

EXTRATERRESTRIAL ORGANIC ANALYSIS

J. ORÓ

*Dept. of Biophysical Sciences and Chemistry,
Houston, Tex. 7704, U.S.A. University of Houston,*

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1. Introduction

Chemical analyses of the Moon, the Earth and meteorites have shown that the composition of these bodies is essentially inorganic. Some of the predominant elements are O, Si, Mg, Fe, Al and Ca, which are usually combined in the form of silicates. On the other hand it is well known from compilations of elementary abundances (Suess and Urey, 1956; Cameron, 1959; Aller, 1961) that, with the exception of the noble gases He and Ne, the four most abundant elements in the solar system and in the universe are H, C, O and N (Figure 1), which are precisely the four major constituent elements of organic matter.

How can the above paradox be explained? In part by considering the solar system as a gigantic circular gas chromatogram, and recognizing that the central part of this system, which is occupied by the terrestrial planets and asteroids, was probably depleted of the light elements by radiant heat and by the hydrogen-helium 'carrier gas' streaming away from the protosun. Thus, the light elements were displaced towards the outer regions of the solar system where the Jovian planets and comets exist today. Consequently, since the mass of the Jovian planets is more than 99.5% of the total planetary mass of the solar system, and since these planets are made of He and light reactive elements (H, C, N, O, etc.), we must conclude that the chemistry of these elements, which is in part organic chemistry, is the prevailing chemistry of the solar system.

Beyond our solar system it could also be expected that the chemistry of these elements should prevail over inorganic chemistry. Yet, up until a few years ago, no organic molecules as such, or any other molecule of these light elements had been detected in the interstellar medium. The absence of significant observational data was caused mainly by the difficulties in developing appropriate instrumentation, and also by the reluctance of investigators to accept the possibility that more or less complex organic

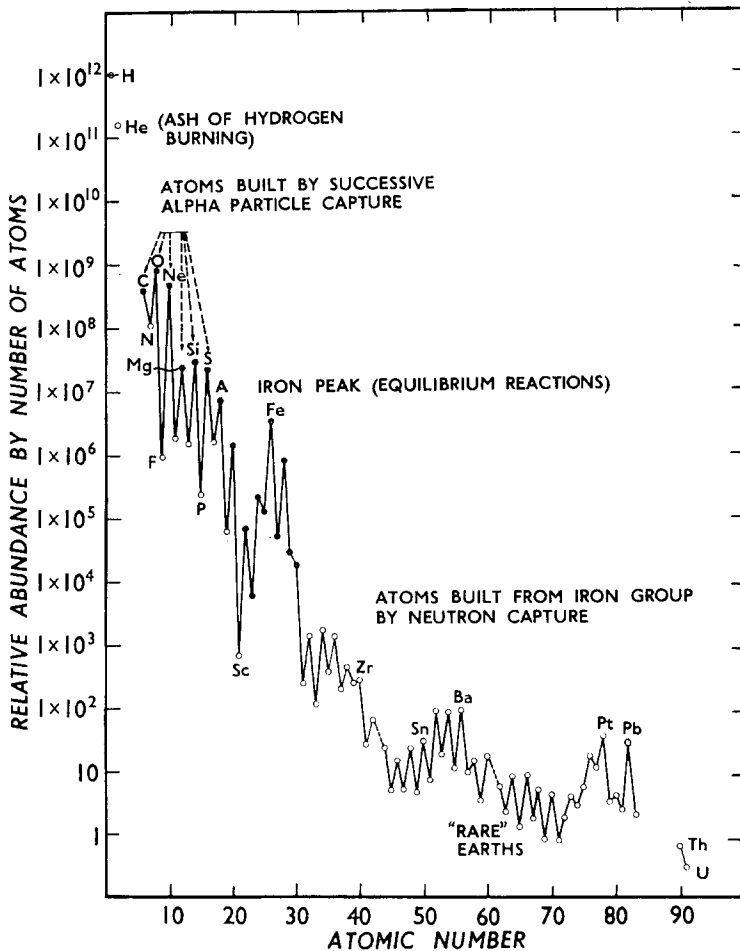


Fig. 1. Relative abundances of elements (After L. H. Aller, 1961).

molecules could exist under the supposedly extreme physical conditions of interstellar space. Fortunately, radioastronomy has resolved this paradox by providing during the last three years the missing evidence about the existence of organic molecules in the vast reaches of our galaxy and consequently giving direct support to the universality of organic cosmochemistry (Oró, 1961, 1963a, 1963b).

Therefore, we are now in a better position to understand the problems concerning the cosmic distribution and formation of molecules of most of the organogenic elements (H, C, N, O, S, P), which are the elements essential for the existence of terrestrial life. The fundamental questions of organic cosmochemistry are: (i) what organic and related molecules are present in our galaxy and solar system? (ii) what is their distribution in different parts of these two systems? (iii) how were or are these molecules formed, and finally (iv) what bearing do they have with regard to prebiological chemical evolution and to terrestrial, and possibly extraterrestrial biology. The present

paper is an attempt to answer these questions, and presents a brief review of relevant information on the composition of stars, interstellar matter, and individual bodies of the solar system. Earlier discussions of this problem may be found elsewhere (Oró, 1965a, 1965b, 1968; Donn, 1972).

2. Stars and the Sun

Concerning the formation and chemical behavior of the organogenic elements in stars, the following three phases need to be considered. First, the nuclides are formed in the stellar interior at very high temperatures. Second, the new elements formed, diffuse out or convectionally reach the surface of the star, where at the relatively low temperatures of its atmosphere form simple diatomic or triatomic combinations. Thirdly, these combinations are eventually ejected together with atoms and possibly more complex species into circumstellar or interstellar space by a number of different processes.

Hydrogen is transformed into nuclides of higher atomic number by a sequence of nuclear reactions which involve predominantly the condensation or capture of protons, α -particles and neutrons, as shown schematically in Figure 2 (Burbidge *et al.*, 1957). The nature of the element building processes prevailing in a star depends on its primary or secondary composition, the age, mass and temperature of the star, and on the relative stability of the respective nuclides under the conditions of their formation. The graph of elementary abundances shown in Figure 1 reveals the existence of certain singularities in such nuclear element building processes. Of crucial importance to our discussion, since it explains the unusual abundances of the organogenic elements, is the discontinuity between the Li-Be-B minimum (not shown in the graph) and the C-N-O maximum. *A priori* it should be more probable to synthesize the ^8B nuclide than the ^{12}C nuclide from helium ions. However the reality is just the opposite. It appears that the excited state of the ^{12}C nuclide, once formed by the ramming together of three α -particles, possesses a low lying resonance and decays to a very stable ^{12}C ground state. On the other hand the stabilities of the Li, Be, and B nuclides are very low under the conditions of the 'helium burning' process which is responsible for the formation of carbon-12 (Aller, 1961).

Once carbon-12 is formed, it is transmuted into nitrogen by the carbon-nitrogen cycle, and into oxygen by an α -capture process. Sulfur and phosphorus are formed by related nuclear processes (Figure 2). In the carbon-nitrogen cycle the ^{12}C is transmuted successively to ^{13}C , ^{14}N and ^{15}N by repeated proton capture, and the last product is finally converted to ^{12}C again. From the standpoint of isotope formation it is of interest to note that the relative proportions of ^{12}C , ^{13}C and ^{14}N depend on the composition and physical characteristics of the star. Analyses of different stars have indicated variations in the $^{12}\text{C}/^{13}\text{C}$ ratios from approximately 4 to about 100, in carbon R and N stars (Aller, 1961). When the carbon-12 passes through a carbon-nitrogen cycle region some of it is transformed into carbon-13, and the resulting $^{12}\text{C}/^{13}\text{C}$ abundance ratio is about 4.6, which presumably is a ratio appropriate to the equilibrium value of this cycle (see Fowler *et al.*, 1967). On the other hand, if the ^{12}C passes outward without significant mixing and without encountering the carbon-nitrogen cycle region,

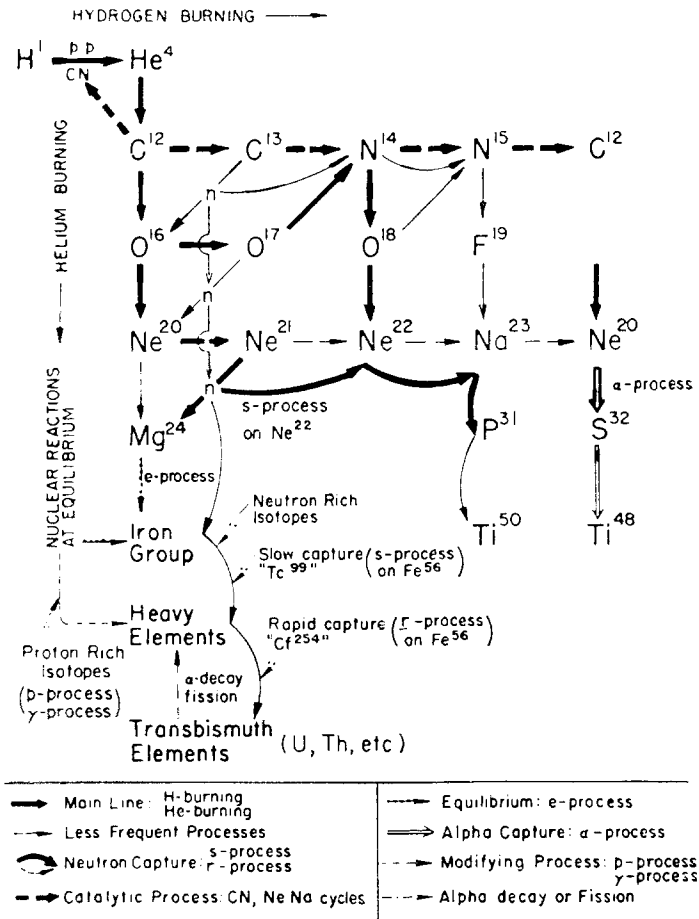


Fig. 2. Schematic diagram of nuclear processes by which synthesis of elements in stars takes place. (Reproduced from E. M. Burbidge, G. R. Burbidge, W. A. Fowler, and F. Hoyle: *Rev. Modern Phys.* **29** (1957), 552.)

the $^{12}\text{C}/^{13}\text{C}$ ratio might be as high or higher than 90, or that found on the Earth (Aller, 1961).

The existence of simple combinations of H, C, N, and O, such as the diatomic species CN, C₂, CO, CH, NH and OH, has been observed in the atmospheres of the Sun and other relatively cool stars, particularly the so-called carbon stars. The triatomic species C₃ and SiC₂ have been identified in cool carbon stars and it has been suggested that a substantial contribution to the star's opacity is made by the continuous absorption of these molecules. Calculations of molecular dissociation equilibria at different temperatures (≈ 1500 to 6000°C) and different C/O ratios have shown the stability ranges of some of the above chemical species. When oxygen is larger than, or equal to carbon ($\text{O} > \text{C}$ or $\text{O} = \text{C}$), the prevailing species are carbon monoxide at lower temperatures and monoatomic C and O at higher temperatures. When carbon is larger

than oxygen ($C > O$) the diatomics C_2 , CN and CH are together with CO and monoatomic carbon, the major constituents of the relatively cool atmospheres. A graphical representation of the behavior of these compounds in the atmosphere of a dwarf ($O > C$) main sequence star is shown in Figure 3 (Aller, 1963).

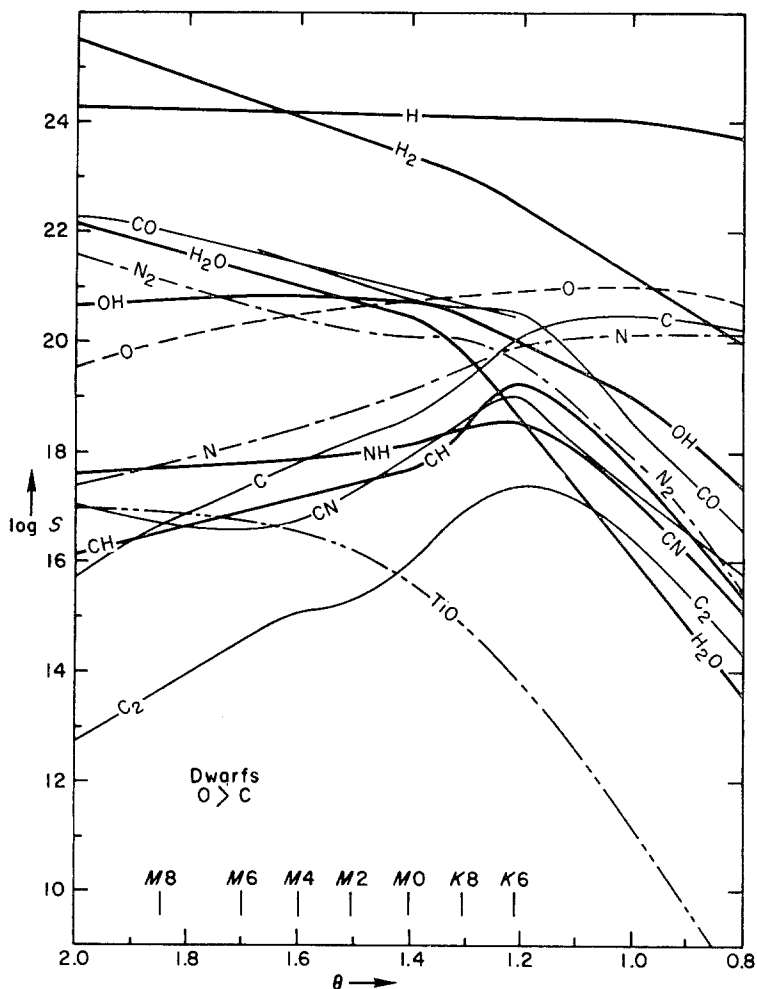


Fig. 3. The behavior of compounds in the atmospheres of main sequence stars. The ordinates are the logarithms of the numbers of molecules or atoms above each cm^2 of the photosphere, $\log S$. Abscissas are $\theta = 5040/T$. The corresponding spectral classes are given also. (From L. H. Aller, *Astrophysics* (1963), 135.)

