organic matter and water share a common origin. However, this origin is poorly understood.

In recent reviews (Robert *et al* 2000, Robert 2001), the D/H in the insoluble organic matter (IOM) and in the water-bearing minerals (clays) embedded in the carbonaceous meteorites have been compared to their interstellar and cometary counterparts (only available for the volatile components). Instead, we have selected the limited number of solar system objects for which water and OM D/H were both measured. Averaged published data along with their proper references on water and OM D/H are presented in Table 7 and are discussed briefly in the notes of the Table. In Table 7, D/H are all reported in units of $10^{-6}$ in order to be easily comparable. A discussion of these data can be found in Robert (2002). The comparison of water and organic matter D/H allows a qualitative model to be developed, which may account for the solar system D/H variations.

In Figure 9, the data of Table 7 are reported with the water D/H as the X-axis and the organic matter D/H as the Y-axis. The distribution of the data in Figure 9 cannot be accounted for by invoking the classical turbulent model (the so called $\alpha$-disk) of the protosolar nebula (Cassen 1994, Dubrulle 1992). In such models, the evolution of the water D/H ratio in the protosolar gas has been modeled through the following isotopic exchange reaction (Lécluse & Robert 1994, Drouart *et al* 1999):

$$HD + H_2O \leftrightarrow HDO + H_2 \qquad (1)$$

This isotopic exchange is supposed to occur in the gas phase before the condensation of water. Numerical models of isotopic exchange and homogenization in a hot, dense, and turbulent nebula have reproduced the variation of water D/H observed between comets and carbonaceous meteorites using times of 1 million years (Drouart *et al* 1999).

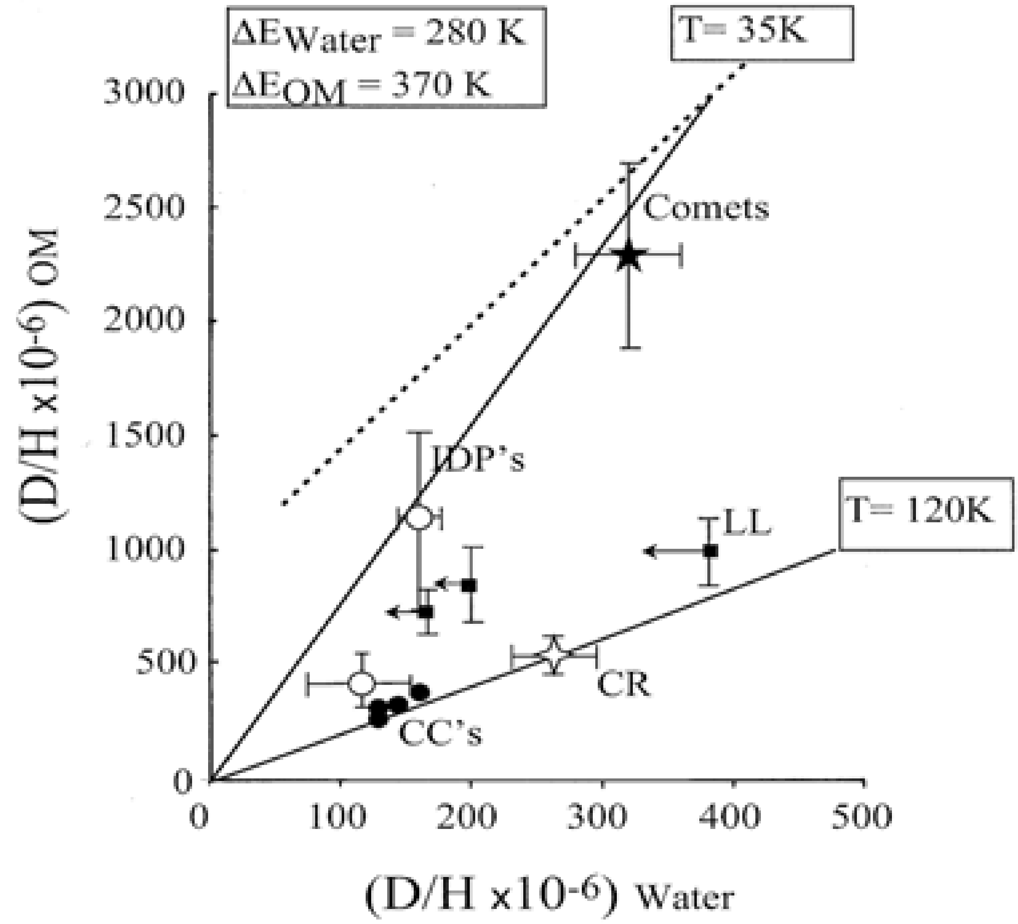


**Figure 9**

The water D/H abundance ratio is reported versus the OM D/H (Table 7). The dashed line is the theoretical pathway of isotopic exchange of water and OM with molecular hydrogen in the canonical turbulent proto-solar nebula (the so called α-disk; unpublished calculations from F. Hersant; pers. communication). The two solid lines correspond to the kinetic co-evolution of the water and OM D/H and can be regarded as "isotopic thermometers". The calculated temperatures for these two isotopic evolution pathways are 35 and 120 K. The calculated high and positive energies ($\Delta E_{OM}$ and $\Delta E_{Water}$, see eq. 7 and following discussion) likely correspond to isotopic exchanges via ion-molecule reactions. This interpretation suggests that the deuterium enrichment process was "similar" in the whole solar system and the temperature of the isotopic exchange varied with heliocentric distance. Consequently, the young Sun, in its YSO phase, seems to have governed the deuterium enrichment via an intense ionization of the surface of the protosolar nebula. CC, CV, CR and LL3: Different petrologic types of Carbonaceous (C's) and Ordinary (LL3) chondrites; IDPs : Interplanetary Dust Particles.

Using the same model, the evolution of the organic matter D/H in the protosolar nebula was also numerically simulated in order to account for the cometary value. Taking appropriate initial interstellar D/H for water and organic matter (HCN in the case of comets), the model yields the observed cometary D/H. It is important to note that, in this model, the initial isotopic conditions are defined by two fixed values for water and organic matter D/H. These ratios are interpreted as the interstellar D/H, carried by water and organic matter that predates the formation of the solar system. During the evolution of the nebula, no fresh interstellar water or organic matter is supposed to be injected in the gas. In this respect, the model represents an evolution in a closed system. For given parameters describing the initial physical conditions of the nebula (its radius, mass, accretion rate and coefficient of turbulent viscosity), there is only one single pathway describing the relations between water and organic matter D/H. An example of such pathways is shown in Figure 9 as a dashed line (after Mousis *et al* 2000). According to this model, the D/H of grains move along this dashed line as a function of time and of heliocentric distance at which organic matter and water condensed on these grains.

However, a systematic study of this type of calculated pathway (F. Hersant pers. comm.) has shown that $\alpha$-disk models cannot account for the distribution of the D/H reported in Figure 9 because (1) two given initial water and organic matter D/H ratios correspond to a unique evolution pathway (as shown by the dashed line) (2) whatever the initial conditions, no isotopic variation in the water D/H is expected between 0.5 and 4.0 AU. The case of the Renazzo meteorite (noted CR in Figure 9), whose water D/H is twice the values of other carbonaceous meteorites, is in clear contradiction with this theoretical prediction. It seems therefore unavoidable that, beside the isotopic exchange within the protosolar molecular hydrogen, an additional process has played a role in establishing the D/H ratio of solar system objects. Such a possible process is now presented.

First, it must be noted that, according to the Figure 9, water and organic matter are not related by a unique isotopic fractionation process, which would give a linear (proportional) correlation in this diagram, with the isotopic fractionation factor being the slope of the correlation. In Figure 9, two solid lines were arbitrarily drawn. They do not represent possible correlations in the diagram but define the upper and lower limits of the isotopic variations: the upper limit is defined by the comets and by one IDP and the lower limit by the carbonaceous meteorites.

They also correspond to the inner and outer regions of the solar system (meteorites and comets respectively; the origin of IDPs are still in debate).

Let us assume that these lines result from two coupled isotopic fractionation processes: (1) a fractionation between organic matter and $H_2$ and (2) another one between water and $H_2$.

That is :

$$\alpha_{\text{water-H2}} = (D/H)_{\text{water}} / (D/H)_{H2} \quad (2)$$

$$\alpha_{\text{OM-H2}} = (D/H)_{\text{OM}} / (D/H)_{H2} \quad (3)$$

The isotopic fractionation factor noted $\alpha$ in (2) and (3) is different from the coefficient of turbulent viscosity, also noted $\alpha$, and used to designate the circum solar nebula as an $\alpha$ -disk.

Coupling these two isotopic exchange processes yields:

$$\alpha_{\text{OM-water}} = (D/H)_{\text{OM}} / (D/H)_{\text{water}} \quad (4)$$

The slopes of the two lines drawn in Figure 9 may thus stand for two different values of $\alpha_{\text{OM-water}}$. Since the isotopic fractionation factor $\alpha$ depends exclusively on the temperature, the two lines can be viewed as isotopic thermometers.

At a first order of approximation, let us express the isotopic fractionation factors as :

$$\alpha_{\text{water-H2}} = (D/H)_{\text{water}} / (D/H)_{H2} = \text{Exp}(\Delta E_{\text{Water}}/T) \quad (5)$$

$$\alpha_{\text{OM-H2}} = (D/H)_{\text{OM}} / (D/H)_{H2} = \text{Exp}(\Delta E_{\text{OM}}/T) \quad (6)$$

Let us accept without demonstration that, at a given temperature, the D/H of OM and water move linearly in Figure 9. That is to assume: at a given temperature T, the position on the line is kinetically controlled by the rates of the isotope exchange. The slope s of the line is:

$$s = \text{Exp}\,[\,(\Delta E_{\text{OM}} - \Delta E_{\text{Water}}) / T\,] \quad (7)$$

It is possible to calculate a value for $\Delta E_{\text{OM}}$ and $\Delta E_{\text{Water}}$ that will fulfill two conditions: (1) matching the slopes of the two solid lines reported in Figure 9 (2) giving equilibrium values for $\alpha$'s higher than the highest D/H ratios on each line; i.e.higher than CR and cometary D/H ratios. An example of a possible solution is $\Delta E_{\text{OM}} = 370$ K and $\Delta E_{\text{Water}} = 280$ K, giving temperatures of 120K and 35K for the two lines. These temperatures must be considered as upper limits since for $\Delta E_{\text{Water}} >$ 280 K, temperatures <120 K and <35K would correspond to the two lines drawn in Figure 9 (with $\Delta E$'s still fulfilling the two conditions). Interestingly, the $\Delta E_{\text{OM}}$ and $\Delta E_{\text{Water}}$ are close to the following known isotopic exchange ion-molecule reactions:

$$H_3^+ + HD \rightarrow H_2D^+ + H_2 \qquad (\Delta E_8 = 227\ \text{K} \approx \Delta E_{\text{Water}}) \quad (8)$$

$$CH_3^+ + HD \rightarrow CH_2D^+ + H_2 \qquad (\Delta E_9 = 370\ \text{K} \approx \Delta E_{\text{OM}}) \quad (9)$$

Such ion-molecule reactions that characterize the interstellar chemistry between 10-100 K, are known to be a fast even at these low temperatures (Brown & Rice 1981, Guélin *et al* 1982, Rodgers & Millar 1996, Willacy & Millar 1998). The scenario for isotopic fractionation of hydrogen in the early solar system is based on these considerations (Fig. 9). The calculated isotopic temperatures stand for the last isotopic exchange with the solar system hydrogen reservoir. These temperatures do not preclude the formation of water (and OM) at 10-20 K in the ISM and subsequent isotopic re-equilibration with H during the collapse of the interstellar cloud that yielded the formation of the protosolar nebula. Such partial reequilibration is observed in water in hot cores regions (cf. Table 7).

**Table 7**

D/H ratios of water and organic matter in the solar system reported in units of $10^{-6}$.

Notes (1) Organic matter: OM. In meteorites SOM and IOM refer to as soluble and insoluble fractions, respectively (2) Interstellar Medium: dense molecular clouds (3) Domain defined for different initial fractions of atomic D and different "condensed solid" to gas ratio. (4) Domain defined for different organic molecules. (5) Mostly measured in HCN. (6) Four independent spectroscopic determinations on 3 comets. (7) OM as HCN in Hale-Bopp (8) From SNC meteorites. (9) The D/H ratio in meteoritic water is calculated by mass balance using C and H concentrations and D/H ratios, determined in whole rock and IOM samples. (10) Error bars stand for 1 $\sigma$, calculated on mean values averaged from published data. (11) Maximum values corrected for solvent contamination during SOM extractions. (12) Water D/H ratio cannot be calculated but must be lower than that of the whole rock D/H ratio; hence the sign ≤. (13) Clays in Semarkona range from 85 to 720 x$10^{-6}$. (14) Two deuterium-rich organic compounds were identified in this IDP with D/H = 250 and 1500 x $10^{-6}$; hence the large error bars. (15) Calculated assuming C/H in organics = 1 and a C/H in the bulk comet between 0.4 and 0.6.

References : [ 1 ]: Brown & Millar (1989). [ 2 ]: Guélin *et al* (1982). Millar *et al* (1989). [ 3 ]: Jacq *et al* (1990). [ 4 ]: Gensheimer *et al* (1996). [ 5 ]: Hatchell et al (1998). [ 6 ]: Schilke *et al* (1992). [ 7 ]: Meier *et al* (1998). [ 8 ]: Balsiger *et al* (1995). Eberhardt *et al* (1987). Bockelée-Morvan *et al* (1998). [ 9 ]: Leshin (2000). [ 10 ] Lécuyer *et al* (1998). [ 11 ]: Becker & Epstein (1982). Boato (1954). Deloule & Robert (1995). Deloule *et al* (1998). Epstein *et al* (1987). Halbout *et al* (1990). Kerridge (1985). Kerridge *et al* (1987). Krishnarnurthy *et al* (1992). Pizzarello *et al* (1991). Mc Naughton *et al* (1981). Mc Naughton *et al* (1982). Robert *et al* (1979). Robert & Epstein (1982). Robert *et al* (1987). Sears *et al* (1995). Yang & Epstein (1983). Yang & Epstein (1984). McKeegan *et al* (1985). Zinner *et al* (1983). [ 12 ] Messenger & Walker (1998), Messenger (2000) Aléon *et al* (2002) [ 13 ] Geiss & Gloecker (1998).

| **Sample** | **$(D/H)_{H2O}$ x $10^{-4}$** | **$(D/H)_{OM}$(1) x $10^{-6}$** | **Remarks** |
|---|---|---|---|
| ***ISM*(2)** | 17,000 to 40,000 | 9000 to 33,000(3) | Calculated; 10K, H=$10^3$cm$^{-3}$ *Ref.[1,2]* |
| ***ISM*(2)** | < 900 | 5000 to 45,000(4) | Measured at 10K, H=$10^3$cm$^{-3}$ *Ref.[2]* |
| ***ISM*(2)** | ? | 2000 to 60,000(4) | Measured at 70K, H=$10^3$cm$^{-3}$ *Ref.[2]* |
| Hot Cores | 30 to 1000 | 1000 to 5000(5) | Measured at 150K, H=$10^7$cm$^{-3}$ *Ref.[3,4,5,6]* |
| Comets | 320 ± 40(6) | 2300± 400(7) | $(D/H)_{Bulk}$ = 1200±200 $10^{-6}$ (15) *Ref. [7,8]* |
| Mars | 300±20 | ? | *Ref. [9]* |
| Earth | 149±3 | 140 | *Ref. [10]* |
| Meteorites(9,10) | | | *Personal compilation of Ref. [11]* |
| CI,CM | | IOM | *Mean values of published data* |
| Orgueil | 160±10 | 383±5 | $(D/H)_{Bulk}$ = 191±7 |
| Cold-Bokkeveld | 126±5 | 280±30 | $(D/H)_{Bulk}$ = 140±5 |
| Murray | 130±5 | 265±50 | $(D/H)_{Bulk}$ = 171 |
| Murchison | 142±6 | 330±20 | $(D/H)_{Bulk}$ = 150±6 |
| | | SOM(11) | |
| Murchison | | 369 | Amino Acid |
| Murchison | | 262 | Monocarboxylic Acids |
| Murchison | | 220 | Hydrocarbons |
| CR | | | |
| Renazzo | 260±35 | 545±80 | $(D/H)_{Bulk}$ = 282±33 |
| LL(9) | | | |
| Semarkona | <390(12,13) | 1010±150 | $(D/H)_{Bulk}$ = 395±30 |
| Bishunpur | <200(12) | 860±160 | $(D/H)_{Bulk}$ = 200 |
| Chainpur | <165(12) | 735±100 | $(D/H)_{Bulk}$ = 165 |
| IDP's | | | *Ref. [12]* |
| K1 | 160±16 | 1096±380(14) | $(D/H)_{Bulk}$ = 295 |
| A6 | 129±38 | 389±85 | $(D/H)_{Bulk}$ = 287 |
| Protosolar $H_2$ | | | 25±5 *Ref. [13]* |