Substantial amounts of these simple combinations are probably ejected to interstellar space by different stellar processes. These vary in intensity from the explosions of supernovae, novae, and nova-like stars (recurrent novae, P Cygni and Wolf-Rayet stars), to the less violent processes responsible for the dynamics of pulsating variable stars, and stellar flares and winds. A more common process is the ejection of gaseous

matter into the interstellar medium at relatively low velocities, either as a consequence of radiation pressure or because of the high pressure of a hot mass of gas expanding into the relatively cold interstellar space (Struve and Zebergs, 1962). Although such explosive and non-explosive mass ejection or transfer events may not be sufficient to maintain the presently observed amount of interstellar gas and dust, out of which new stars are formed, the magnitude of these processes is not negligible either (Gorbatsky, 1970; Weymann, 1963).

Some astronomical observations have given direct evidence for the ejection of carbon compounds from stars. For instance, in the spectrum of Nova Herculis 1934, CN bands were observed a few days after maximum light and their presence was only temporary (Stoy and Wyse, 1935; Wilson and Merrill, 1935; Sanford, 1935). Furthermore, the Doppler shifts of the CN bands were the same as those of atomic lines, a fact which shows that diatomic species and atoms were ejected from the star with the same velocity. Observations of a CN band (3590 Å) were made also on Nova Aquilae 1918, and Nova Aquilae 1945 (see Merrill, 1958). The possible formation of more complex compounds of carbon, such as benzene and graphite grains, in cool stellar atmospheres and their ejection to circumstellar or interstellar space has been discussed by Hoyle and Wickramasinghe (1962), Wickramasinghe *et al.* (1966), Donn and other investigators (see Donn, 1972). The absorption spectra of type I supernovae has been studied recently by Graham and Duley (1971). The observed broad absorption bands were compared to the absorption bands of complexes of aromatic hydrocarbons with metals (Ca, Ti, etc.). Of particular interest is the excellent match of the shape of the extensively studied 4430 Å strong diffuse band (see next section) with a calcium-benzene complex (Ca-C₆H₆). From the above and other recent observations, a more accurate re-evaluation of the magnitude and significance of different mass ejection processes within our galaxy may soon become possible.

3. Interstellar Matter

Interstellar matter has been referred to in the past as the 'ghost that haunted astronomers.' Still today, it retains a modicum of mysticism when we refer to it as interstellar medium. Obviously, this was caused by our lack of knowledge concerning its chemical composition, in spite of the fact that it could be calculated that its total mass is comparable to the mass associated with stars. Although there are no precise definitions of its boundaries the interstellar matter or medium should include at least what has been described as interstellar gas clouds, planetary and diffuse nebulae, interstellar grains, cosmic rays and particles and circumstellar dust and gas clouds. This presentation will be limited mainly to the composition of the gaseous components of interstellar clouds and gaseous nebulae as determined by optical and radio astronomy.

A. OPTICAL ASTRONOMY

Optical spectra of planetary and diffuse nebulae have shown no radical differences between them, and it is probable that their composition is similar to that of the stars

with which they are associated. The elements whose spectral lines have been identified in gaseous nebulae are *hydrogen*, helium, *carbon*, *nitrogen*, *oxygen*, fluorine, neon, *sulfur*, chlorine, argon, potassium, calcium, manganese and iron, which include five of the six elements necessary for the synthesis of biochemical compounds. The spectral line intensities of more than half of these elements (not including carbon) have been measured and shown to have about the same proportions as in stars (Merrill, 1963).

Our knowledge of chemistry of interstellar or circumstellar gas clouds began early in this century with the interesting discovery by Hartman of the spectral line of Ca (λ 3934) somewhere in space on the line of sight of the binary star Delta Orionis (Hartman, 1904; Struve, 1926; Eddington, 1926). The differentiation of stellar and interstellar spectra could be achieved because the calcium line did not share in the periodic displacements caused by the orbital motion of the binary star from -80 to $+120$ km s^{-1} and did not come either from a massive secondary component of the binary system. The interstellar clouds generating the calcium line showed no velocity changes but rather a constant average velocity of about $+20$ km per second, the null point of both displacements. The assumption made is that this Ca line is not derived from a chromospheric shell of Ca surrounding the stellar system, as in the case of other calcium lines from Alpha Herculis (Struve and Zebergs, 1962). Other inorganic elements identified, between the stars include sodium, potassium, titanium and iron.

The first simple combinations of interest to organic chemistry observed in interstellar space were methylidyne radical (CH), cyanogen radical (CN), and methylidyne ion (CH^+) which were discovered in 1937–1941 by Dunham and Adams (see Adams, 1943). The sharp absorption lines from these radicals and radical ion are superimposed on the optical spectra of the hot stars. These findings were supported by the theoretical and experimental studies of Swings and Rosenfeld (1937), Douglas and Herzberg (1941) and McKellar (1947). The absorption lines from 3745 to 4300 Å arise from electronic levels having either zero or one quantum of rotational energy. A comprehensive treatment of the applications of quantum mechanics to molecular spectroscopy may be found elsewhere (Herzberg, 1950–1966).

In 1934 Merrill discovered a series of diffuse, or broad absorption bands in the region 4310 to 6700 Å which have not yet been identified. More than half of the 25 broad bands, including the major one absorbing at 4430 Å, have tentatively been assigned to bis-pyridyl-magnesium-tetrabenzoporphin ($MgC_{46}H_{30}N_6$) by Johnson (1967). Although it is statistically improbable that all the diffuse bands of the interstellar medium are caused by one single molecule, the high stability of this and similar porphyrins makes them good candidates together with other compounds (see below) for molecules capable of existing in interstellar regions of very intense radiation flux. The above molecule is stable at the sublimation temperatures of 500° to $600^\circ C$ and has a resonance and a dissociation energy of about 400 kcal $mole^{-1}$ and 17 eV, respectively, which compares favorably with the resonance energy of benzene (60 kcal mol^{-1}) and the dissociation energy of water (≈ 10 eV).

Optical astronomy has also attempted to explain the origin of the diffuse bands, as well as the obscuration and reddening (i.e., extinction) and polarization of starlight,

from the point of view of small solid particles containing absorptive impurities (Van de Hulst, 1957; Wickramasinghe, 1967; Greenberg, 1968). These small particles, referred to, in general, as interstellar grains, have been considered, by different authors, to be: (a) ices of condensed gases or vapors, with or without a solid core, (b) metals, (c) silicates, (d) graphite, (e) relatively large organic molecules, and (f) mixtures thereof.

Among the organic molecules, polycyclic hydrocarbons containing 5 or more rings have been suggested by Donn (1972). Arrays of these aromatic molecules show a continuous extinction through the visible region of the spectrum very similar to that of the interstellar medium. Also, it appears possible to explain the wavelength dependence and polarization of the interstellar extinction by these compounds. Their stability is exemplified by the symmetrical molecule hexabenzocoronene ($C_{42}H_{18}$) which does not melt even above $700^{\circ}C$, and in a sense can be considered as a representative 'particle of graphite,' according to Clar (1964).

The possibility that the 4430 Å and other diffuse bands observed in type I supernovae may be produced by metal-aromatic hydrocarbon complexes has been indicated earlier (see previous section). However, it has not yet been established that the diffuse bands are an intrinsic property of the interstellar grains. It would seem reasonable to think that they are caused by chemical species or structural features associated in some way with the grains of interstellar and circumstellar dust clouds. Through a study of the shape of the diffuse bands and the application of a new criterion (Greenberg and Stoeckly, 1971) it may be possible to elucidate whether or not these broad bands originate from features or constituents of the interstellar grains.

Table I lists the carbon compounds (radicals and radical ion) identified in the interstellar medium by 1941, and includes also the more recent detection of the hydrogen molecule by means of a rocket camera. This was done by measuring the Lyman resonance-absorption bands in the far-ultraviolet spectrum of the star ξ Persei. The column number-density in the line of sight was estimated $1.3 \times 10^{20} \text{ cm}^{-2}$ for H_2 and $4.2 \times 10^{20} \text{ cm}^{-2}$ for H, and the extinction by dust about 1 magnitude, which indicates that nearly half of the total hydrogen may be in molecular form in the observed region (Carruthers, 1970). With the exception of this latter finding the limitations of optical astronomy in the identification of molecules have been so great that no definitive additional data on the composition of interstellar matter have been obtained during the last 30 years.

B. RADIO ASTRONOMY

After the beginning and early development of radio astronomy by Jansky and Reber during 1931 to 1942 (Struve and Zebergs, 1962), two other major developments took place: the calculation of the 21.2 cm quantum emission, for the electron spin reversal of atomic hydrogen (which can occur once in 11 million years) by Van de Hulst in 1945 (Van de Hulst, 1960); and the discovery of the 21-cm emission line in interstellar space by Ewen and Purcell in 1951. These two significant advances made possible the mapping of the gigantic clouds of atomic hydrogen in the spiral arms of the Milky

TABLE I
Interstellar chemical species (optical astronomy)

Year	Molecule or radical	Symbol	Wavelength	Telescope	Reference
1934	Diffuse bands	?	4310-6700 Å	Mt. Wilson 100 in.	Merrill (1934)
1937	Methylidyne radical	CH	4300 Å	Mt. Wilson 100 in.	}
1940	Cyanogen radical	CN	3875 Å	Mt. Wilson 100 in.	
1941	Methylidyne ion	CH ⁺	3745-4233 Å	Mt. Wilson 100 in.	Adams (1943)
1970	Hydrogen molecule	H ₂	1100 Å	Rocket camera	Carruthers (1970)

Way, and the determination of most of the, until then, unobservable structure of our Galaxy (Figure 4).

In 1953–1955 Shklovsky and Townes suggested a search for possible interstellar molecules by microwave spectroscopy, and the fundamental principles of this science were presented at about the same time by Townes and Schawlow (1955). However,

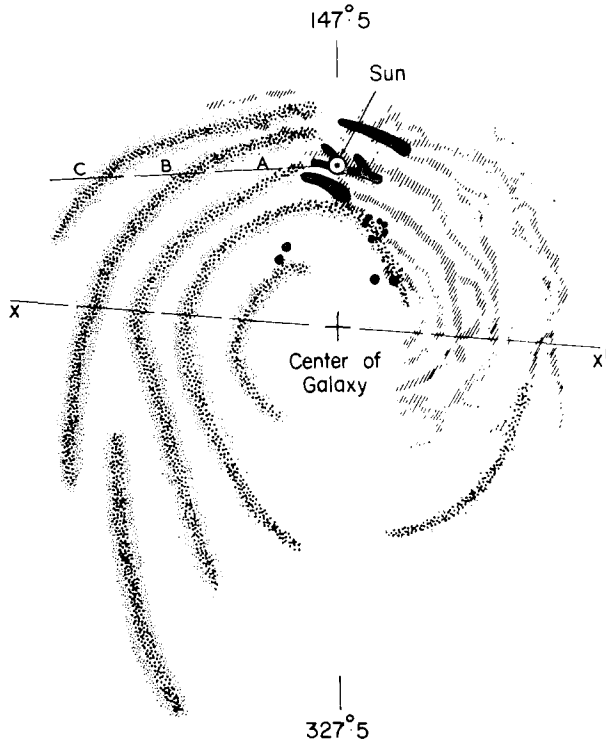


Fig. 4. Spiral structure of our Galaxy as indicated by the distribution of hydrogen radiation observed with the 21 cm line by radio telescopes in recent years. Only the small black areas near the Sun were found from ordinary photographic observations. (From P. W. Merrill, 1963.)

the practical problems in the development of appropriate microwave receivers and antennae were such that it was not until some years later that important new findings were made. In 1963 Weinreb *et al.* (1963), detected, using the MIT Lincoln Laboratory 84 ft radiotelescope, the 18 cm and other normal and maser emission lines of the hydroxyl radical from a region near the center of our Galaxy. Because of some reluctance to accept the existence of ordinary molecules in interstellar space, a few more years had to pass before the revolutionary breakthrough in our knowledge of the chemical composition of interstellar matter was made with the discovery of interstellar gas clouds of ammonia, water and formaldehyde. Thus, in the fall of 1968 and early 1969 the 1.26 cm normal emission of ammonia ($^{14}\text{NH}_3$) and the 1.35 cm maser emission of water (H_2^{16}O), respectively, were detected by Cheung *et al.* (1968, 1969) with the 20 foot Hat Creek radiotelescope of the University of California. In March, 1969,

the 6.2 cm normal absorption, and inverse maser absorption of formaldehyde were observed by Snyder *et al.* (1969) using the now famous 140 ft radiotelescope of the National Radio Astronomy Observatory (NRAO), at Green Bank, West Virginia. This was, indeed, the discovery of the first ordinary molecules and of the first organic molecule in the interstellar medium (i.e. not radical or radical ions). The findings of these three important polyatomic molecules, ammonia, water, and formaldehyde represent the beginning of the remarkable development of molecular radioastronomy during the next three years. Very interesting accounts of these developments have been reported by Snyder and Buhl (1970) and Buhl and Snyder (1971).