According to the present interpretation, inner solar system water and OM were isotopically fractionated to a different extent but both at the same temperature (120 K). In the outer solar system, a similar type of isotopic fractionation occurred but at much lower temperature (35 K). The LL meteorites fall in between the two lines, attesting that their organic matter and water formed at temperatures intermediate between carbonaceous meteorites and comets. Since the isotopic temperatures for inner solar system objects (meteorites) are higher than for outer solar system objects, the deuterium enrichment seems to be governed by a heliocentric parameter. This observation can be understood in the light of modern theories of star formation, in which the temperature in the solar nebula decreases with increasing heliocentric distance.

Astronomical observations provide compelling evidence that all young solar-type stars go through a T-Tauri phase (see section 4) and emit an intense flux of X-rays that irradiates the surface of their surrounding disk (André & Montmerle 1994). Calculations suggest that X-rays penetrate deep into the gaseous disk and the ionization rate of the disk greatly exceeds that of the ISM (Chiang *et al* 2001, Glassgold *et al* 2000). The degree of ionization, the thickness, and the temperature of the ionized disk vary as a function of the distance to the Sun. Ion-molecule reactions such as those depicted by (8) and (9) can rapidly proceed (Aikawa *et al* 1999). Once formed at the surface of the disk, organic and water molecules can sink in the deeper, denser and neutral regions of the disk - the so-called protosolar nebula (Cassen 1994, Dubrulle 1992, Drouart *et al* 1999) - where they are protected from solar ionizing particles. This interpretation may not be in conflict with classical $\alpha$-disk models of the protosolar nebula such as the one developed by Drouart *et al* (1999). However, it strongly suggests that the nebula cannot be treated as a closed system: chemical species, formed via non-thermal chemical reactions, were injected into the protosolar gas, during its temporal and spatial evolution. The preservation of isotopic thermometers in such an open system - as depicted in the Figure 9 - remains an open issue. Indeed, isotopic systems may have eventually lost the memory of their reaction temperatures since their D/H ratios can be partially reset via reaction (1). Such an issue is beyond anything which can be calculated with the presently available models of the protosolar nebula. Nevertheless, the proposed solar irradiation scenario offers a plausible interpretation pointing toward a local and a common origin for both water and organic matter.

### 9.2. Using the D/H ratio to decipher the origin of water in the terrestrial planets

In the case of the terrestrial planets, most of the $H_2O$ may well have been brought in the form of hydrous minerals or adsorbed water, but the contribution from comets remains uncertain. We may be able to rule out comets as the sole carrier by comparing D/H in cometary water with D/H = $155 \times 10^{-6}$ in the oceans. In the three Oort cloud comets measured thus far, D/H = $320 \pm 50 \times 10^{-6}$, essentially twice the value found in the oceans. On the other hand, near-surface water on Mars appears to have the same isotopic ratio as the comets, suggesting that both Mars and Earth received some cometary endowment.

On Earth, the cometary water would have been thoroughly mixed with water from the planet's interior, thanks to the geological activity (eruption, subduction) on this planet. On smaller Mars, the hydrosphere has remained isolated from the lithosphere, as demonstrated by studies of the oxygen isotopes in Martian meteorites.

To determine how much cometary water reached the Earth, we need to know the value of D/H in the water that was brought in by the rocks. In the extreme case that this water fully equilibrated with the nebular hydrogen, we would have $D/H = 26 \times 10^{-6}$ and 50% of the oceans would have been supplied by comets. Another conservative estimate can be based on the lower limit observed in water, extracted from meteorites, i.e. $120 \pm 26 \times 10^{-6}$ : in such case 15% of the oceans have been supplied by comets.

### 9.3. Elemental mass balance of volatile elements: a constraint for the origin of planetary atmospheres

Besides the D/H ratio, elemental mass balance calculations can in principle be used to constrain the origin of the volatiles on terrestrial planets. For example, if one assumes that comets brought in the Earth's nitrogen and carbon, we may ask how much water would accompany these elements. However, uncertainties in cometary elemental abundances, and even in the solar C/O ratio (Prieto *et al* 2002) make this procedure difficult at present.

A closer specification will be possible when we know the abundances and isotopic architecture of the heavy noble gases krypton and xenon in comets. If it turns out that Kr/Xe and the relative abundances of the Xe isotopes are the same in comets as they are in the atmospheres of Earth and Mars, which are known to be different from carbonaceous chondrites, there will then be a prima facie case that comets indeed impacted the Earth, bringing their volatiles with them. Furthermore, it will be possible to estimate the total $H_2O$ (or C or N) brought by comets simply by ratioing to one of these heavy noble gases.

If comets indeed brought at least some fraction of the water on Earth and the other inner planets, these icy messengers must have delivered some carbon and nitrogen as well. As already mentioned C/O should have the solar value in comets, while N/O may be depleted by about a factor 5 (Altwegg *et al* 1999, Krankowsky 1991).
These numbers are derived from investigations of Halley's comet by the Giotto spacecraft and by ground-based telescopes, so there is an assumption here that Halley is truly representative of all Oort cloud comets.

Different types of comets are known to exist, based on relative abundances of the radicals observed in visible spectra. These radicals are daughter products of molecules studied in the radio region or in situ. Thus, we should worry that more fundamental differences in composition may exist that we have not yet identified. This should not be surprising, in view of the immense span of more than 30 AU over which icy planetesimals could have formed in the outer solar nebula, corresponding to a possible range in temperature from 30 to 150 K.

This temperature range permits major differences in amounts of trapped ambient gases in condensing ice, if comets formed from interstellar ice grains that evaporated as they entered the solar nebula and then subsequently recondensed (Lunine *et al* 1991, Owen & Bar-Nun 1995). Despite the uncertainties, the observations of comets recorded thus far indicate that virtually all of them contain volatile nitrogen and carbon compounds in addition to water ice.

## 10. The origin of life

### 10.1 The antiquity of terrestrial life

The basic constituents of life on planet Earth include the genetic materials DNA and RNA as well as proteins and membrane components. DNA is structured in a double helix formed from three different components, nucleic acid bases, sugars and phosphates. Proteins, composed of amino acids, form complex three-dimensional structures and play a central role in biological catalysis. Although amino acids are found in meteorites together with sugar alcohols and nucleobases, it is not clear that their direct exogenous delivery played a role in the origin of life on our planet. Additionally, very little is known about phosphorus chemistry in space.

Deciphering the origin of life requires knowledge of the environment at its onset. Unfortuately, we lack definitive evidence of atmospheric composition, surface temperature, oceanic pH, and other general and local environmental conditions important for the appearance of the first living systems on Earth. Recent data from very old detrital zircon crystals suggests that liquid water could have been around as early as 4.4 Ga ago (e.g. Wilde *et al* 2001, Mojzsis *et al* 2001) The rock remnants of the early Archean are extremely scarce. Most of the record has been lost. The few rocks that were preserved have been metamorphosed to great extent (Isua, Akila). The oldest rock chemical record of life was found in 3.86 Ga old apatite grains from southwestern Greenland which contained graphite inclusions with light carbon ($^{13}C/^{12}C$ ~ -35 to -60 ppm) (Mojzsis *et al* 1996). The association graphite-apatite suggests that microorganisms turned into graphite, while the phosphorus of these microbes formed the source for apatite (calcium phosphate). However, recent new evidence (Fedo & Whitehouse 2002, van Zuilen *et al* 2002) questions the sedimentary nature of the 3.86 Ga Akilia rock formation, suggesting that the isotopically light carbon previously reported (Mojizis *et al* 1996) cannot be proven to be biogenic in origin.