One of the first microwave absorption spectra of interstellar formaldehyde ($\text{H}_2^{12}\text{C}^{16}\text{O}$) at 6.21 cm recorded at the National Radio Astronomy Observatory is shown in Figure 5. This absorption was observed against Sagittarius A, and since then formaldehyde has been detected against many radio sources in different regions of our Galaxy. It is presumed to be a common constituent, along with hydrogen and hydroxyl radical, of many of the clouds of the Milky Way. From the observed Doppler shifts of the line frequencies a radial velocity can be calculated for the moving molecular clouds. The abscissa gives the radial velocity and the ordinate the relative intensity or antenna temperature. Of significance for measurements of carbon isotopes was the detection of heavy formaldehyde ($\text{H}_2^{13}\text{C}^{16}\text{O}$) by Zuckerman *et al.* (1969).

In April 1970 Wilson *et al.* (1970) detected normal emission lines from interstellar carbon monoxide at 2.60 mm in the Orion nebula and other sources; Jefferts *et al.* (1970) observed the cyanogen radical at 2.64 mm in the Orion nebula and W51. The carbon monoxide is of particular interest because it appears to form the 'core' of formaldehyde clouds, suggesting a possible genetic relationship between these two organic molecules (Snyder and Buhl, 1970). In June, 1970, Snyder and Buhl (1971)

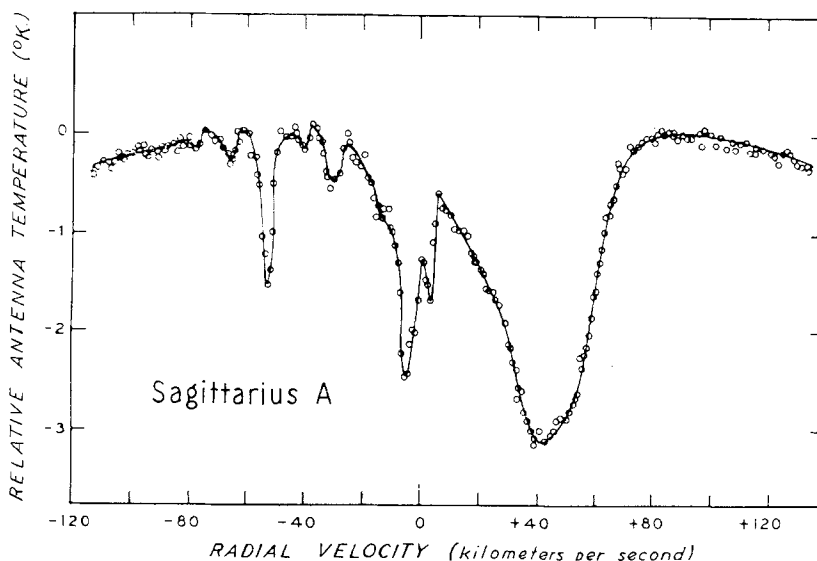


Fig. 5. Interstellar formaldehyde absorption. (From L. E. Snyder and D. Buhl, 1970.)

detected hydrogen cyanide in the Orion Nebula, as shown in Figure 6, which depicts the emission spectra not only of ^{12}C (3.38 mm) and ^{13}C (3.47 mm) hydrogen cyanide, but also that of the unknown compound X-ogen (3.36 mm), which has been suggested to be the formyl radical ion (HCO^+), isoelectronic with HCN, and presumably a very

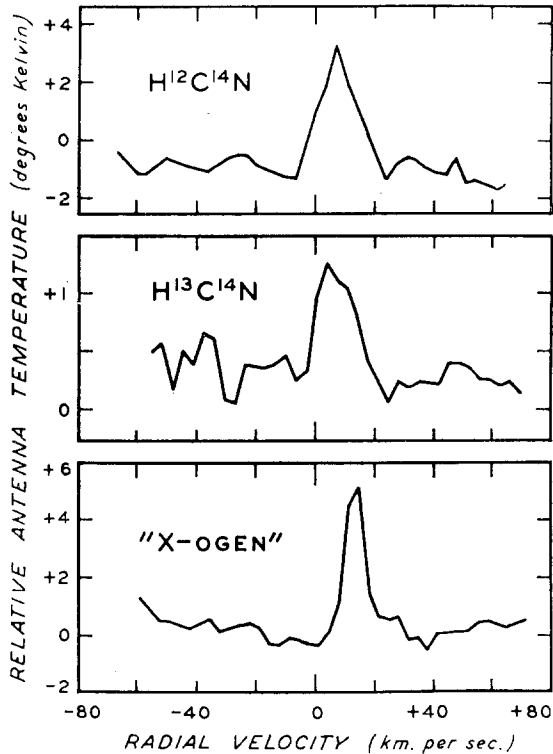


Fig. 6. Interstellar emission spectra. (From L. E. Snyder and D. Buhl, 1970.)

stable species (Klemperer, 1970). Hydrogen cyanide is the second polyatomic organic molecule detected in interstellar clouds. The three observations above (CO, CN, HCN) were made with the 36 ft radiotelescope of the NRAO at Kitt Peak, Arizona, the strongest signals coming from the Orion nebula among other sources. (Buhl and Snyder, 1971). This interstellar formation (Figure 7) is, indeed, one of the most interesting nearby nebulae of gas and dust, about 10 light years in diameter and only 1500 light years away from Earth. In addition to hydrogen cyanide, a large cloud of carbon monoxide about the size of the nebula, and smaller clouds of formaldehyde, cyanogen, water, hydroxyl radical carbon monosulfide and methyl alcohol have been detected there. In July, 1970, Turner (1971) observed, using the 140 ft NRAO telescope, a 3.30 cm emission line corresponding to cyanacetylene. This was the fifth polyatomic species identified and the third and most complex polyatomic organic molecule found in interstellar space. It was discovered at the galactic radio source Sagittarius B2,

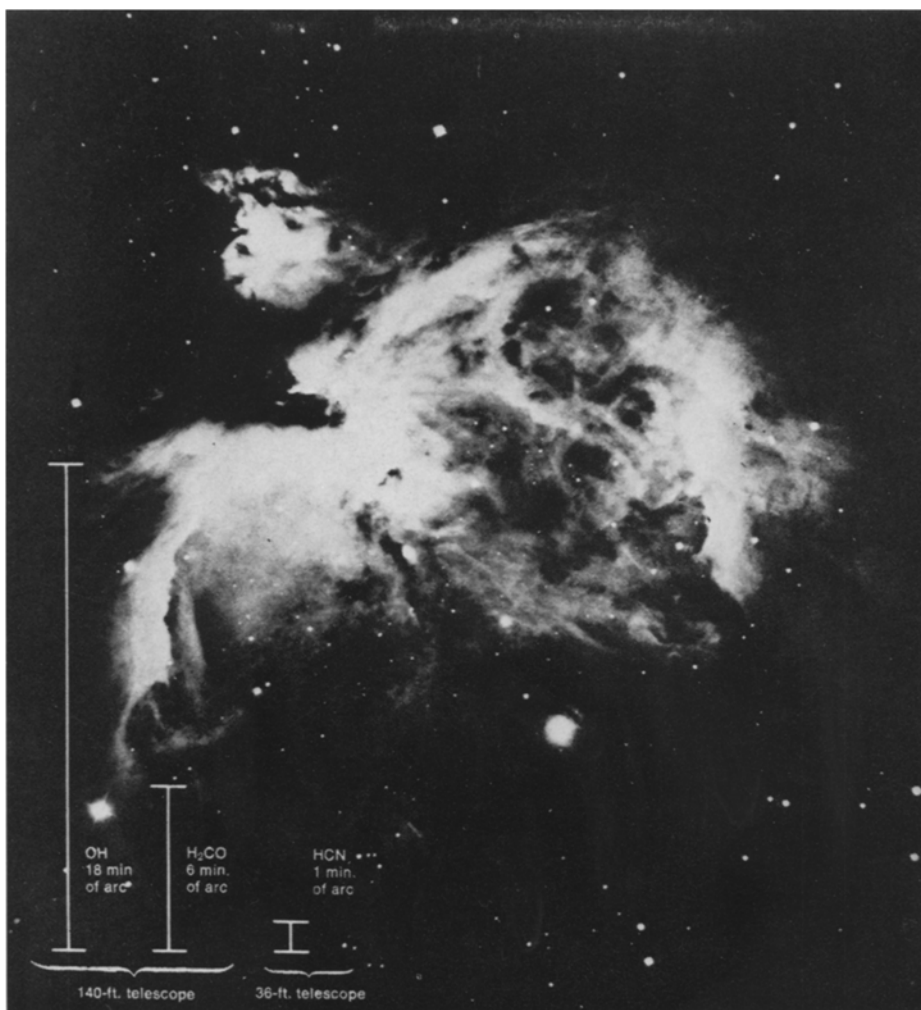


Fig. 7. The Orion nebula. (From D. Buhl and L. E. Snyder, 1971.)

which is also known to have OH, CO, NH_3 , H_2O , HCHO, thioformaldehyde, formamide and formic acid.

Table II shows the 27 interstellar chemical species detected by microwave spectroscopy before the end of 1972. They include 16 organic molecules, 4 inorganic molecules, 6 other species (ions and radicals) and 1 not yet identified line. Most of them have been detected towards the center of the Galaxy (Sagittarius, etc.) and in the Orion Nebula, which are also the dustier regions of the Milky Way. It is remarkable that the interstellar medium contains practically all the organic and related molecules necessary for the synthesis of the biochemical compounds which are essential to life. The significance of these findings for exobiology is discussed in the last section of this article.

TABLE II
Interstellar chemical species (radio astronomy)

Year	Atom, molecule or radical	Symbol	Wavelength	Telescope	Reference
1951	Hydrogen atom	H	21 cm	Harvard Horn	Ewen-Purcell (1951)
1963	Hydroxyl radical	OH	18 cm	Lincoln 84 ft	Weinreb <i>et al.</i> (1963)
1964	Hydrogen ion	H ⁺	3.4 cm	Lebedev 22 M	^a
1966	Helium	He	18 cm	Harvard 60 ft	^a
1967	Carbon	C	6 cm	NRAO 140 ft	^a
1968	Ammonia	NH ₃	1.3 cm	Hat Creek 20 ft	Cheung <i>et al.</i> (1968)
1968	Water	H ₂ O	1.3 cm	Hat Creek 20 ft	Cheung <i>et al.</i> (1969)
1969	Formaldehyde	HCHO	6.2 cm	NRAO 140 ft	Snyder <i>et al.</i> (1969)
1970	Carbon monoxide	CO	2.6 mm	NRAO 36 ft	Wilson <i>et al.</i> (1970)
1970	Cyanogen radical	CN	2.6 mm	NRAO 36 ft	Jefferts <i>et al.</i> (1970)
1970	Hydrogen cyanide	HCN	3.4 mm	NRAO 36 ft	Snyder-Buhl (1971a)
1970	X-ogen	HCO ⁺	3.4 mm	NRAO 36 ft	Buhl-Snyder (1970)
1970	Cyanoacetylene	HC ₂ CN	3.3 cm	NRAO 140 ft	Turner (1971)
1970	Methyl alcohol	CH ₃ OH	36 cm	NRAO 140 ft	Ball <i>et al.</i> (1970o)
1970	Formic acid	HCOOH	18 cm	NRAO 140 ft	Zuckerman <i>et al.</i> (1971)
1971	Carbon monosulfide	CS	2.0 mm	NRAO 36 ft	Penzias <i>et al.</i> (1971)
1971	Formamide	HCONH ₂	6.5 cm	NRAO 140 ft	Rubin <i>et al.</i> (1971)
1971	Silicon oxide	SiO	2.3 mm	NRAO 36 ft	Wilson <i>et al.</i> (1971)
1971	Carbonyl sulfide	OCS	2.5 mm	NRAO 36 ft	Jefferts <i>et al.</i> (1971)
1971	Acetonitrile	CH ₃ CN	2.7 mm	NRAO 36 ft	Solomon <i>et al.</i> (1971b)
1971	Isocyanic acid	HNCO	3.4 mm	NRAO 36 ft	Snyder-Buhl (1971b)
1971	Hydrogen isocyanide	HNC	3.3 mm	NRAO 36 ft	Snyder-Buhl (1971b)
1971	Methylacetylene	CH ₃ C ₂ H	3.5 mm	NRAO 36 ft	Snyder-Buhl (1971b)
1971	Acetaldehyde	CH ₃ CHO	28 cm	NRAO 140 ft	Ball <i>et al.</i> (1971) ^a
1971	Thioformaldehyde	HCHS	9.5 cm	Parkes 210 ft	Sinclair <i>et al.</i> (1971) ^a
1972	Hydrogen sulfide	H ₂ S	1.7 mm	NRAO 36 ft	Thaddeus <i>et al.</i> (1972) ^a
1972	Methylene imine	H ₂ CNH	5.6 cm	Parkes 210 ft	Godfrey <i>et al.</i> (1972) ^a

^a These discoveries have appeared in *International Astronomical Union Circulars* or are private communications.

C. ABUNDANCES, LIFETIMES AND ISOTOPIC RATIOS

Table III shows the relative abundances of a few of the molecules in the interstellar medium, normalized to formaldehyde, and their comparison to the values to be

TABLE III
Relative molecular abundances^a

Molecule	Observed	Expected
CO	10 ⁴	1
OH	30	3 × 10 ³
NH ₃	30	3 × 10 ²
HCN	10	10 ⁻¹
CN	10	10 ⁻¹
H ₂ CO	1	1
Cosmic atomic abundances		
	O/H	7 × 10 ⁻⁴
	C/H	3 × 10 ⁻⁴
	N/H	9 × 10 ⁻⁵

^a Normalized to formaldehyde. (Courtesy of D. Buhl.)

expected from the relative cosmic abundances of their constituent elements. Although the molecular values may vary from source to source, carbon monoxide, cyanogen radical and other species show anomalously high abundances. For instance, CO is much more abundant than OH, when in reality it should be the other way around, because of the predominance of hydrogen in the cosmos. If these differences are confirmed when more extended observations are made the explanation of these anomalies will have to be sought in the different factors which determine the relative rates of decomposition and formation, and the steady state concentration of a particular chemical species in an interstellar gas cloud.