While the evidence for life on Earth 3.86 Ga is debatable, isotopic data of organic carbon from sediments provide evidence that a biological carbon cycle was established on Earth at about 3.6 Ga. It is difficult to confidently elucidate the exact nature of life at this time in Earth's history. The biological origin of features interpreted as fossil remnants in the 3.5 Ga old Australian Apex sediments (Schopf 1993, Schopf *et al* 2002) has recently been challenged (Brasier *et al* 2002). These authors claim that the 3.5 Ga old structures interpreted as similar to photosynthetic microfossils are either non-biological or are the fossil remnants of a microbial community associated with a seafloor hydrothermal system (Brasier *et al* 2002). While it is possible that the Australian Apex sediments do not correspond to a shallow water environment, the biological origin of these structures is not precluded, and thus they may yet remain as the oldest known microfossils in the geological record (Schopf *et al* 2002). If, however, they indeed preserve fossilized vent microflora, then they are certainly not cyanobacterial in origin.

## 10.2 The heterotrophic theory and the primitive soup

The lack of constraint in parameters concerning the origin of life has led to alternative and competing theories regarding the emergence of the first living systems and the defining characteristics of the first organisms. Although discussions of panspermia, i.e. the transfer of organisms from one planet to another, are periodically resurrected, this merely displaces the problem of the chemical origin of life. It is important to stress that life as we know it is a chemical phenomenon, and the chemistry, which could produce self-organizing systems, is the central problem in the origin of life. There are several competing theories for how this chemistry may have arisen. In spite of their diversity, proposals for a prebiotic "soup", for the role of submarine hydrothermal vents, or for the extraterrestrial origin of organic compounds have as a common background assumption the idea that abiotic organic compounds were a necessary preamble for the appearance of life.

This is the basic tenet of the heterotrophic hypothesis for the origin of life, first proposed by Oparin and Haldane in the 1920s', according to which the first lifeforms were not able to synthetize their own compounds, but were formed from and dependent on pre-existing organic compounds of abiotic origin (Oparin 1924).

## 10.3 An autotrophic origin of life?

A few theories proposing an autotrophic origin of life, i.e. that the very first organisms were able to fix $CO_2$ and synthesize their own organic compounds, have been suggested as alternatives to the heterotrophic hypothesis. The most commonly cited autotrophic hypothesis stems from the work of Günter Wächtershäuser, who has argued that life began with the appearance of an autocatalytic two-dimensional chemolithotrophic metabolic system based on the formation of the highly insoluble mineral pyrite ($FeS_2$).

The reaction $FeS + H_2S \rightarrow FeS_2 + H_2$ is highly exergonic with a standard free energy change of -9.23 kcal/mol, which corresponds to a reduction potential $E^o = -620$ mV. Thus, the $FeS/H_2S$ combination is a potentially strong reducing agent, and has been shown to provide not only an efficient source of electrons for the reduction of organic compounds under atmospheric pressure and temperatures below 100 C, but also to promote the formation of peptide-bonds that result from the activation of amino acids with carbon monoxide and (Ni, Fe)S, as well as the fixation of carbon monoxide into activated acetic acid by a mixture of co-precipitated NiS/Fe/S (Huber & Wächtershäuser 1998).

None of these experiments (which occur in an aqueous medium) proves by itself that both enzymes and nucleic acids are the evolutionary outcome of surface-bounded metabolism, as hypothesized by Wächtershäuser (1988). These results are compatible with a general, modified model of a "primitive soup" in which pyrite formation is recognized as an important source of electrons for the production of reduced organic compounds. The experimental results achieved so far using the $FeS/H_2S$ combination are consistent with an heterotrophic origin of life.

It is important to note that these reactions rely on fairly high concentrations of compounds which are inconsistent with those found in modern vent fluids.

## 10.4 Prebiotic chemistry

The formation of organic compounds under conditions which could be accepted nowdays as primitive was investigated during the 19th century. The list includes, among others, Strecker's formation of alanine from acetaldehyde, ammonia, and hydrogen cyanide, and Butlerov's laboratory synthesis of sugars from formaldehyde. It was not until 1953, that the first successful synthesis of organic compounds under plausible primordial conditions was accomplished, by electric discharges acting for a week on a mixture of $CH_4$, $NH_3$, $H_2$, and $H_2O$; racemic mixtures of several protein amino acids were produced, as well as hydroxy acids, urea, and other organic molecules, see Figure 10 (Miller 1953, Miller & Urey 1959).

Miller's 1953 experiment was followed a few years later by the demonstration of adenine synthesis from the aqueous polymerization of HCN under basic conditions (Oro & Kimball 1961, 1962). The role of HCN in prebiotic chemistry has been further supported by the discovery that hydrolysis of HCN polymers yields several amino acids, purines, and orotic acid, which is a biosynthetic precursor of the pyrimidine uracil, a constituent of RNA (Ferris *et al* 1978). A potential prebiotic route for the synthesis of cytosine in high yields is provided by the reaction of cyanoacetaldehyde with urea, specially when the concentration of the latter is increased by simulating an evaporating pond (e.g. Miller & Lazcano 2002). Interestingly, selective absorption of organic compounds to various mineral surfaces has been shown to promote concentration and polymerization of various activated monomers in the laboratory (Ferris *et al* 1996).

The ease of formation of amino acids, purines, and pyrimidines from simple precursors under plausible prebiotic conditions strongly suggests these components were present in the prebiotic environment. As a number of experiments suggests, additional products of prebiotic chemistry probably included urea, alcohols, carboxylic acids, sugars, a wide variety of aliphatic and aromatic hydrocarbons, and branched and straight fatty acids, including some of which are capable of forming vesicles. The list also includes several highly reactive derivatives of hydrogen cyanide (HCN), such as cyanamide ($H_2NCN$) and its dimer (NC-NH-NH-CN), dicyanamide (NC-NH-CN), and cyanogen (NC-CN), which are known to catalyze polymerization reactions (Oro *et al* 1990).

The significance of prebiotic simulation experiments is supported by the occurrence of the large array of protein and non-protein amino acids, carboxylic acids, purines, pyrimidines, hydrocarbons, and other molecules in the 4.6 Ga old Murchison meteorite, a carbonaceous chondrite which also yields evidence of liquid water (see section 7). These meteoritic compounds make it plausible, but do not prove, that a similar synthesis took place on the primitive Earth.

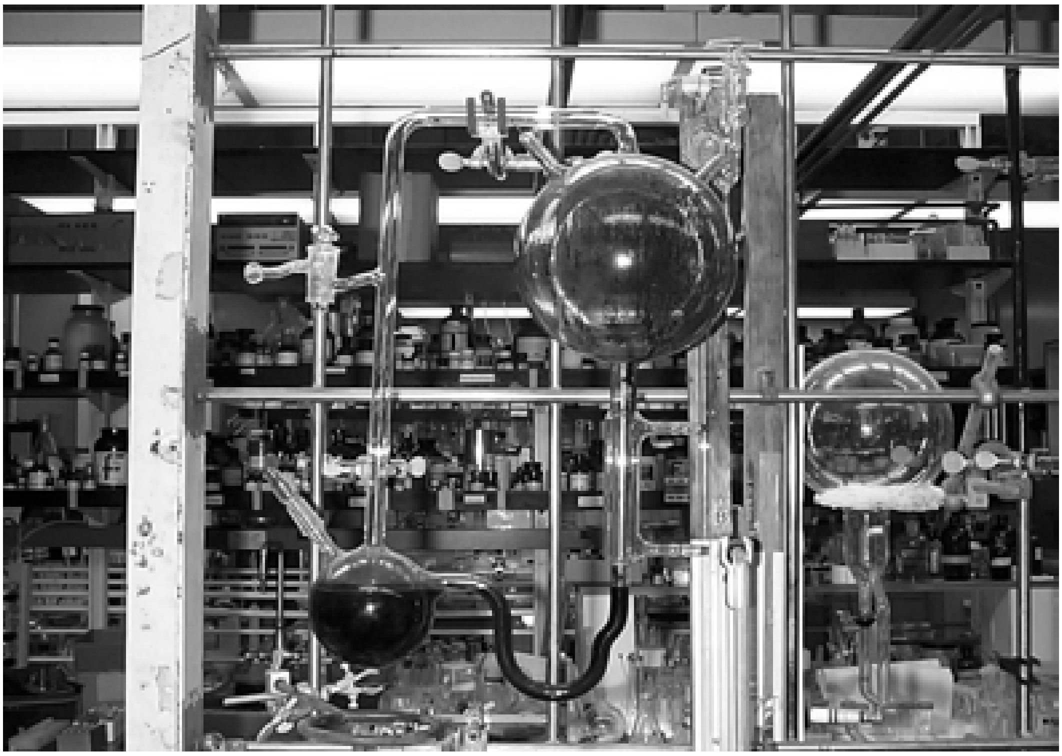


**Figure 10**
The Miller-Urey experiment (now located at UCSD, San Diego) that was used to demonstrate the synthesis of biologically relevant molecules in a hypothetical primitive reducing atmosphere. Water vapor, evaporated from a bulb that simulated the early Earth's ocean, is passed through a chamber with $NH_3$, $CH_4$, and $H_2$. Lightning, the most powerful energy source in this environment, was simulated by a spark discharge between two electrodes. The molecules formed in the reaction chamber were condensed and collected in the "ocean" bulb, where hydrolysis reactions take place.

Together with the ever-increasing complexity of organics found in the ISM, we see that nature readily makes the first steps in prebiotic chemistry.

### 10.5 Extraterrestrial sources of organic compounds

The abiotic syntheses of amino acids, purines, pyrimidines, and other compounds are very efficient if strongly reducing gaseous mixtures are used in simulation experiments. However, the possibility that the primitive atmosphere was non-reducing, as currently favoured by planetary scientists, does not create insurmountable problems, since the primitive soup could still form. For instance, geological sources of hydrogen, such as pyrite, may have been available; in the presence of ferrous iron, a sulfide ion ($SH^-$) would have been converted to a disulfide ion ($S_2^-$), thereby releasing molecular hydrogen. It is also possible that the impacts of iron-rich asteroids enhanced the reducing conditions, and that cometary collisions created localized environments favouring organic synthesis.

Of course, the question is not what was the source of organic compounds, but what percentage came from each source (see also sections 8 and Table 6). For instance, although the total amount of formaldehyde, hydrogen cyanide, acetaldehyde, cyanoacetylene and other prebiotic compounds in a given interstellar cloud is high, any of these compounds surviving the formation of the solar system would only have reached the Earth as minor constituents of comets, carbonaceous meteorites or IDPs. The Murchison meteorite contains approximately 3% organic carbon, most of which is an insoluble polymer (see section 7). There are only about 100 ppm (by weight C) amino acids which represents, assuming a void volume of 10% and a density of approximately 2 g $cm^{-3}$, a concentration of 0.1 g amino acids per kg of meteorite, or ~2 x $10^{-2}$ M of amino acids (Miller & Lazcano 2002).

Any origin of life theory based on the evolution of a self-replicating genetic system relies on the presence of chemically stable compounds and stabilizing microenvironments. HCN chemistry provides a preferential route for the prebiotic synthesis of purines and pyrimidines (see above). Alternatively, synthesis from formamide of purine and pyrimidine derivatives under catalytic conditions provided by the presence of dust grains could represent a more efficient prebiotic route than HCN chemistry (Saladino *et al* 2001).

### 10.6 Chirality and the origin of extraterrestrial organics

A fundamental characteristic of life is the homochirality of most of its building blocks. Various theories have been proposed to explain its origin; most of them require a chemical amplification scheme, but they differ in the origin of the initial excess to be amplified: random fluctuation, electroweak interaction effect, or extraterrestrial input. Detailed reviews can be found in Bonner (1991, 1996).

Enantiomeric excesses have up to now been found only in meteoritic matter (e.g. Engel & Macko 1997, Cronin & Pizzarello 1997, Pizzarello & Cronin 1998, 2000) but are searched for in micrometeorites (e.g. Vandenabeele-Trambouze *et al* 2001) and comets (COSAC experiments on-board ESA mission ROSETTA, Thiemann & Meierhenrich 2001).

Early experimental approaches on the syntheses of organic compounds do not produce chiral products (Miller & Urey 1959). Recent evaluation of abiotic mechanisms proposed for the origin of chiral molecules on the primitive Earth concluded that such approaches are not likely to occur in nature (Bonner *et al* 1999). The absence of chirality in products of prebiotic evolution experiments strengthened the presumption that natural abiotic synthesis invariably produces racemic compounds. Indeed, early analysis of Murchison amino acids declared them racemic (e.g. Kvenvolden *et al* 1970).

In 1997, Cronin & Pizzarello reported modest L-enantiomeric excesses of 2 to 9% in some amino acids in the Murchison meteorite. They avoided the problems of contamination by making measurements on 2-amino-2,3-dimethylpentanoic acid, α-methyl norvaline and isovaline.

All three of these compounds are α-methyl substituted; the first two have no known biological counterparts and the third has a restricted distribution in fungal antibiotics. Bailey *et al* (1998) have suggested that the observed enantiomeric excesses could have been induced by circularly polarized light arising from dust scattering in regions of high mass star formation. These sources occur more widely than do the supernova remnants or pulsars that were first proposed by Rubenstein *et al* (1983) as sources of circularly polarized synchrotron radiation. However, neither theory takes into account that amino acids are very fragile compounds, which are easily destroyed by particle radiation and even by low energy UV photons (Ehrenfreund *et al* 2001b). An extraterrestrial origin of chirality is strongly debated. Racemic mixtures of amino acids may be turned by an amplification mechanism into (L- or D-dominant) non-racemic mixtures under conditions that exist on planets or through catalytical processes on the surface of minerals (Hazen *et al* 2001). The fragility of amino acids (left unprotected) in interstellar environments and the lack of a plausible robust mechanism (neutron stars are rare) for producing enantiomeric excesses in amino acids, casts doubt on their interstellar origin. On the other hand, the production of amino acids on the parent body via the Strecker-cyanohydrin synthesis is a robust reaction that results in essentially racemic mixtures (Kvenvolden *et al* 1970).

There are, no doubt, many questions on this topic that are still unanswered and discussions are far from resolved. However, the possibility of coupling the delivery of extraterrestrial organic compounds to planets with the appropriate conditions like the early Earth, sheds new light on the importance of homochirality and the role of exogenous delivery of organic compounds to the origin of life.

## 10.7 Perspectives for prebiotic life studies from experiments and modelling in biotechnology and soft nanotechnology

The reconstruction of critical events in the origin of life is challenging, since there is no known geological record of prebiotic chemistry. We are then faced with the following problem: while we have available suggestive models for the organic compounds present on the primitive Earth for the origin of life (from laboratory simulations, atmospheric modelling, and the compounds present in carbonaceous chondrites), and we have detailed knowledge of modern biochemistry, we have only speculation to guide our understanding of the steps which connect these two. Indeed, it is possible that a number of intermediary stages existed between these two extremes, on the nature of which we know little.

The 'RNA World' hypothesis assumes self-replication information storage was first (Gesteland et al, 1999), the 'Lipid World' - confinement was first- (Segre et al, 2001), 'Protein World' – protein microspheres first- (Fox 1988), and the 'Thioester World' – metabolism first (de Duve, 1991). We have only begun to understand the fundamental relations between the oganisational units in a living cell, the distribution of common properties among species, and the determination of essential life-determining factors. There can be no doubt that such an approach will lead to a critical evaluation and fine-tuning of models and an improvement of our thinking about life's origins.

On the theoretical side, there has been an explosion of computer simulations and analytical models for complex collective behaviours of prebiotic chemical mixtures (Dyson 1985). Most of the popular versions tend to be variations of Eigen's original Hypercycle concept (Eigen & Schuster 1979), where the general feature is a compound reaction-diffusion model, embodied in a series of coupled (partial) differential equations, for a reacting mixture of complex bio-organic molecules. The set of equations is integrated on a computer, assuming parameters such as reaction rates and diffusion coefficients. The complex mixture should have a sufficient diversity, so that certain molecular types catalyse the formation of others. In a proper region in parameter space, diffusion and mutual catalysis will lead to self-sustaining autocatalytic networks, and these networks may contain information, merge, split, reproduce, etc: life will follow spontaneously. There is an interesting connection with novel approaches which makes the theoretical approach not only relevant for origin of life studies, but also for the development of new technology. In genomics and bioinformatics, projects such as E-cell (http://www.e-cell.org) endeavour to reproduce the features of a living organism in a computer model. The E-cell models need careful calibration with experimental data, but they may offer a virtual test of the chemical conditions necessary for life.