Calculations of the lifetimes in an unobscured interstellar radiation field ($U_{\lambda} = 40 \times 10^{-18} \text{ erg cm}^{-3} \text{ \AA}^{-1}$) have given relatively short lifetimes of about 40 to 100 yr for HCHO, H₂O and NH₃, and 10² to 10³ yr for CO (quantum yields from 1.0 to 0.1) (Stief *et al.*, 1971). These short lifetimes suggest that these molecules were formed or released in the gas phase in the clouds where they now occur or were protected against photodecomposition by dust particles or interstellar grains. Calculations of lifetimes as a function of cloud opacity, for clouds of moderate opacity (3 magnitudes) show that polyatomic molecules and CO have reasonably long lifetimes, of the order of 10⁶ and 10⁸–10⁹ yr, respectively. It appears, that the destructive effects of the physical conditions prevailing in interstellar space may have been overestimated, and that certain molecules can exist, particularly in dusty regions, for a relatively long time, compared to the evolutionary lifetimes of their respective clouds. For instance, the expanding shell of carbon monoxide detected in the planetary nebulae IRC+10216

(Solomon *et al.*, 1971a) must have existed as such since it was formed, for it has been estimated to have an age of 500 yr only. Thus, the higher photo-stability of carbon monoxide must be responsible, in part for the overabundance of this diatomic species in interstellar space. The same argument probably applies to CN and other species of greater observed abundances than expected. In general therefore the photo-stability of these diatomics is consistent with the wide distribution and higher observed abundances of CO and CN not only in interstellar clouds but also in circumstellar clouds. Further support for this interpretation is provided also by the high photo- and thermal-stability of these diatomics and related species during their residence in stellar atmospheres and their ejection to interstellar space (see previous section). Indeed, aside from H₂ and OH, the carbon compounds CO and CN are two of the calculated most stable diatomic species in the atmospheres of carbon stars (Figure 3).

This would suggest the hypothesis that most of the organic molecules are derived from stars in the form of stable and relatively dehydrogenated precursors (C, CO, CN, CH, C₂, C₃, 'aromatic-graphitic,' etc.) and that these species are progressively converted into other molecules by hydrogenation ($\cdot\text{H}$), hydroxylation ($\cdot\text{OH}$) and other reactions in interstellar space, thus generating several daughter molecules (HCHO, CH₃OH, HCO₂H; HCN, HNCO, HNC, HCONH₂; CH₃CHO, HC₂CN, HC₂CH₃, etc.). This hypothesis is in line with the direct observations on *novae* presented earlier and is also consistent with an examination of some carbon isotopic abundances from interstellar molecules.

Measurements from different sources have given values of the ¹²C/¹³C ratio which vary from about 11 to terrestrial values. If these ratios are confirmed they will give ranges similar, but possibly less wide than, the ranges observed in stellar atmospheres. The following ¹²C/¹³C values have been reported for Sagittarius A and Orion A, although the line intensity measurements were only semiquantitative: HCHO (Sgr A) \approx 11 (Zuckerman *et al.*, 1969); HCN (Or A) \approx 8.9; HCN (Sgr A) \approx 4.7 (Snyder and Buhl, 1971). As stated in the previous section a value ¹²C/¹³C \approx 4.6 corresponds to the equilibrium value for the carbon-nitrogen cycle of carbon stars, which could indicate that the HCN of Sagittarius A was derived from such a star. It should be pointed out that in the case of the carbon isotopes of formaldehyde from Sgr A, saturation effects of the carbon-12 line may lead to an overestimate of the relative proportion of carbon-13 present (Buhl, 1971). Other independent measurements of carbon isotopes from Sgr A have also given ratios, such as ¹²C/¹³C = 25, different from terrestrial values (see Buhl, 1971). On the other hand, a series of optical spectra obtained with the Lick Observatory 120 in. telescope, gave average ¹²C/¹³C values of about 82, close to the terrestrial 89 value (Bortolot and Thaddeus, 1969). However, these observations were made in a region removed from the galactic center. The difference between these two series of measurements (radio and optical) may reflect the higher turnover rate of stellar and interstellar matter in the more active (nuclear) region of the galactic center, and the increased recycling of carbon through the carbon-nitrogen cycle of this central region. However, it is obvious that many more accurate measurements are needed before it can be said with certainty that the carbon isotopic values of interstellar clouds

vary as in the stars or have average values typical of the isotopic carbon mixture in our solar system.

Table IV gives approximate values for some physical parameters of interstellar gas clouds and grains. The interstellar clouds are composed of hydrogen, 'molecular'

TABLE IV
Physical parameters of interstellar matter

<i>Gas clouds</i>	
Size of gas clouds	$\approx 10^{-2}$ to 10^2 light years
Molecular weight (organic and related species)	1 to 60 daltons
Distance scale unit	1 light year
Probable collision time	1×10^6 yr
Velocity range	≈ 0 to 100 km s^{-1}
Density (thin clouds)	$\approx 1 \text{ molecule cm}^{-3}$ or less
Density (dense clouds)	$10^1 - 10^6 \text{ molecules cm}^{-3}$
Microwave background temperature	2.7 K
Temperature (radiation or kinetic excitation)	≈ 1 to 100 K (clouds can be cooler or hotter than environment)
Energy emitters	OH and H_2O masers ($10^{32} \text{ erg s}^{-1} \equiv 0.1 \text{ Sun}$)
Energy absorbers	Formaldehyde inverse maser
<i>Interstellar Grains</i>	
Diameter (average)	≈ 0.1 micrometer
Density (relation to H)	10^{-12}
Temperature of grain	$\approx 10 \text{ K}$ (5 to 15 K)
Suggested composition which may account for some of the observational features (reddening, polarization, etc.)	Metals, ices and condensed, gases, silicates, chondrules, graphite, aromatic hydrocarbons, large organic molecules and inorganic or organic cores plus condensed gases.

species and grains in variable ratios with the former usually predominating. There appears to be a good correlation on one hand, between molecules and the interstellar grains and galactic center (or other active regions such as the Orion nebula), and less of a correlation, on the other hand, between molecules, and the hydrogen atoms and the peripheral spiral arms of our Galaxy. This is probably what should be expected not only from the probable existence of common genetic relationships between molecules and grains, but also as a result of the protective effect against radiation conferred by the interstellar grains on the molecules. It is obvious that the prevailing low densities, temperatures and molecular collision frequencies establish a physical state in the interstellar medium far removed from thermodynamic equilibrium. At the relatively low temperatures of interstellar space (microwave background radiation temperature $\approx 2.7 \text{ K}$) each molecule has a particular set of discrete levels of rotational energies. The transition between any two levels occurs by the absorption or emission of quanta of energy. This energy may be in the form of radiation or in the form of collision with other species, most likely neutral hydrogen atoms or molecules. The nonequilibrium conditions of the interstellar medium, and the radiation or collisional processes of energy transfer, make possible the existence of masering (emission by OH and H_2O),

and inverse masering (absorption by HCHO) effects, which bring about cooling and heating of the respective clouds (Buhl and Snyder, 1971).

The masering effect may play an important role during the contraction phase of gravitationally unstable clouds into stars and possible planetary systems. The cloud density required for this to occur is of the order of 10^6 mol cm^{-3} . Through collisions with hydrogen molecules or atoms the H_2O and OH are cooling the hydrogen cloud as it collapses into a protostar, and the excess energy generated by this collapse is radiated away by the masering OH radicals and H_2O molecules. As much as $10^{32} \text{ erg s}^{-1}$, approximately 10% of the Sun's energy irradiation rate, is being emitted by some OH masering sources (Buhl, 1971). One could conceive, therefore, depending on the nature of the intermediate steps, a certain relationship between the organic and inorganic components of the collapsing gas and dust cloud of the solar nebula and the components of the cool bodies of our solar system, as are the comets, the carbonaceous chondrites and the Jovian planets. However, relatively little is known on the nature of these intermediate steps, which are very much dependent on models for the evolution of the interstellar medium (e.g., Bottcher *et al.*, 1970), fractionation and condensation in space (e.g., Arrhenius and Alfvén, 1971), and formation of the solar system (e.g., Jastrow and Cameron, 1963). It is hoped that a continuation of studies on molecular radioastronomy and interstellar cloud dynamics will bring a significant improvement of this situation in the future.

4. Comets

Within the solar system comets are without doubt the most interesting bodies to study from the point of view of organic cosmochemistry. The three primary reasons are as follows: (1) They contain substantial amounts of organic compounds as evidenced by well defined optical emission lines. (2) The matter in them has not undergone the changes experienced by the matter in the terrestrial planets during their processes of gravitational contraction, differentiation, internal or surface heating, and substantial loss of volatile components. Therefore, if they have originated in the solar system as the planets, they probably represent the least changed samples available of the primordial matter of the solar nebula, preserved in a more or less frozen state in the outer regions of the solar system. (3) The orbits of some comets come near the Earth and may even cross the Earth's orbit during their approach to perihelion. Therefore a certain amount of cometary matter (from direct collision, meteor streams or other cometary debris) must have been acquired by our planet throughout its past history.

A. CHEMICAL COMPOSITION

Spectroscopic observations of fluorescence emission lines have shown that comets are rich sources of volatile compounds of H, C, N, and O, as well as other heavier common metallic constituents (Na, Fe, etc.). The nucleus probably consists of a mixture of ices, hydrates of a few molecules (H_2O , NH_3 , CO, C_2N_2 , CH_4 , C_2H_2 , etc.) and metals, silicates and other inorganic components. The icy-conglomerate model of Whipple

(1950, 1951, 1963) has been further developed by Donn (1963) and Donn and Urey (1956), and more recently has been refined to a 'coremantle' model particularly applicable to short period comets (Sekanina, 1969a). Briefly, the comet nucleus is presumed to be a body of 1 to 10 km radius (Roemer, 1966), of density approximately 1, made of a non-volatile solid matrix (core) embedded with ices or hydrates of volatile constituents, and surrounded by layers of these ices (mantle). This central body is in turn surrounded by a diffuse atmosphere of the volatilized molecules (coma) from which an extended band, or series of linear or helical rays (tail) stream away, always in opposite direction to the Sun. The gases in the coma are mainly atomic hydrogen (see Biermann, 1971) accompanied by the hydroxyl radical and other neutral or ionized species such as atoms and di- or triatomic radicals or molecules (H, H₂, OH, OH⁺, O; CN, C₂, C₃, CH, CH⁺, CO⁺, CO₂⁺; N₂⁺, NH, NH₂; Na, Fe); those in the tail are essentially ionized molecules (CO⁺, N₂⁺, CO₂⁺, CH⁺, OH⁺, CN). These chemical species probably result from the photodissociation or ionization of stable parent molecules, or from chemical reactions occurring near the surface of the nucleus. One of the most active zones is presumably the solar wind shock front region of the comet facing the Sun. Table V gives some information on the chemical species detected in comets. More detailed information may be found elsewhere (Richter, 1963; Swings and Haser, 1956; Vsekhsvyatskii, 1964).

TABLE V
Chemical species detected in comets and other cometary data

Composition ^a	CN, CH, CH ₂ , C ₂ , C ₃ , NH, NH ₂ , OH, CH ⁺ , CO ⁺ , CO ₂ ⁺ , N ₂ ⁺ , OH ⁺ , and Na
Parent compounds ^b	HCN, NH ₃ , H ₂ O, CO, C ₂ N ₂ , CH ₄ , C ₂ H ₂ , and other hydrocarbons
Average mass ^{b,c}	10 ^{18±3} gm (10 ¹⁸ gm minimum mass for Halley's comet)
Probability of collision with the Earth ^b	100 collisions in 5 × 10 ⁹ yr
Cometary matter trapped by the Earth ^b	10 ^{20±3} gm in 5 × 10 ⁹ yr

^a From spectrochemical evidence

^b Calculated or estimated.

^c See Richter (1963), pp. xxvii and 37-39.

Carbon isotopic measurements from cometary species obtained recently are consistent with a common origin with matter of our planetary system since the observed cometary isotopic carbon ratios are essentially those prevailing on Earth and in meteorites. The value obtained for the Swan (¹²C¹³C) bands of comet Ikeya was ¹²C/¹³C = 70 ± 15 (Stawikowski and Greenstein, 1964). A more recent measurement of Tago-Sato-Kosaka, 1969 g, Swan bands gave a ratio 100 ± 20 (Owen, 1972).

An examination of the radicals, radical ions, and suggested parent compounds of comets, and their comparison with the molecules and other chemical species detected in interstellar space shows a notable agreement. In fact about ten of the most impor-

tant chemical species (H, H₂, H₂O, NH₃, HCN, CN, CO, CH, CH⁺, OH) appear to be common to both interstellar clouds and comets. Another salient feature is that a similar degree of individual differentiation is observed in both groups of cosmic bodies. That is to say, if gas clouds do not have a homogenous composition neither do the comets. Some comets are rich in CO, others in CN, others in OH, etc. One of the key related questions is whether this reflects a certain heterogeneity within the primordial solar nebula or it shows a possible genetic correlation of comets to interstellar gas and dust clouds.

B. POSSIBLE ORIGINS

Two possible alternative origins of comets, 'interstellar' or 'solar system' have been considered in the past on the basis of the orbital and dynamic characteristics of comets. Indeed, the two major groups of theories advanced since Laplace, propose either an 'interstellar' or a 'planetary origin of these cosmic bodies (Richter, 1963). The first group of theories assumes that comets have been acquired by the solar system from interstellar space, whereas the second group postulates that the comets originated from the Jovian planets by disruptive events, or alternatively from the primordial solar nebula.

Observational studies on some 600 individual comets have revealed a preponderance of elliptic and paraboloid orbits with approximately 10% hyperbolic orbits. The actual number of comets must be much larger with estimates up to 10¹¹ comets (Oort, 1963). The overall cometary population extends out to a great distance from the Sun, and includes two major systems: the central planetary system of short-period (<200 yr) comets, and the general circumsolar system of long-period comets. From statistical calculations on long-period comets Oort (1963) concluded that the majority of members from this system must come from distances as far away as 100000–150000 AU, which are the distances of the nearest known stars. (For comparison Pluto's aphelion is approximately 50 AU and its period 248 yr.) Therefore, the existence of an interaction between the circumsolar cometary system and the interstellar clouds, during the motion of the solar system, through interstellar space, appears possible, notwithstanding the relatively small proportion of hyperbolic cometary orbits observed. A number of authors (Kuiper, 1953; Levin, 1958; Whipple, 1964) consider that comets are byproducts of the formation of planets, and that they originated from low temperature planetesimals or primordial solar nebula material in the region of the outer planets about 4.5×10^9 yr ago.

C. EVOLUTION AND INTERACTIONS

The great comet cloud at about 100000 AU is presumed to provide our present long-period comets *via* the perturbations of passing stars. Some of the long-period comets are later perturbed by Jupiter and eventually become short-period comets of the Jupiter family. The evolution of these bodies does not stop here, and apparently, further gravitational interactions and non-gravitational effects (e.g., acceleration by gas 'jets' escaping from the nucleus) are responsible for the transformation of some short-

period comets into asteroids, particularly some of the Apollo and Amor types (see Öpik, 1963; Marsden, 1967, 1968, 1970, Sekanina, 1969a, b). For instance, Icarus is an asteroid widely regarded to be a former comet; Arend-Rigaux and Neujmin 1 are two Jupiter's family comets which have been observed to change from a cometary (coma fuzziness) to an asteroidal appearance; and Encke is a slowly decaying comet, probably associated with the Taurid meteor-stream (Whipple and Hamid, 1952). According to recent calculations Encke will lose most of its volatiles and acquire an asteroidal appearance by the year 2030 (Sekanina, 1969b). The relatively short observable lifetimes of a number of comets had already been predicted by the decrease in the measured 'absolute' magnitudes at their successive returns to perihelion (Vsekhsvyatskii, 1964) (Figure 8).

In line with the above comet-asteroid relationships it was also established by Hoffmeister (see Richter, 1963) that meteor streams or showers are associated not only with comets but also with some of the asteroids, or minor planets, such as Apollo, Adonis, and Hermes. Furthermore, Arnold's-type (Arnold, 1964) Monte Carlo calcu-

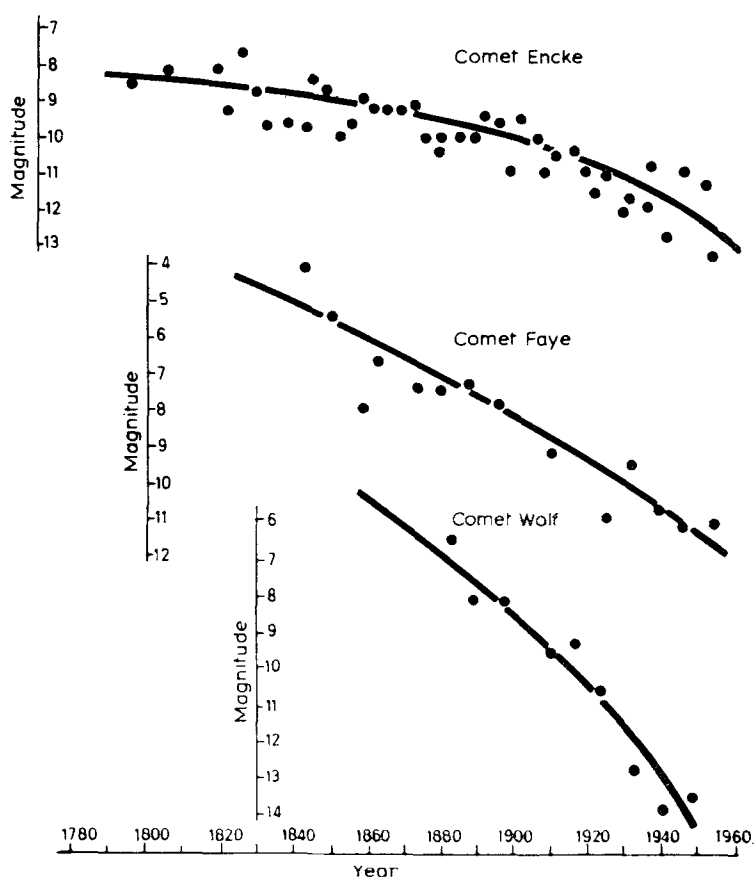


Fig. 8. Decreasing magnitudes of some periodic comets. (From K. Hindley, 1971.)

lations by Wetherill (1968) show that bright fireballs and chondritic meteorites are derived from orbits similar to those of short-period comets and asteroids. Also, recent evidence obtained by the U.S. Prairie Network, and other photographic networks, indicates that only about 5% of the material falling on Earth as fireballs from interplanetary space produces solid meteorites. The bulk of this matter is of a friable nature most probably related to cometary debris or to carbonaceous chondrites (McCrosky, 1968; Hindley, 1971).

It is therefore not surprising that the data available on the cataclysmic event which occurred in Tunguska, Siberia, in 1908, does not indicate a meteorite fall, but rather shows that it was produced, most probably, by the collision of a comet with the Earth, as suggested first by V. I. Vernadsky, F. J. W. Whipple, and I. S. Astapovich, and more recently by V. Fesenkov and K. P. Florensky (see Krinov, 1960; Florensky, 1963a, b; Astapovich, 1966). The comet apparently exploded at an altitude of about 5 to 10 km before reaching the Earth's surface with an energy probably in excess of 10^{23} erg. No macroscopic solid fragments could be recovered from the soil, but dust was spread throughout the Earth's upper atmosphere and microscopic iron-nickel spherules of cosmic origin were recovered from the impact area. Cometary collisions with the Earth have also been implicated in the generation of tektites and magnetic field reversals (Glass, 1968). The collision of comets with the Earth, as well as the more frequent fall of interplanetary debris and carbonaceous meteorites on our planet may be of significance in relation to the formation and capture of carbon and nitrogen compounds not only by the Earth (Oró, 1961; Hochstim, 1963) but also by other terrestrial planets and the Moon. This will be briefly discussed later.

5. Meteorites

It is a generally accepted idea that meteorites are derived from asteroids, some of which, in turn, were derived from the breakup of a few minor planets of about 100 km in diameter (Anders, 1964). Calculations of the orbit of two meteorites (two bronzite chondrites) one of which fell in Pribam, Czechoslovakia, 1959, and the other in Lost City, Oklahoma, 1970, gave results which are compatible with an asteroidal origin for these meteorites (McCrosky, 1970; Fireman, 1970; Fireman and Spannagel, 1971). As seen in Figure 9 their orbits are slightly larger but comparable to that of the Apollo asteroid. Other relationships of meteorites with Apollo asteroids, Mars asteroids, and those from the major asteroid belt, or ring asteroids, have been discussed by Anders (1964).

It is also possible, as has been said before, that some of the meteorites, particularly carbonaceous chondrites type I, are derived from fragments of broken-up nuclei of comets which have been perturbed some time in the past into asteroid orbits. This suggestion becomes more plausible when one takes into consideration the fall of the Revelstoke meteorite, a type I carbonaceous chondrite (Folinsbee *et al.*, 1967) from which only about 1 g could be recovered out of a calculated mass of 1×10^6 g (Shoemaker, 1966). This large mass of loosely aggregated matter may be closely related to

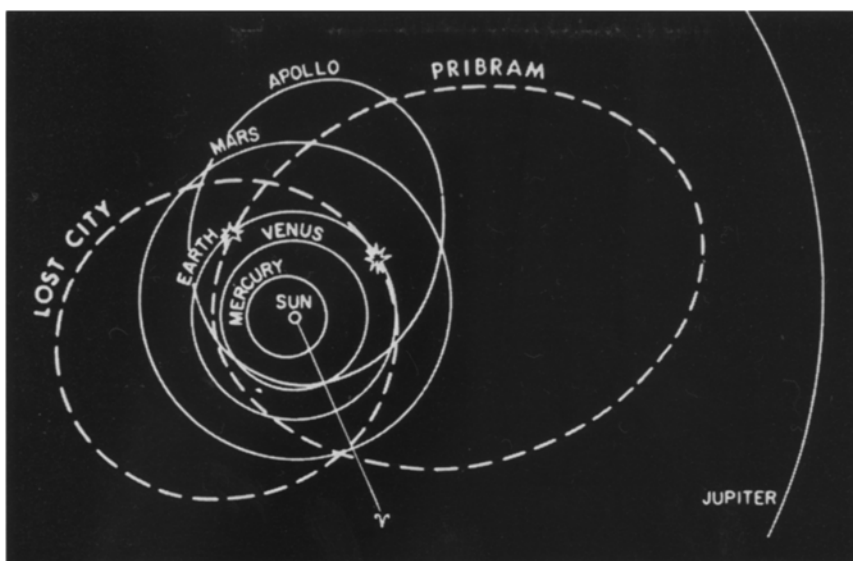


Fig. 9. Orbits of the Lost City and Pribram meteorites. (From E. L. Fireman, 1970.)

the friable material which continuously enters the terrestrial atmosphere and is dissipated in the form of bright fireballs (Hindley, 1971). In fact, a cometary origin for some meteorites (as well as asteroids) had already been suggested some time ago by several investigators (e.g., Öpik, 1968).

Regardless of the exact location of their origin, or the primary or secondary nature of their source(s), meteorites are presumed to have been derived from matter of approximately cosmic composition as it existed in the solar nebula at the time of formation of the solar system. The existence of different types of meteorites, irons, stony irons, achondrites, chondrites must therefore reflect the different physical processes of fractionation of elements, formation of chondrules, separation of phases, loss of volatiles, collisional processes, etc. which are responsible for the major differential characteristics of these extraterrestrial objects (Mason, 1962, 1963; Anders, 1964, 1968).

As pointed out in the Introduction the organogenic elements H, C, N and S are, in general, depleted in meteorites relative to their cosmic abundances. However, significant amounts of carbon are found in four major groups of meteorites, carbonaceous chondrites, ureilites, irons and other chondrites. The distribution of total carbon does not follow a well defined pattern. It varies from about 0.1% to 5% for carbonaceous chondrites, to about 2% for ureilites, and to less than 0.6% for ordinary chondrites and irons (Moore and Lewis, 1965, 1967; Otting and Zahringer, 1967; Vdovykin, 1970b; Lewis and Moore, 1971). The ureilites contain diamonds, the irons and several chondrites contain graphite, cliftonite, carbides (cohenite) and possibly other carbon compounds, and the carbonaceous chondrites contain a variety of volatile and non-volatile organic compounds. Whereas the highly stable carbon compounds present in

the former meteorites appear to have been generated by the action of relatively high temperatures (e.g., graphite, carbides) or shock pressures (e.g., diamonds), the more labile organic and related compounds present in carbonaceous chondrites can never have been subjected to the action of high temperatures after they were formed. It is for this reason that the study of these meteorites is of particular interest to organic cosmochemistry.

6. Carbonaceous Chondrites

The carbonaceous chondrites have been classified as types I, II and III (Wiik, 1956; Mason, 1963) and recently C1, C2, C3 and C4 types (Van Schmus and Wood, 1967). A more recent reevaluation of the data from 36 carbonaceous chondrites (Mason, 1971) shows that Wiik's early scheme incorporating Van Schmus-Wood subdivision of type III into two subtypes (Vigarano and Ornans), is a preferable classification because it appears to reflect more adequately the basic differences in chemical and mineralogical composition, and structure of these meteorites.

It is well known that in addition to volatile and non-volatile carbon compounds, the three types of carbonaceous chondrites contain water, sulfur and other volatiles, and that the bulk of the volatile matter decreases in going from type I to type III. Also, in contrast to the other meteorites, carbonaceous chondrites contain significant amounts of hydrated ferromagnesium silicates and other minerals which can only be formed at low temperatures and in aqueous systems (Mason, 1962; Anders, 1964). These meteorites are presumed to be mixtures of low- and high-temperature fractions which were generated in two different environments of the primordial solar nebula (Wood, 1962; Anders, 1964). The first, or undepleted fraction, corresponds to the matrix, rich in volatiles, and the second, or depleted fraction, to the chondrules, from which the volatiles were lost.

Type I carbonaceous chondrites are unique because they have virtually no high-temperature minerals with the possible exception of traces of olivine and pyroxene (Mueller, 1962; Reid *et al.*, 1970), have no ordinary chondrules, although the existence of certain chondrular inclusions (Mueller, 1966) and magnetic spherules (Jedwab, 1968) has been shown, and contain veins of magnesium sulfate and dolomite, which indicate exposure to liquid water for at least 1000 yr (DuFresne and Anders, 1962). Therefore, they consist almost exclusively of matrix and represent samples of the undepleted fraction slightly changed by exposure to liquid water. These conditions and features are consistent with those which have been postulated for low temperature minor planetary bodies and primordial cometary nuclei.