Can the computer models also serve as rational design tools for the preparation of a self-sustaining chemical system *ab initio* in the laboratory, without reference to, or using chemicals from, known biological origin? If yes, this could contribute to our understanding of complex chemical networks and the origin of life on Earth or on other planets.

The task is to invent a purely synthetic present-day system, capable of performing basic phenomena of self-sustaining chemical networks: increase complexity by a bottom-up approach, rather than decompose complexity as in the top-down bio-archeology.

The design of smart soft nano-materials has led to a new perspective concerning life's origins. For example, there are obvious connections between designing a life system and a drug delivery capsule capable of self-propagation, recognition, and response (Artificial Cell projects). The same methods can be used in both fields with mutual benefit (Szostak *et al* 2001). The simulation result of a drug delivery microscopic hydrogel, consisting of self-assembled heteropolymers, is shown in Figure 11. The soft reversible hydrogel is porous but can be closed by small changes in environmental conditions such as pH or temperature. Such gels are abundant in any concentrated mixture of amphiphilic polymers, where in most cases the morphology is not a simple hollow sphere, but rather an intricate labyrinth of folded lamellae, tubes and droplets (van Vlimmeren *et al* 1999).

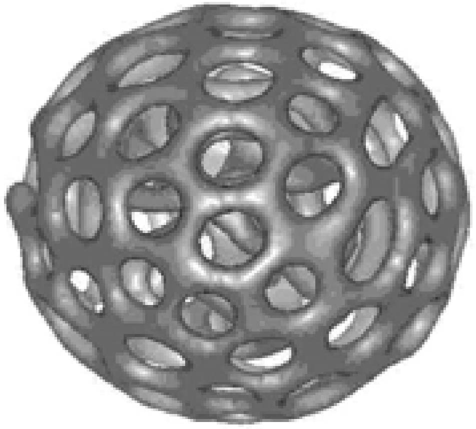


**Figure 11**
A technological perspective for origin of life studies: predicted structure of a self-assembled porous polymer microgel (diameter 80 nm). Such gels are used in Artifical Cell projects, and also find application as smart soft material in medical technology. The hydrogel is internally structured due to the microphase separation of hydrophobic (Poly Propylene Oxide) and hydrophilic (Poly Ethylene Oxide) block. Small changes in solvent quality will close or open the gel, thereby allowing release or uptake of reagents. The hydrogel resembles a $C_{60}$ buckyball structure, but with a twist: the hydrogels are soft and fragile, not hard, and they are much larger. The design of such smart gels is also an active area of research in drug delivery.

## 11. Conclusion and perspectives for future research in Astrobiology

Life on Earth is one of the outcomes of the origin and evolution of the solar system. Both the gas phase species (Table 1) and the less well characterized, but complex organic solids in the ISM (sections 2-3) point towards the universality of organic chemistry. Together with the wide range of organic molecules found by laboratory analysis of carbonaceous meteorites, these results certainly suggest that the basic building blocks of life, at least as recognized on Earth, must be widespread in planetary systems in our Milky Way and other galaxies.

Life as we know it originated from a very complex carbon-based chemistry. Extraterrestrial inorganic and organic materials (from comets, meteorites, and IDPs) were and are continuously captured by the Earth (Chyba *et al* 1990, Maurette & Morbidelli 2001). Models suggest the planetary delivery of an enormous ($10^{20}$- $10^{26}$ g) amount of extraterrestrial carbon and rocky materials since the formation of the solar system. These materials contain prebiotic compounds that, under suitable physical and chemical conditions, may have contributed to the origin of life. Whether or not this contribution was essential relative to the *in situ* production of organic compounds remains unknown.

The recognition of an extraterrestrial origin for a fraction of organic compounds on Earth does not require a reappraisal of panspermia, although the possibility of a Martian origin for terrestrial life should not be ignored (e.g. Nisbet & Sleep 2001). It is an acknowledgement instead that the primitive terrestrial environment was shaped in part by the intense bombardment characteristic of the early history of the Earth and other solar system bodies. The study of the exogenous delivery of material to Earth is still in its infancy. In addition, the link between cometary and interstellar matter remains unclear; there is a good correlation with volatile abundances but puzzling results on silicates. Further study is needed in order to assess correctly the survivability for molecules and enantiomeric excesses; the time dependence of the extraterrestrial flux on Earth must also be better constrained.

Use of advanced technology in astronomical and satellite observatories will make major contributions to this research area in the coming decades. Our knowledge of the chemistry of dense interstellar clouds and protoplanetary disks will grow with the higher sensitivity and angular resolution that will become available with new radio astronomy facilities such as the SMA (the sub-mm array; http://sma2.harvard.edu/index.html, the Large Millimeter Telescope LMT (http:// www-lmtgtm.org) and ALMA (the Atacama Large Millimeter Array, an interferometer of 64 antennas working between 30 and 900 GHz, in operation in 2010, http://www.eso.org/projects/alma/). ALMA should be able to detect relatively complex prebiotic molecules, in particular those present in protoplanetary disks where planetary formation is expected to take place, opening a new field of investigations.

Space observatories such as FIRST-HERSCHEL and SIRTF will allow the study of molecules in stellar formation regions. The forthcoming generation of optical (such as the NGST) and submillimeter telescopes should allow the first quantitative studies of both dust and gas contents in molecular clouds and galaxies (see APPENDIX for important websites).

Meanwhile, our elation at the discovery that ours is not the only planetary system in the Galaxy is tempered by the lack of confirmation of extrasolar, Earth-like planets. We await the technology to image Earth-sized planets revolving around other Suns. The most promising technique at present is high precision photometry that would permit the detection of Earth-like planets passing in front of their stars as seen from Earth. The diminution of the light from the star will yield the size of the planet, while the observation of successive transits will allow a precise determination of the orbit. To achieve the required photometric precision, it will be necessary to make the observations from a telescope in space. A goal of the COROT, KEPLER and EDDINGTON missions will be such photometric detection of Earth-like planets in other stellar systems. Statistics of exo-Jupiters will help to constrain current models of star and planetary formation. In the next two decades, new space-born interferometers (e.g. IRSI-DARWIN and Terrestrial Planet Finder, TPF) may permit us to measure the atmospheric spectra of extrasolar planets and look for non-equilibrium atmospheric compositions that may provide hints for life.

Several important space probes are planned in the coming years to investigate comets and asteroids. In addition to the ROSETTA *in situ* analysis by a lander and a 1-year orbiter, much is expected from the in situ cometary dust sample collection by STARDUST (to be returned 2006), and from several flyby or rendezvous missions (CONTOUR, DEEP IMPACT). With all these new studies one can hope to determine if comets have just brought some spice to the primitive soup, have brought essential components (water, carbon) and chirality, or even have been by themselves a "complete kit" sufficient for life to start. This in turn will allow us to address more convincingly the question of the spread of life in our solar system and in other extrasolar systems. The Mars exploration programme will also permit us to study processes of geological and atmospheric evolution, as well as searches for extinct or extant life on Mars. Already in 2003 the MARS-EXPRESS orbiter will perform studies of the water cycle, while the BEAGLE-2 lander will characterise surface conditions of exobiological relevance. Another target for Astrobiology is the ocean of Europa below its icy crust (Greeley *et al* 1998).

Laboratory simulation of the formation and processing of cosmic materials has aided the characterization of carbonaceous matter present in space. New high-resolution technology may further improve our abilities in this regard. In such experimental programs, the search for links between materials present in different space environments and biogenic components is a primary motivation. A future focus for experiments should be the catalytic function of dust. Materials such as Mg-rich olivine and pyroxene, synthesised and characterised in the laboratory (see section 3), could be proxies for space dust; their catalytic properties will yield insight into possible chemical pathways leading to the formation of prebiotic materials.

The chemistry of prebiotic simulations is robust and supported by meteorite organic analyses, but the synthesis of biochemical constituents of contemporary organisms by non-enzymatic processes under laboratory conditions does not necessarily imply that they were either essential for the origin of life or available in the primitive environment. Understanding the constraints when defining the chemical composition of life's "raw material" from the viewpoints of different scientific disciplines is essential. This will help us to describe the processes of self-organization that led to the establishment of the functional relationship between replicative polymers, energy-rich compounds and membrane-forming compounds, which eventually led to the first cells. Our existence is a consequence of the evolving Universe. If nothing else, and there may be no further connection with the origin of life on Earth than this, the investigations of the ISM, the meteorites, the comets and the cold, dimly lit satellites of the outer solar system demonstrate the ease with which nature can assemble the organic compounds that play such an important role in prebiotic chemistry. The step from prebiotic matter to life on Earth and possibly elsewhere is still hidden in the mists of space and time. Penetrating those mists remains one of the grand adventures of science. It will surely continue to be enthusiastically pursued in the future.

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# Appendix

**Accretion:** Accumulation under the influence of gravity and some minor forces.

**Accretion disk:** An accretion disk is a flat disk of gas and dust in space that surrounds a newborn star, black hole, or another enormous object that is growing by attracting matter to it with its gravitational field.

**Achondrite**: A stony meteorite without chondrules, coarsely crystallized, with large bits of various minerals visible to the naked eye.

**Aliphatic**: An open chain carbon molecule, or non-aromatic hydrocarbon.

**ALMA:** Atacama Large Millimeter Array: International collaboration between Europe and the US to build a synthesis radio telescope that will operate at millimeter and submillimeter wavelengths.

**Amino acids**: Low molecular weight, organic acids that serve as building blocks of peptides and proteins.

**Amphiphilic**: Molecule with both hydrophobic (water-avoiding) and hydrophilic (water-attracting) functional groups.

**Aromatic hydrocarbons**: Benzene and its derivatives, often fragrant; ringed, unsaturated, organic compounds in which the electrons of the carbon double bonds are shared among the carbons involved.

**Astronomical Unit (AU)**: The mean distance between the Earth and the Sun (1 AU = $1.496 \times 10^8$ km). It is a derived constant and used to indicate distances within a solar system.

**Autotroph**: An organism capable of synthesizing its own organic substances from inorganic compounds. Autotrophs produce their own sugars, lipids, and amino acids using carbon dioxide as a source of carbon, and ammonia or nitrates as a source of nitrogen. Organisms that use light for the energy to synthesize organic compounds are called photosynthetic autotrophs (e.g., green plants, certain algae, and the pigmented sulfur bacteria); organisms that oxidize such compounds as hydrogen sulfide ($H_2S$) to obtain energy are called chemosynthetic autotrophs, or chemotrophs (e.g., iron bacteria, the nitrifying bacteria, and the nonpigmented sulfur bacteria).

**Baryonic mass**: Mass of 'normal' material, i.e., that composed of protons and neutrons as opposed to exotic material such as neutrinos or axions.

**BEAGLE-2**: Lander vehicle of the Mars Express Mission, to be launched in 2003.

**Carbonaceous chondrites (CC)**: The subset of meteorites, usually with chondrules, containing the highest concentration of water, volatile elements, and organic compounds, believed to be the most representative of the bulk composition of the solar system.

**Centaurs**: The set of planetesimals with orbits between Saturn and Neptune.

**Chirality**: “Handedness”; any geometrical figure, or group of points, has chirality if its image in a plane mirror cannot be brought to coincide with itself.

**Chondrite**: Stony (silicate) meteorite containing chondrules embedded in a fine-grained matrix of pyroxene, olivine, and metallic nickel-iron. These meteors, believed to be unchanged since their formation, shortly after the formation of the Sun, also contain elements common in the Earth's core.

**Chondrule**: Small, mm-sized, spherules of various materials, chiefly olivine or pyroxene glass, found embedded in a usually fragmented matrix in certain of the stony meteorites.

**Clathrate, clathrate hydrate**: A class of solids in which the guest molecules occupy, fully or partially, cages in host structures made up of H-bonded water molecules. Clathrates are believed to occur in large quantities on some outer planets, binding gas at fairly high temperatures.

**Clouds**: Concentrations of gas and dust in the interstellar medium often distinguished by their degree of opacity: *dark* clouds, *diffuse* cloud*s*, *translucent* clouds.

**Comet**: An icy planetesimal, often in a highly elliptical orbit, consisting of frozen gases, dust, and organic materials. When it is warmed by the Sun, the ices in this nucleus sublimate, producing a gaseous coma (water vapor, $CO_2$, and other gases) and a tail (dust and ionized gases) that points away from the Sun.

**Cosmic spherules**: Melted droplets of meteorites, less than 1 mm in size, found in ocean sediments and ice.

**COROT**: COnvection ROtation and planetary Transits is a mission led by the French National Space Agency, CNES. It is a 30-centimetre diameter space telescope designed to detect tiny changes in brightness from nearby stars. Launch is scheduled in 2005 from Russia.

**CONTOUR:** The Comet Nucleus Tour (CONTOUR), a NASA Discovery mission, will visit and study at least two comets, it was launched in August 2002.

**COSAC:** The cometary sampling and composition experiment. COSAC is one of the two "evolved gas analysers" (EGAs) on board the Rosetta-Lander.

**Cretaceous/Tertiary Boundary**: A major demarcation in the geologic record dated at 65 million years ago defined by a massive extinction of plant and animal species; this extinction, marking the end of the era of dinosaurs, is believed to correlate with the Chixulub Impact, which occurred in the Yucatan Peninsula.

**D/H**: A ratio of the two most abundant isotopes of hydrogen, deuterium and hydrogen.

**DEEP IMPACT**: Scheduled for July 2005, Deep Impact's spacecraft will arrive at Comet Tempel 1 and become the first mission to impact the surface of a comet.

**DNA**: Deoxyribonucleic acid; a double-stranded helix of nucleotides that functions as the carrier of genetic information in cells in living organisms. It also encodes the information for the proteins.

**EDDINGTON**: A space mission to map stellar evolution and find habitable planets.

**Electromagnetic spectrum**: The radiation described by Maxwell's Equations, from gamma-rays through x-rays, ultraviolet, visible light, infrared, microwave, all radio waves, all having specific energy.

**Enantiomer**: One of the two mirror-image forms of an optically active (chiral) molecule.

**Fullerenes**: Fullerenes are large carbon-cage molecules. By far the most common one is $C_{60}$--also called a "buckyball".

**Fusion crust**: Dark, glassy coating on the surface of a meteorite, caused by heating as the meteorite enters the atmosphere.

**Ga (Gigayears)**: Billions of years.

**Glycine**: The simplest amino acid, and the only one without a chiral center.

**Habitable zone**: The region around a star in which liquid water could exist on an Earth-like planet.

**HERSCHEL**: Herschel will be the only space facility ever developed covering the far infrared to submillimetre range of the spectrum (from 80 to 670 microns). It will open up a virtually unexplored part of the spectrum which cannot be observed well from the ground.

**Heterotrophic**: Living organism that obtains its energy from carbohydrates and other organic material. All animals and most bacteria and fungi are heterotrophic. In contrast, autotrophs are organisms that use inorganic substances as energy sources and carbon dioxide as a carbon source.

**Hypercycle concept**: Linked series of chemical reactions evolving toward selection of more complex systems.

**Interferometry**: The data from two or more separate telescopes are used simultaneously to create an image with higher angular resolution than that from one telescope alone.

**Insoluble organic matter (IOM)**: One of several fractions of organic matter broadly defined on the basis of solubility in acid. IOM has low to no solubility in a weak acid bath; it is also referred to as protokerogen or humin.

**Infrared (IR)**: The portion of the electromagnetic spectrum with wavelengths from 0.6 to ~300 microns, just beyond the red end of the visible spectrum.

**Inorganic**: Describes a substance which is not organic, did not come from the materials or processes of living organisms, and/or is not a hydrocarbon or a hydrocarbon derivative compound.

**Interplanetary dust particles (IDPs)**: microscopic particles of asteroids or comets.

**Interstellar dust**: Particles composed of microscopic bits of carbon and/or silicates present in the interstellar medium and in circumstellar regions.

**Interstellar medium (ISM)**: The dust and gas (mostly hydrogen) that are between stars in a galaxy; at its densest, it is emptier than the best vacuum we can produce on Earth.

**ISO:** Infrared Space Observatory, European infrared satellite with 4 instruments onboard, operational between 1995-1998, covering the wavelength range between 2.5 and 200 micrometer.