A. ORGANIC CONSTITUENTS

The literature on the nature of the organic compounds and other related constituents of carbonaceous chondrites has been reviewed by Cohen (1894), and more recently by Briggs and Mamikunian (1963), Urey (1966), Nagy (1966), Hayes (1967) and Vdovykin (1967). The latter two comprehensive reviews cover the literature from about 1894 to 1967 and from 1806 to 1967, respectively. The organic research work on these mete-

orites seems to have taken place in periodic cycles of increased and decreased activity since the first of these meteorites fell in Alais in 1806 and was analyzed (e.g., Thenard, 1806). In spite of its long history, the interest on this subject has remained high, even if periodical, mainly because the organic compounds, structures and microorganisms found in carbonaceous chondrites have been considered at different times as possible indicators of the existence of extraterrestrial life or extraterrestrial organic chemistry. In the present century, aside from the suggestion by Spielman (1924) of the possible formation of meteoritic 'bitumens' from carbides, and the sharp controversy between Lipman (1932) and Roy (1935) on the isolation of bacteria from these extraterrestrial objects, the field did not regain momentum until the work of Mueller (1953) and Nagy *et al.* (1961) on the analysis of hydrocarbons and other organic compounds in extracts of carbonaceous chondrites. A thorough examination of the evidence on the organic constituents in meteorites and a critical discussion of this subject will be found in the review by Hayes (1967). Hayes suggested that an increased effort on the detailed organic analysis rather than a directed search for extraterrestrial life may be more desirable.

Whether the organic material in carbonaceous chondrites is in any way the product of extraterrestrial life or the result of natural processes of chemical evolution is indeed an exciting question. Although the answer is not yet available in a definitive manner, significant progress has been made during the last four years, with the organic analysis of several meteorites, particularly two newly fallen carbonaceous chondrites, the Allende and the Murchison. The results obtained provide strong support for the non-biological chemical synthesis of the organic compounds present in these meteorites. This presentation does not cover all the work published since Hayes' review; rather it is a discussion, limited in scope, of some of the most salient observations made recently on two major groups of organic compounds: hydrocarbons and amino acids.

B. HYDROCARBONS

By the application of combined gas chromatography and mass spectrometry, a more complete identification of the hydrocarbons and related volatile compounds in carbonaceous chondrites and other meteorites has been possible (Hayes and Biemann, 1968; Studier *et al.*, 1968; Oró and Gelpi, 1969; Gelpi and Oró, 1970a). The first authors observed the evolution of sulfur, nitrogen, oxygen, carbon disulfide, and several hydrocarbons and other organic compounds, including alkanes, with a large n-C₁₅, olefins, alkylbenzenes, naphthalene, and other aromatics up to phenanthrene by direct volatilization of the Murray meteorite at temperatures approximately 100 to 300°C. The second group of authors also used direct volatilization at 100 to 200°C for 16 hours, and occasionally extraction, in the analysis of the Orgueil and Murray meteorites. Above C₁₀, normal paraffins were found to be the principal species (C₁₀ to C₁₆), with lesser amounts of 2-methyl, 3-methyl and other slightly branched paraffins and olefins. Below C₁₀, aliphatic hydrocarbons were found markedly deficient while benzene and alkylbenzenes dominated. Carbonyl sulfide, carbon disulfide, o- and p-dichlorobenzene were also seen in both meteorites. Three isoprenoid hydrocarbons (C₁₁, C₁₃, C₁₄) were tentatively identified in the Murray.

The third group of investigators analyzed the alkane fraction of extracts of six carbonaceous chondrites (Essebi, Grosnaja, Mokoia, Murray, Orgueil and Vigarano) (Gelpi and Oró, 1970a) and graphitic nodules of three iron meteorites (Canyon Diablo, Odessa, and Cosby's Creek) (Gelpi and Oró, 1970b). Their results confirmed and extended the earlier work of Meinschein (1965) on the Orgueil meteorite and of Nooner and Oró (1967) on some twenty-nine meteorites, providing a substantially complete characterization of the aliphatic hydrocarbons in the examined meteorites. Ten homologous series of paraffinic hydrocarbons were identified mass spectrometrically in the carbonaceous chondrites. In addition to the normal alkane series (from C_{11} to C_{26}), there were five monomethyl series (2-, 3-, 4-, 5-, and 6-methyl alkanes), two monocyclic series (cyclohexyl- and cyclopentyl alkanes), and two isoprenoid series (2, 6, and 10-trimethyl and 2, 6, 10, 14-tetramethyl alkanes). The total amounts of n-paraffins ranged from about 6 to 80 ppm. The isoprenoids usually showed a bimodal distribution with a major maximum at C_{19} (pristane) and a secondary maximum at C_{16} (methyl farnesane). The graphitic nodules of the iron meteorites were found to contain practically all the alkane homologous series (except the 5-monomethyl), as well as the bimodal (C_{16} , C_{19}) distribution of the isoprenoids which had been found in the carbonaceous chondrites. The amounts of total alkanes in the nodules were lower (0.3 to $9.4 \mu\text{g g}^{-1}$), and certain odd C-numbers n-alkanes predominances (C_{15} and C_{17}) were observed in a nodule from the Cosby's Creek meteorite. A similar n- C_{15} and n- C_{17} predominance or bimodality had been observed before in the Orgueil meteorite (Nooner and Oró, 1967). The work of Smith and Kaplan (1970) on the alkanes of extracts from Ivuna, Murray, Orgueil, Mokoia, Cold Bokkeveld, Mighei and Erakot, also gave analogous results. The isoprenoids pristane and phytane were found in the last six of these meteorites; and the first three showed high molecular weight alkanes with the following predominances or modes: Ivuna, C_{15} , C_{17} and C_{21} ; Murray, C_{17} and C_{21} ; and Orgueil, C_{19} and C_{23} .

In general, the distribution of alkanes in extracts of meteorites is similar to that of certain biological products such as petroleum crudes and extractable organic matter of sediments, terrestrial graphites (Gelpi *et al.*, 1969), limestones (Nooner *et al.*, 1972) and many other environmental samples (Nooner, 1966; Gelpi, 1968; Gibert and Oró, 1970; Oró *et al.*, 1970b; Gibert, 1971). Normal heptadecane which is abundant in meteorites and terrestrial samples (graphites, soils, limestones, etc.) is also known to be one of the major alkanes produced by algae (Gelpi *et al.*, 1970a), particularly *Chlorococcus* which has been isolated from the surface of exposed limestones (Nooner *et al.*, 1972).

The above observations suggest that some of the hydrocarbons, particularly the isoprenoids, pristane and phytane, and part of the odd C-number alkanes (e.g., C_{15} , C_{17} , C_{19} , C_{21} , C_{23}) are terrestrial contaminants. This is supported by the finding (see later) of trace amounts of high molecular weight isoprenoids (e.g., C_{17} to C_{20}) in the external parts or surface of two recently fallen carbonaceous chondrites, the Allende (Han *et al.*, 1969), and the Murchison (Studier *et al.*, 1972). A more rigorous demonstration of the origin of these highly ordered hydrocarbons may eventually be possible by the application of recently developed stereochemical separation methods (Maxwell,

1971) to the analysis of the different isoprenoid isomers from meteorites. This does not preclude the possibility that some of the normal and branched alkanes in meteorites could have been abiotically synthesized by different chemical reactions.

The lighter hydrocarbons (from C₁ to C₇) of the Murray meteorite have also been studied by Belsky and Kaplan (1970) by a method which does not involve extraction or heating, that is, by carefully crushing the meteorite after evacuation of loosely adsorbed gases. Small amounts of saturated and unsaturated hydrocarbons, including methane (514 ng g⁻¹), ethane (206 ng g⁻¹), propane, ethylene pentane, n-heptane, n-pentane, 2-methyl pentane and benzene (14 ng g⁻¹), the amounts of which decreased approximately in the listed order, were observed. It was concluded that these gases were trapped between crystal boundaries. From the results on the small methane/ethane ratio, low amounts of aromatic hydrocarbons, and different ¹³C/¹²C ratios for different fractions, it was also concluded that equilibrium conditions had not been attained among the different carbon constituents.

C. ALLENDE AND MURCHISON HYDROCARBONS

The Allende is a type III, Vigarano subtype, carbonaceous chondrite with 0.27% C, 0.007% N, dark and light inclusions and other peculiar properties (King *et al.*, 1969; Clarke *et al.*, 1971; Mason, 1971). This meteorite was found to be slightly contaminated on the outside (fatty acids, isoprenoids and other hydrocarbons), but analysis of the inside pieces did not yield any significant (less than 0.5 μg⁻¹) amount of high molecular weight extractable organic compounds (Han *et al.*, 1969). However, by heating in vacuum or in a stream of helium, aromatic and aliphatic hydrocarbons were obtained in amounts of 20 ppm (Simmonds *et al.*, 1969) and 70 ppm (Levy *et al.*, 1970) in the range C₁ to C₁₂. The aromatics (benzene, toluene, dimethylbenzenes, etc.) predominated in the first of these two studies (by heating up to 500°C in 15 s), whereas aliphatics (decane and undecane) prevailed in the second experiment where the bulk of the organic compounds appeared by heating at 150°C for ten minutes. In both cases olefins and alkylbenzenes were also observed. The hydrocarbons were presumed to be tightly entrapped within the inorganic matrix or result from degradation of a polymer, since previous extraction of the meteorites with a perdeuterated solvent mixture (benzene-methanol) did not significantly affect the results (Simmonds *et al.*, 1969). However, the increased aromatic content (xylenes, C₃ alkylbenzenes, etc.) observed when the meteorite was heated at 460°C for five minutes (Levy *et al.*, 1970), suggest that some of these compounds may be secondary products or alternatively that there is a marked heterogeneity from sample to sample, which may be indigenous or acquired. Other recent observations on 'hydrocarbon' inclusions (Clarke *et al.*, 1971) and the extraction of formaldehyde from this meteorite (Breger *et al.*, 1971) are too preliminary to be properly evaluated. It is obvious that additional work on the Allende is required before any major conclusions can be made.

The Murchison is a type II carbonaceous chondrite with 2% C and 0.16% N (Kvenvolden *et al.*, 1970; Jarosewich, 1971; Mason, 1971), apparently rich in organic compounds. This meteorite has been shown to contain substantial amounts of extractable

high molecular weight aliphatic and aromatic hydrocarbons (Kvenvolden *et al.*, 1970; Oró *et al.*, 1971a; Gibert, 1971; Gibert *et al.*, 1971; Pering and Ponnampereuma, 1971; Studier *et al.*, 1972). The hydrocarbon types and other compounds are listed in Table VI.

The aliphatic hydrocarbons range from C₁₀ to about C₂₅ and include predominantly n-alkanes, monomethyl (2-, 3-, 4-, etc.), dimethyl, monocyclic (cyclohexyl), and dicyclic (decahydronaphthyl) alkanes and alkenes. In general, the hydrocarbons are more cyclized and branched, and their distribution is somewhat more complex than that corresponding to the aliphatic hydrocarbons from other carbonaceous chondrites. According to Studier *et al.* (1972), isoprenoids from C₁₇ to C₂₀ have been observed in a surface rinse but not in subsequent extracts and appear to be terrestrial contaminants.

The high molecular weight aromatic hydrocarbons include dicyclic, tricyclic and tetracyclic members (naphthalene, acenaphthene, phenanthrene, fluoroanthene, pyrene, etc.) and their respective monomethyl and other alkyl derivatives (Oró *et al.*, 1971a; Pering and Ponnampereuma, 1971). In the low molecular weight range, some of the major compounds found were benzene, toluene and other alkylbenzenes, branched alkanes and alkenes (Studier *et al.*, 1972). Substantial variations were observed from sample to sample, indicating significant heterogeneity. Thus the extractable aliphatics of the Murchison ranged from 11 to 35 $\mu\text{g g}^{-1}$ (Kvenvolden *et al.*, 1970), and the aromatics from 15 to 28 $\mu\text{g g}^{-1}$ (Pering and Ponnampereuma, 1971). Taken together, these values (26 to 63 $\mu\text{g g}^{-1}$) are of the same order of magnitude as those observed for the total directly volatilizable organics in Allende (20 to 70 $\mu\text{g g}^{-1}$) (Simmonds *et al.*, 1969; Levy *et al.*, 1970), and for the average values (10 to 80 $\mu\text{g g}^{-1}$) of the alkanes (Nooner and Oró, 1967; Gelpi and Oró, 1970a) in other carbonaceous chondrites. Wide qualitative and quantitative variations had also been observed in the aromatic hydrocarbons of the latter meteorites, although in general the amounts were lower, with an average value of less than 10 $\mu\text{g g}^{-1}$ for 32 samples analyzed (Olson *et al.*, 1967).

D. AMINO ACIDS

Amino acids have been found in several carbonaceous chondrites and other meteorites by different investigators. The amounts varied from essentially zero for several meteorites (including the Lancé) to 527.7 $\mu\text{g g}^{-1}$ for the Lancé (see Hayes, 1967). In general, water extracts contained much less amino acids than the acid hydrolyzates (Raia, 1966). The problem of terrestrial biological contamination has been so serious (Anders *et al.*, 1964; Hamilton, 1965; Oró and Skewes, 1965; Vallentyne, 1965; Hare, 1964–1965) that only the separation into their optical isomers was considered potentially capable of differentiating between chemically and biologically synthesized amino acids, since the former are racemic mixtures and the latter are predominantly of the L-configuration. Two new methods have been developed, one forming amino acid diastereomeric derivatives (Gil-Av *et al.*, 1965; Pollock *et al.*, 1965), and the other using optically active stationary phases (Gil-Av *et al.*, 1966), for the gas chromatographic separation of amino acid enantiomers.