**IRSI-DARWIN**: An array of six space telescopes, each of which will be at least 1.5 metres in diameter. They will work together to scan the nearby Universe, looking for signs of life on Earth-like planets.

**Isomers**: Different substances that have the same chemical formula.

**KEPLER**: The Kepler Mission is a space mission designed to detect and characterize hundreds of Earth-size planets in the Habitable Zone of a wide variety of stars.

**Kuiper Belt**: A region beyond Neptune in which numerous asteroid-like objects orbit. This belt is located 30 to 50 A.U.'s from the Sun and is the presumed source of the short-period comets. The Kuiper belt was named after the Dutch-American astronomer Gerard P. Kuiper, who predicted its existence in 1951.

**Large millimeter telescope (LMT)**: A joint project of the University of Massachussetts (U.S.A.) and the Instituto Nacional de Astrofisica, Optica & Electronica (Mexico) to build the world’s largest radiotelescope for use at millimeter wavelengths, completion expected in 2004/2005.

**Low mass stars**: Stars with masses comparable to or less than that of our Sun.

**Luminosity**: The total brightness of a star or galaxy, measured as total amount of energy radiated each second in all wavelengths of the electromagnetic spectrum.

**Molar (M)**: Concentration of a dissolved constituent in moles of material per liter of water.

**Magnitude**: A logarithmic scale of intensity used by astronomers.

**Main Sequence**: The region of the temperature-luminosity (Hertzsprung-Russell) diagram in which a star falls while it is fusing hydrogen to helium in its core and, hence, where it spends most of its lifetime; the Sun is a typical Main Sequence star.

**Metabolomics**: The study of the reconstruction of metabolic pathways, deduced from genomic information.

**Meteorites**: A metallic or silicate body that has fallen on Earth, Moon, or other planetary body from outer space.

**Molecular clouds**: A concentration of interstellar material primarily molecular in form implying densities greater than ≈ 1000 atoms/cm$^3$.

**Ordinary chondrites:** The most common class of meteorites, consisting of variable amounts of metal and chondrules in a matrix of mostly silicate minerals.

**Organic Matter (OM)**: Compounds of carbon, hydrogen, and oxygen that form complex molecules (may or may not be from living organisms).

**Oort Cloud**: Roughly circular reservoir of comets ~50,000 AU distant from our Sun, the presumed source of long-period comets.

**Ozonolysis**: Breaking of an organic molecule by reactions with ozone.

**Panspermia**: The hypothesis that life was or may have been transported across the Universe.

**Parent body**: The asteroid or cometary nucleus from which a meteorite is derived.

**Permian/Triassic boundary**: Major geological demarcation approximately 250 million years ago, marked by massive extinction in the fossil record.

**Planetary embryos**: The presumed Moon-sized objects that accreted together to form planets.

**Plantesimals**: Small objects that orbit the Sun, thought to have formed when the solar system itself formed, and possibly the building blocks from which the planets were built.

**Polycyclic Aromatic Hydrocarbons (PAHs)**: Aromatic molecules containing several fused (joined) rings made up only of carbon and hydrogen. Mid-infrared emission bands in the ISM are most often attributed to PAHs, which are believed to be relatively stable in space environments.

**Pre Main Sequence**: Characterizing a forming star before it has reached the stage of hydrogen fusion.

**Proteomics**: The identification, characterization and quantification of all proteins involved in a particular pathway, organelle, cell, tissue, organ or organism that can be studied to provide accurate and comprehensive data about that system.

**Protoplanetary disk**: A rotating disk of dust and gas that surrounds the central core of a developing solar system. This disk may eventually coalesce into planets that orbit the star, which forms from the central core.

**Protostar**: A star that is still forming and in which nuclear fusion has not yet begun.

**Racemic**: A mixture of an organic compound containing equal parts of both L- and R-enantiomers

**Refractory**: A material with a very high sublimation temperature. For example, a refractory mineral is one that will remain intact when a rock is fused or melted; a refractory component of organic carbon is that portion which will be the last to separate from its host substrate, as is the case with the macromolecular, tar-like material found in carbonaceous chondrites.

**RNA**: Ribonucleic acid, a linear, usually single-stranded polymer of ribonucleotides, each containing the sugar ribose in association with a phosphate group and one of four nitrogenous bases: adenine, guanine, cytosine, or uracil. RNA is found in all living cells; in prokaryotic and eukaryotic cells, it encodes the information needed to synthesize proteins (i.e., it copies "instructions" that it receives from DNA); in certain viruses, it serves as the genome.

**ROSETTA:** A comet rendezvous mission. The mission goal is a rendezvous with comet 46 P/Wirtanen in 2011. On its eight-year journey to the comet, the spacecraft will pass close to two asteroids, Otawara and Siwa. Rosetta will study the nucleus of comet Wirtanen and its environment in great detail for a period of nearly two years and then land on the comets surface.

**Shock**: A pressure wave passing through a fluid medium in which the pressure, density, and particle velocity undergo drastic changes. The source of the shock wave moves at a speed greater than the speed of sound in the fluid.

**SIRTF:** The Space InfraRed Telescope Facility completes NASA's great observatories that study the Universe at wavelengths from visible light to x-rays.

**SMA**: Sub-millimeter array: An array of radiotelescopes on Mauna Kea (Hawaii, U.S.A.) operated by the Harvard-Smithsonian Center for Astrophysics.

**SNC**: Shergotites, Nakhlites, and Chassignites, the three primary meteorites of the suite of Martian meteorites, identified by their relatively young ages and their chemical similarity to the Viking data from Mars.

**Solar Mass**: The amount of mass in our Sun; it is also the unit in which the masses of other stars, galaxies, and other large celestial bodies are expressed. The solar mass is $1.99 \times 10^{30}$ kg. A black hole, for example has anywhere from a million to a billion solar masses.

**Solar nebula**: The flattened cloud of gas and dust from which the Sun and other solar system bodies, including planets, comets and asteroids, formed.

**Soluble Organic Matter (SOM)**: Organic material that is readily leached from a surface (such as a meteorite) when it is immersed in a water or weak acid bath.

**STARDUST**: NASA's Stardust spacecraft is currently on a mission to collect and return the first samples from the vicinity of comet Wild-2. Samples will be captured in a low-density aerogel and parachuted to Earth in the middle of this decade.

**Terrestrial Planet Finder (TPF)**: A proposed NASA mission that will study all aspects of planets: from their formation and development in disks of dust and gas around newly forming stars to the presence and features of those planets orbiting the nearest stars.

**Trojans**: Trojan asteroids are asteroids that orbit in gravitationally stable Lagrange points in a planet's orbit, either trailing it or preceding it (these places are where the gravitational attraction of the Sun and the planet balance each other). Jupiter has the most Trojan asteroids, approximately 60° ahead of and behind in its orbit; Mars also has some. Achilles was the first Trojan asteroid found.

**T-Tauri star**: T Tauri stars are stars whose brightness varies irregularly. Their spectrum has broad and very intense emission lines, probably indicative of violent surface activity. They are protostars of approximately solar mass in the later stages of formation, young stars that are not yet stable main sequence stars in the Hertzsprung-Russell Diagram.

**Ultra-violet (UV)**: A type of electromagnetic radiation invisible to us, with wavelengths shorter than the color violet but longer than those of x-rays. The ozone layer traps much of the Sun's ultraviolet energy coming through Earth's atmosphere.

**Visible (VIS)**: The parts of the electromagnetic radiation that we can see, ranging from red (longer wavelengths, about 700 nanometers) to violet (shorter wavelengths, about 400 nanometers).

**Visual extinction**: The dimming of star light by interstellar dust particles.

**Young Stellar Object (YSO)**: a forming star

## Related web-sites:

### *Astrobiology:*
http://www.astrobiology.com/
http://origins.jpl.nasa.gov/
http://exoplanets.org
http://cfa-www.harvard.edu/planets/encycl.html
http://www.cv.nrao.edu/~awootten/allmols.html
http://www.e-cell.org
http://www.imo.net/

### *Space missions and large telescopes:*
http://discovery.nasa.gov
http://www.esa.int
http://sma2.harvard.edu/index.html
http://www-lmtgtm.org
http://www.eso.org/projects/alma
http://www.iki.rssi.ru/ssp/vega.html
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