Three carbonaceous chondrites, Orgueil, Mokoia and Murray were analyzed by the

TABLE VI
Hydrocarbons and amino acids in the Murchison meteorite

Hydrocarbon types ^a	[1 2 3]	Amino acids	[1 2 3 4]
Normal alkanes	X X	Glycine	X X X
Monomethyl alkanes	X	Alanine	X X X
Dimethyl alkanes	X	Valine	X X X
Alkyl cyclohexanes	X	'Leucine' ^b	X
Other alkyl cycloalkanes	X X	Proline	X X X
Polycyclic alkanes	X	Aspartic	X X
Olefins	X	Glutamic	X X X
Benzenes (and alkyl-)	X	Sarcosine	X X
Biphenyls naphthalenes (and alkyl-)	X	β -Alanine	X X X
Antracenes (and alkyl-)	X X	N-Methyl alanine	X
Phenantrenes (and alkyl-)	X X	N-Ethyl alanine	X
Acenaphthenes	X	α -Amino-N-butyric	X
Fluoroanthenes	X	α -Amino isobutyric	X X
Pyrenes	X	β -Amino-N-butyric	X X
		β -Amino-isobutyric	X
		γ -Amino-N-butyric	X
		Isovaline	X
		Norvaline	X X
		Pipecolic acid	X

[1] Kvenvolden *et al.* (1970); Kvenvolden *et al.* (1971).

[2] Oró *et al.* (1971); Gibert (1971).

[3] Pering and Ponnampertuma (1971).

[4] Cronin and Moore (1971).

^a The list is only representative of major compounds and is not complete. Other compounds such as thiophenes, indenes, chlorobenzenes, and several other amino acids have also been detected. See the above references and other references in section 8D.

^b Parent and fragment ions corresponding to one or several of the possible leucine isomers.

latter method (Nakaparksin, 1969; Oró *et al.*, 1971b) which has been shown to cause a minimum of racemization (Nakaparksin *et al.*, 1970a), provide a reasonable resolution of most amino acids (Nakaparksin *et al.*, 1970b), and permit the unequivocal identification of amino acids by mass spectrometry (Gelpi *et al.*, 1969). Small samples of the three meteorites were successively extracted with organic solvents and water in order to remove any free amino acids introduced by handling or other surface contamination, before they were hydrolyzed with hydrochloric acid. The analysis of the meteorite hydrolyzates demonstrated the presence of alanine, valine, threonine, isoleucine, leucine, proline and aspartic acid, mainly in the L-configuration. (In addition β -alanine and small amounts of many other unidentified derivatives were also present.) Only in a few cases was the concentration of the D-isomer above the levels produced by racemization (in general 1 to 2%). Thus, significant amounts of D-alanine were found in the three meteorites (Orgueil, 22.5%; Mokoia, 6.5%; and Murray, 13%). The Murray sample also contained significant amounts of D-aspartic (24.6%) acid and D-proline (12.3%). These results indicated that these three amino acids had been, in part,

generated by either racemization or chemical synthesis. In the latter case, they could probably be of abiotic origin. However, since soil hydrolyzates also gave reasonably high values of 8.6% for D-alanine and 8.0% for D-aspartic acid, and since limited studies had been done on the amino acid configuration of possible contaminants, the results were not considered conclusive to demonstrate either a biological or an abiotic origin, even though, in the main, the data pointed to terrestrial biological contamination. Probably the most correct interpretation is that there are at least two major sources of the amino acids in the exposed carbonaceous chondrites: (a) one made principally of residues of microorganisms and other biological contaminants acquired on Earth, and (b) the other made of racemic mixtures of free amino acids and/or other amino acid-generating compounds which may be indigenous to the meteorite.

E. MURCHISON AMINO ACIDS

An opportunity to resolve the above ambiguities posed by the inconclusive results obtained thus far was presented by the two recent falls of the Allende and Murchison carbonaceous chondrites, since the degree of biological contamination of these meteorites was expected to be minimal on account of their short terrestrial history.

The more informative data on amino acids has been obtained with the Murchison, due to the fact that the Allende contains only traces of nitrogen (0.007%). Thus, the analytical studies carried out in three different laboratories (Kvenvolden *et al.*, 1970; Kvenvolden *et al.*, 1971; Oró *et al.*, 1971a; Cronin and Moore, 1971), have demonstrated the presence of substantial amounts of protein and non-protein type amino acids in the hydrolyzates of the water extracts of this meteorite. In addition to the presence of non-protein type amino acids, the most important observation made on this meteorite was, however, the finding of approximately equal amounts of the amino acid enantiomers, indicating that the D- and L-isomers existed there in essentially racemic mixtures.

Following the experience on the analysis of amino acids in Precambrian cherts (Abelson and Hare, 1967–1968) and lunar samples (Fox *et al.*, 1970; Hare *et al.*, 1970) interior pieces of the meteorite were extracted with boiling distilled water, the extracts hydrolyzed with hydrochloric acid, desalted with ion exchange resins and analyzed by four different methods. Kvenvolden *et al.* (1970) and Kvenvolden *et al.* (1971) used analytical ion exchange chromatography, gas chromatography of the N-trifluoroacetyl-D-2-butyl esters, diastereomers of the amino acids, and mass spectrometry of the same derivatives. Oró *et al.* (1971a) used gas chromatography of the N-trifluoroacetyl isopropyl esters of the amino acids on ordinary phases, and mass spectrometry of the same derivatives, as well as gas chromatography on an optically active phase (N-TFA-L-valyl-L-valine cyclohexyl ester). The latter method was also applied to the separation of amino acid enantiomers from water extracts of the Murray meteorite (Oró *et al.*, 1971b). Cronin and Moore (1971) used an accelerated, high sensitivity, modification of the conventional ion exchange chromatographic method. These investigators also analyzed the water extracts of the Murchison before hydrolysis and extended their method to the analysis of Murray and Allende carbonaceous chondrites, the former

giving similar results to the Murchison and the latter showing no measurable amounts of amino acids.

The different amino acids detected in the Murchison meteorite are listed in Table VI. The most abundant among protein type amino acids was glycine ($6 \mu\text{g g}^{-1}$) followed by alanine ($3 \mu\text{g g}^{-1}$), glutamic acid ($3 \mu\text{g g}^{-1}$), valine ($2 \mu\text{g g}^{-1}$) and proline ($1 \mu\text{g g}^{-1}$) (Kvenvolden *et al.*, 1970). Similar distributions were found by the other laboratories. The overall amounts of 10 amino acids for the Murchison and Murray meteorites were 22 and $21.5 \mu\text{g g}^{-1}$, respectively (Cronin and Moore, 1971), the latter value being not greatly different from the total amount of amino acids ($37.2 \mu\text{g g}^{-1}$) found earlier by Raia (1966) in a sample of Murray. The individual amounts of some eight non-protein type amino acids were in general lower with the exception of α -amino isobutyric which was found at a level comparable to that of the protein type amino acids.

Since the results obtained from the three laboratories were obtained following four different methods and are in very close agreement, they represent, taken together, the first solid evidence for the presence of amino acids in meteorites which are probably indigenous and abiogenic.

Other analyses of the Murchison meteorite have also shown the presence of heterocyclic bases of the pyrimidine type, 4-hydroxy-primidine and 2-hydroxy, 4-methyl-pyrimidine, (Folsome *et al.*, 1971) but no biological purines or pyrimidines could be identified by trimethylsilylation and combined gas chromatography-mass spectrometry. It is known that adenine and other nitrogen compounds of low volatility have been reported in the Orgueil meteorite (Hayatsu, 1964) and were later abiotically synthesized in the laboratory under modified Fischer-Tropsch conditions (Hayatsu *et al.*, 1968; Yang and Oró, 1971). There are other organic compounds which have been detected in meteorites during the last four years which cannot be covered in this limited presentation. It is hoped that by an increased application of combined gas chromatographic and mass spectrometric methods to the Murchison and to other well preserved carbonaceous chondrites (if any remain as such), it will be possible to determine with certainty not only the identities of these compounds, but also their distribution and degree of contamination. It is not possible either to cover here the different hypotheses advanced to explain the formation or synthesis of these compounds. (A brief discussion of this problem will be found in Section 8D.) In general, the majority of the organic as well as inorganic data from carbonaceous chondrites suggest a chemical rather than a biological origin of the organic compounds indigenous to these meteorites.

7. Terrestrial and Jovian Planets

In addition to the basic differences in mass and external temperature between these two groups of planets, there is also a fundamental difference in the composition of their respective atmospheres. Whereas the major carbon component in the terrestrial atmospheres is completely oxidized (CO_2), that in the Jovian atmospheres is completely reduced (CH_4).

The above differences must be related not only to the relative distances of these two groups of planets from the Sun but also to the various processes operating in the formation and subsequent evolution of the Solar System. Table VII lists the gases identified in planetary and some satellite atmospheres by 1968 as reported by the planetary astronomy panel of the National Academy of Sciences (Hall, 1968). In each case the most abundant gas is listed first. For comparison the quantitative composition of ter-

TABLE VII
Gases identified in planetary and satellite atmospheres

	Gas
Mercury	No definite identifications
Venus	CO ₂ , CO, HCl, HF, H ₂ O
Earth	N ₂ , O ₂ , H ₂ O, A, CO ₂ , Ne, He, CH ₄ , K, N ₂ O, H ₂ , O, O ₃ , Xe
Mars	CO ₂ , CO, H ₂ O, O ₂
Jupiter	H ₂ , CH ₄ , NH ₃
Saturn	H ₂ , CH ₄ ; NH ₃ (?)
Uranus	H ₂ , CH ₄
Neptune	H ₂ , CH ₄
Pluto	No identifications
Jovian satellites	No definite identifications
Titan	CH ₄
Triton	No identifications

restrial dry air is given in Table VIII. The large number of constituents that have been identified in the Earth's atmosphere give an indication of the incompleteness of our present knowledge of other planetary atmospheres. It should be recognized, however, that the uniqueness of the terrestrial atmosphere (high N₂ and O₂; O₃) is at least in part the result of the existence of life on our planet, although some of these gases are also geochemically produced by volcanoes (N₂) and by photolysis of water in the upper atmosphere (O₂) as suggested by some models for the generation and evolution of the atmosphere of the Earth (e.g., Bates, 1951; Rubey, 1951; Berkner and Marshall, 1964; Holland, 1964).

Except for O₂ traces found on Mars (Barker, 1972; Carleton and Traub, 1972), examination of the gaseous envelopes of terrestrial planets (Sagan and Kellogg, 1963) has not revealed any surprising findings yet, unless one wishes to classify the presence of traces of HCl and HF in the Cytherean atmosphere in this category. As indicated, most of the carbon exists in the highly oxidized form of CO₂, with only small amounts of carbon monoxide, which is, however, sufficient to confer a partially reducing character to the planetary atmospheres of Venus and Mars. No definitive observations have been made on the existence of more reduced compounds of carbon, such as hydrocarbons, in terrestrial planetary atmospheres other than the Earth, and it would appear that if they are found, they will probably be in small amounts as the result of localized outgassing

TABLE VIII
Composition of dry air (sea level)^a

Gas	Symbol	Per cent of volume
Nitrogen	N ₂	78.084
Oxygen	O ₂	20.9476
Argon	A	0.934
Carbon dioxide	CO ₂	0.0314
Neon	Ne	0.001818
Helium	He	0.000524
Krypton	Kr	0.000114
Xenon	Xe	0.0000087
Methane	CH ₄	0.0002
Hydrogen	H	0.00005
Nitrous oxide	N ₂ O	0.00005
Sulfur dioxide	SO ₂	0 to 0.0001
Ozone	O ₃	0 to 0.000007
Nitrogen dioxide	NO ₂	0 to 0.000002
Iodine	I	0 to 0.000001
Ammonia	NH ₃	0 to trace
Carbon monoxide	CO	0 to trace

^a After K. K. Turekian, 1969.

or other non-equilibrium processes. Measurements of the carbon isotopic ratios for both the CO and CO₂ of the two terrestrial planets, Venus and Mars, have given values of the ¹²C/¹³C ratios which are in all four cases essentially the same: 90 ± 15% (Owen, 1972). These results, taken together with the cometary values given earlier support the idea that the carbon in the Solar System is fairly well homogenized. It will be interesting to see the confirmation of these results with measurements of the carbon isotopic ratios of Jupiter.

There is evidence for hydrogen and methane in Jupiter (Owen, 1970; Teyfel', 1969) and all of the large outer planets. Ammonia is also present in Jupiter and Saturn and water frost has been detected in the Saturn rings (Pilcher *et al.*, 1970). Water and hydrogen sulfide are two of the most expected but not yet detected constituents of Jupiter (Owen, 1970). Other recent observations include the preliminary identification of CH₃D in the atmosphere of Jupiter, and ammonia frost in Io and in Jupiter's largest satellite, Ganymede (Morrison *et al.*, 1971). There is no reliable information about the existence of organic molecules in Jupiter other than methane (Wildt, 1964; Owen, 1970) even though it is quite probable that many different organic and related compounds are there. After the Sun, Jupiter possesses the largest single mass of the Solar System. Because of its large gravity, and low mean density, the composition of this planet is probably representative of the matter of the Solar Nebula at the place and time this planet was formed. In a sense it can be considered as a 'fossil' sample of the Solar System.

On the basis of what is known of Jupiter's physical properties (Michaux, 1967) a number of models have been proposed for this planet (DeMarcus, 1958; Peebles, 1964a, b; Gallet, 1963; Rasool, 1968). Even though it may not be appropriate to con-

sider this massive planet as a small non-luminous star, it apparently emits more energy than it receives from the Sun. Taking into consideration the elemental composition (H, C, N, etc.) the broad variations in temperature and pressure along its radius, and the different forms of energy which are internally generated, it would be impossible that Jupiter would not give rise to large amounts of different organic and related compounds, some of which may be responsible for the coloration of this planet (Sagan *et al.*, 1967). Indeed, experiments with simulated Jovian atmospheres (Woeller and Ponnampertuma, 1969) have demonstrated the synthesis of several organic compounds, some of them colored, and others which are precursors of biologically important molecules.

The Moon has no measurable atmosphere although a long series of observations about transient phenomena has been made on our satellite. It remains to be seen whether the observations made by Kozyrev on the C₂ Swan bands of a degassing cloud from the Moon will be confirmed by other investigators. The same applies to the more recent observations about water being degassed for a relatively long time and during a period of seismic activity recorded at the sites of Apollo 12 and 14 ALSEP (Hills and Freeman, 1971).

8. Significance for Exobiology

A. INTERSTELLAR MOLECULES

Our knowledge of the formation of interstellar molecules and of the evolutionary behavior of interstellar gas clouds is so inadequate that it would be premature to make any major generalizations about the significance of these findings for prebiological organic chemistry and exobiology (Buhl, 1971; Rank *et al.*, 1971; Buhl and Ponnampertuma, 1972). The conditions of interstellar clouds (Table IV) and terrestrial planets (as well as terrestrial laboratories) are so extremely different that a direct comparison between them is not possible. Leaving aside the drastically different temperatures and radiation flux conditions, it would still require an extrapolation in the concentration of at least 20 orders of magnitude. (Hulett, 1971; Wolman *et al.*, 1971).

On the other hand, if similar molecular and dust clouds condensed to form the primordial Solar Nebula out of which the chondrites and the planets were formed, the survival of the organic molecules would depend on the conditions of condensation and subsequent accretion. (Urey, 1952; Wood, 1963; Cameron, 1966; Ringwood, 1966; Anders, 1968; Elston, 1969; Larimer and Anders, 1970). Obviously, if high temperatures were involved the molecules would have been destroyed, but if the transition between interstellar cloud and primitive Solar System planetary material occurred at relatively low temperatures, some of the molecules could have survived. Whether this is the case for 'pre-type I material' (Whipple, 1968) or type I carbonaceous chondrites is not known.

However, if we consider specifically the accretion of this matter to form a planet with the location and size of the Earth, sufficiently high temperatures might have been generated (Oversby and Ringwood, 1971) to cause the volatilization, destruction or transformation of most of the organic molecules. Thus the organic synthetic cycle of

labile organic molecules would have to be repeated again in the secondary atmosphere, hydrosphere and surface of the Earth.

There is no question, however, that the discovery of a large number of organic molecules in interstellar space, aside from demonstrating the universality of organic cosmochemistry (Oró, 1963a, b) offers a very interesting and challenging, yet real, model for organic synthesis, which can be used as a point of reference and analogy. Furthermore it indicates which molecules are potentially capable of being synthesized on other cosmic and planetary bodies with less constrained physical conditions, and provides the necessary scientific basis and realism for the experimental work on prebiotic synthesis which has been carried out during the last eighteen years (e.g. Calvin, 1961, 1969; Ponnampetuma and Gabel, 1968; Kenyon and Steinman, 1969; Lemmon, 1970).

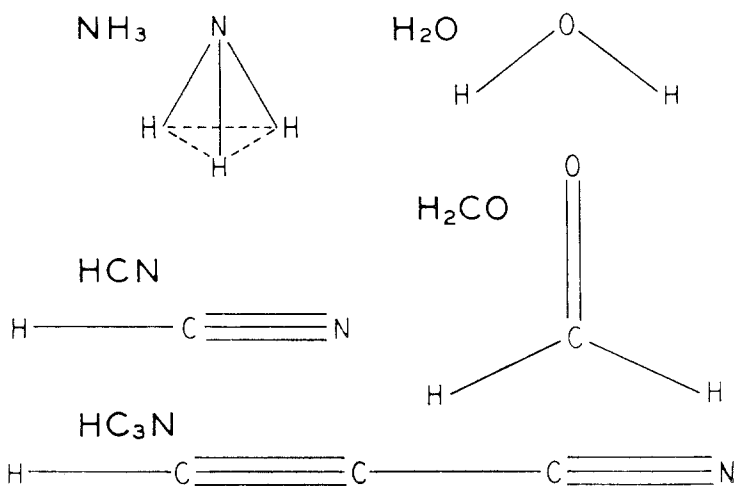


Fig. 10. The first five polyatomic molecules found in interstellar space.

Indeed, the first five polyatomic molecules discovered in interstellar space (Figure 10), and a few others (H₂, CO, etc.) are probably the most important precursors for the abiotic formation of amino acids, purines, pyrimidines, monosaccharides and other biochemical compounds, as demonstrated some time ago by laboratory experiments. With the addition of phosphate, which has not been detected yet in the interstellar medium, the list of precursors for the chemical synthesis of the building blocks of nucleic acids, proteins, saccharides and lipids, would be essentially complete.

Hydrogen and the first two of the above five molecules (water, ammonia) give an indication of the reducing, aqueous and basic nature of the environment which would prevail in a cosmic body resulting from the condensation of these interstellar molecules. Such a reducing, aqueous, and basic environment had indeed been postulated by Oparin (1938) and Urey (1952) as a necessary condition for the abiotic synthesis of biochemical compounds, as was first successfully demonstrated by Miller (1955) in his synthesis of amino acids.

B. INTERSTELLAR GRAINS

As pointed out earlier, very little can be said with certainty in relation to the nature of the interstellar grains. As indicated in Table IV, their composition may be inorganic (silicates, etc.) or organic (graphite, organic polymer, etc.). It is most likely that they are made of both organic and inorganic components. In fact, it has been stated that a mixture of meteoritic silicate, silicon carbide, and graphite particles can explain all the observed properties of interstellar grains (Gilra, 1971).

Interstellar grains may act as catalytic sites for the synthesis of organic molecules and may have a protective effect on the synthesized compounds by shielding them from γ -rays and ultraviolet radiation. It is also possible that at low temperatures they act as condensing agents or traps of gaseous molecules which by the action of ultraviolet light may be condensed into polymers with a rather low degree of atomic ordering in the structure. In fact, it has been pointed out that the distinct absorption band from μ Cephei interstellar grains is similar to the aromatic C-H bond absorption ($1.080\text{--}1.175\text{ cm}^{-1}$) of the polymeric material of carbonaceous chondrites (Vdovykin, 1970a). It remains to be seen whether any of the organic polymers which are present in the matrix of carbonaceous chondrites or surrounding some of the inorganic grains (or microchondrules) of type I chondrites, could be synthesized by a similar low temperature process. Electron spin resonance data indicate that this polymer was synthesized at temperatures below 300°C . (Schultz and Elofson, 1965).

In an evolutionary sense, perhaps the most significant role of interstellar grains is that they provide a transition between the thin gas clouds and the more dense nebular gas-dust clouds which undergo gravitational collapse. The conditions of the latter would be difficult to duplicate in the laboratory, but the reactions taking place on the surface of these grains within a high density cloud cannot be greatly different, in principle, from experimental reactions occurring in monomolecular layers on solid surfaces. It is in this sense that they may have contributed significantly to the formation of organic compounds, providing at the same time the condensation nuclei required for the aggregation and accretion of solar nebula material. However, neither interstellar molecules nor interstellar grains can now contribute directly in any measurable extent to the formation of carbon compounds on the surfaces of the planets and the Moon (Hulett, 1971).

C. COMETS AND METEORITES

There are two aspects of these extraterrestrial objects which are pertinent to discuss here: (a) Extent of the contribution of their carbon and related compounds to the composition of the Moon and terrestrial planets, and (b) significance of the recent analytical results on the organic compounds in carbonaceous chondrites and experiments simulating their synthesis. This will be done briefly and only the points not discussed by other authors will be covered here:

The first of these two aspects has been covered by Hayes (1972), Sagan (1972), and Gibson and Moore (1972) in this issue. Notwithstanding the number of uncertainties

existing in the calculations, it may be concluded in a very approximate way, that of each 100 μg of lunar carbon, 50 μg may be of solar wind origin, 10 μg of meteoritic-cometary origin, and 40 μg of primeval lunar origin.

Aside from the points discussed by Hayes (1972), the values for the solar wind carbon may have been overestimated because the correlation with surface of the lunar fines did not take into consideration the qualitative chemical and mineralogical differences of the particles which vary as a function of their size. Thus, glass particles are more plastic compared to other minerals and they cannot be comminuted to sizes as small as the latter. No measurements of carbon content on the glassy particles have been published. If their external morphological appearance can be taken as a reliable indication, they probably have a very low content of carbon. Therefore, the conclusions about surface correlation of carbon content may have to be modified and reinterpreted.

The meteoritic-cometary-interplanetary dust infall on the Moon has been calculated to be about 1 to 2% (see references in Hayes, 1972) on the basis of enrichments in the fines (in relation to the rocks) of some elements which have not been depleted in carbonaceous chondrites type I (Anders, 1968). However, when instead of these elements magnetite crystals (typical of type I carbonaceous chondrites) were used as a tracer of type I material, negative results were obtained for the contribution of carbonaceous chondrites to the lunar fines. (Jedwab and Herbolch, 1970). It may be that the magnetite crystals are not preserved as such as a result of the collisional process, in which case the nature of any of the organic compounds in the infalling material would also be significantly changed. It is possible that more stable species, such as carbides, CO and CO₂, would be formed, some of which could, in part, be recaptured by the lunar surface by the mechanism suggested by Hayes (1972). At any rate the amounts of carbon compounds accumulated on the Moon from the above sources cannot be very large, taking into consideration the absence of an atmosphere and the small gravity of our satellite. Exploration of the lunar polar areas and other protected regions, if any exist, may show a higher concentration of organic or organogenic compounds from interplanetary sources there.

Because of its high gravity and extensive hydrosphere as well as the presence of a decelerating atmosphere, the Earth would fare better in the capture of interplanetary organic compounds (Oró, 1961; Hochstim, 1963). However, even in this case, low density bodies of high mass would probably never reach the surface of the planet, but would explode in the atmosphere causing a substantial change and diffusion of their constituents (organic as well as inorganic) throughout the Earth, as it probably occurred in the case of the Tunguska catastrophe. Whether the material of this object was type I, or pretype I as suggested by Whipple (1968), cannot make a significant difference as far as the fate of the organic compounds is concerned.

Limited information is available concerning the potential contribution of primeval indigenous sources to the lunar carbon compounds. The conclusions arrived at by Wellman (1970) are quite pertinent and the observations made by Wachi *et al.* (1971), and Gibson and Johnson (1971) would seem to be consistent with the interpretation that a substantial part of the CO and N₂ released at very high temperature is probably

of primordial lunar origin and/or results from reactions involving carbides, or other stable forms of carbon (Chang *et al.*, 1970, 1971; Gibson and Johnson, 1971) with lunar oxygen containing minerals. The uncertainties in determining the extent of the solar, interplanetary and lunar contributions of the carbon compounds found in the Apollo samples could be narrowed down by measurement of 'the abundances, isotopic ratio and capturing characteristics of the carbon in the solar wind reaching the lunar surface', as suggested by Oró *et al.* (1970a), and reemphasized by Hayes (1972). Furthermore, an experiment of this type could provide a value for the solar $^{12}\text{C}/^{13}\text{C}$ ratio, which may confirm the recent measurements of Hall *et al.* (1972).

D. PREBIOTIC ORGANIC SYNTHESIS

Concerning the synthesis of the organic compounds in meteorites, particularly in carbonaceous chondrites, it is reasonable to think that it has occurred by a number of different processes, since different types of energy must have been available in the primitive solar nebula. Several lines of evidence point towards a period of high activity of the Sun during its early T-Tauri stage and its subsequent loss of angular momentum by magnetohydrodynamic coupling. Aside from shock waves, electrical discharges and other processes suggested by several authors, the early active stage of the Sun should have provided heat, radiation and electrical energy in sufficient amounts to bring changes in the inorganic as well as organic constituents of the primordial Solar Nebula. These changes were presumably greater for the region of the terrestrial planets which is closer to the Sun and they were probably less drastic for the asteroidal region and minor for the region of the Jovian planets and comets.

Therefore, moderate heat (less than 100–300°C temperatures) electric discharges and solar radiation were probably involved in the abiotic synthesis of the organic compounds in carbonaceous chondrites types I to III. It is possible that modified Fischer-Tropsch and other non-equilibrium catalytic processes gave rise to the formation of hydrocarbons and amino acids (Oró, 1965b; Studier *et al.*, 1968; Gelpi *et al.*, 1970b). Admittedly there are problems in this type of synthesis such as the lower yields of hydrocarbons obtained when the hydrogen/CO ratio is significantly higher than 10 (the ratio in the Solar Nebula should have been several orders of magnitude higher), or when sulfur, which is quite abundant in carbonaceous chondrites is present together with the meteoritic nickel-iron catalyst used in these experiments (Gelpi *et al.*, 1970b).

It is obvious that we need further knowledge to possibly overcome these difficulties. At any rate, by changing or removing the above two constraints it has been possible to synthesize, as mentioned earlier, not only hydrocarbons but also nucleic acid bases (Hayatsu *et al.*, 1968; Yang and Oró, 1971) and most of the protein and non-protein amino acids found in carbonaceous chondrites (Yoshino *et al.*, 1971; Hayatsu *et al.*, 1971). Other natural processes where the synthesis of organic compounds may be less constrained by the excess hydrogen and the poisoning effect of sulfur are long wave ultraviolet light (Sagan and Khare, 1971) and electrical discharges, which are known to produce substantial amounts of amino acids. Indeed, recent experiments with electrical discharges have yielded mixtures which contain all the protein and non-protein

amino acids found so far in the Murchison meteorite (Ring *et al.*, 1972; Wolman *et al.*, 1972).

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