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Organic Compounds in the Solar System

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Information about the presence of organic and carbon-containing compounds in planets and their atmospheres, in comets, and in meteorites is reviewed. Data on organic compounds present in meteorites are the most important. Numerous studies on such compounds in recent years have led to a significant advance in our knowledge about their nature. In particular, "primary" organic compounds preserved within mineral grains have been detected. These proved to be the compounds which should have been formed in maximum amounts under quasi-equilibrium conditions in the system carbon-hydrogen-oxygen. This finding is based on both theoretical and experimental data. The data concerning the presence of organic compounds in the protoplanetary cloud are used to assess the possible history of these compounds on earth. The bibliography incorporates 108 references.

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1. INTRODUCTION

The existence of organic compounds in the solar system is one of the most important problems of cosmochemistry, since it is most closely related to the problem of the origin of life on earth and the formation of petroleum deposits on the latter. Modern data indicate not only a wide distribution of organic compounds in most of the bodies of the solar system but also the fact that these compounds may have entered into the composition of our earth in great abundance during its formation.

For a long time panplanetary cosmogony was ruled by hypotheses according to which the earth and other planets were formed from incandescent gaseous nuclei. At a temperature of several thousands of degrees organic compounds cannot exist and therefore these hypotheses led to postulates that organic compounds were produced on the previously formed earth after it had cooled sufficiently. Following Mendeleev, the formation of methane as a result of the action of hot steam on metal carbides was regarded as the beginning of this process.

During the last twenty years a radical change in the hypotheses concerning the "initial" state of planetary matter took place in planetary cosmogony: all modern cosmogonic hypotheses postulate the aggregation of planets from a cold gas-dust cloud surrounding the sun at one time. Organic compounds must also have been present in this cloud. Furthermore, in most recent investigations it was shown that various organic compounds, including some which were extremely complex, were present in the protoplanetary cloud at concentrations virtually corresponding to thermodynamic equilibrium.

Since carbon-containing compounds are an essential component of the "raw material" from which organic compounds are formed, the problem of the presence of these in various bodies of the solar system will also be touched upon.

2. ORGANIC COMPOUNDS IN PLANETS

The simplest carbon compounds enter into the composition of all planetary atmospheres when these exist at all. Such compounds are detected spectroscopically. The amount of a particular gas in the atmosphere can be estimated, if only approximately, from the intensities of the absorption bands. Usually the amount is expressed in terms of the thickness of a homogeneous layer of gas at standard temperature and pressure (s.t.p.). For gases with absorption bands in parts of the spectrum accessible to measurement and which are possible components of the planetary atmosphere, the absence of appreciable bands in the spectrograms of the planet permits the determination of the upper limit to the content of the gas in the atmosphere. Frequently this upper limit has been significantly reduced as apparatus was improved.

Spectroscopic data on the composition of planetary atmospheres serve as the initial basis for theoretical calculations of thermodynamic equilibrium in a mixture of gases of this kind and for the determination of the possible concentrations of other more complex molecules.

The hypotheses concerning the presence of carbon compounds, including organic compounds, within the planets themselves are based on indirect considerations. For the giant planets and their satellites, calculations involving models of their internal structure are based on data concerning their average density and on the equations of state for various substances, indicating an appreciable content of light compounds, among which the most important are organic and related compounds. The hypotheses concerning the presence of organic compounds within the planets of the earth group are based on considerations associated with the history of their development.

Spectroscopic observations show that the atmospheres of the giant planets Jupiter, Saturn, Uranus, and Neptune contain much methane and the atmospheres of the first two also contain ammonia. The amounts of these gases above the cloud level forming the visible surface of these planets are listed in Table 1. The increase of the amount of methane on going from Jupiter to Neptune is due to a change in the structure of the atmosphere associated with the reduction of temperature. The absence of ammonia from the atmospheres of Uranus and Neptune is accounted for by its freezing at the lower temperature of the cloud layer in these planets.

Hydrogen, which constitutes the main or at any rate an important component of these atmospheres, has scarcely any spectroscopic effect. Therefore our knowledge about its content above the cloud layer is poor even for Jupiter. Errors in the determination of the equivalent width of the quadrupole band lines of molecular hydrogen in the Jupiter spectrum are such that, even after new laboratory studies of these lines, the amounts of hydrogen found above the cloud layer of Jupiter vary from 30 to 200 km† [3,4]. The models of the part of the Jupiter atmosphere above the cloud level differ correspondingly [4,5]. In their spectroscopic observations of Jupiter, Spinrad and Trafton [4] did not observe absorption bands due to CH_2, NH_2, O_2, HNO, HDO, HCN, C_2H_2, HCO, and H_2O, but they do not quote data concerning the upper limits to their contents. Owen [6] compared the Jupiter spectrum in the near infrared with the laboratory spectra of a number of molecules and obtained the upper limits to their contents, which are listed in Table 2.

Table 1. Composition (cm at s.t.p.) of the atmospheres of the giant planets above the cloud level from spectroscopic data [1,2].

Gas	Jupiter	Saturn	Uranus	Neptune
CH_4	15 000	35 000	~350 000	~600 000
NH_3	700	<250		
O_2		<0.1	<0.1	
SO_2		<0.01	<0.01	

The occasional appearance of a red-brown colour of certain features of Jupiter (in particular the so called red spot) has been attributed from the beginning of the 1950's to the formation in the atmosphere of various organic molecules [7-11]. Urey [7] quotes as an example the following possible compounds: yellow diazomethane (CH_2N_2), red tetrazine ($C_2H_2N_2$), yellow azomethane [$(CH_3)_2N_2$], and yellow cuprene [$(C_2H_2)_x$]. However, it did not prove possible to obtain direct spectroscopic evidence for the presence of particular organic molecules on Jupiter.

In laboratory experiments, where a corona discharge was created in a simulated Jupiter atmosphere [12], the formation of the following molecules was observed: HCN, CH_3CH, C_2H_2, C_2H_4, and C_2H_6. In other experiments [13], where the simulated Jupiter atmosphere was subjected to hard ultraviolet irradiation (λ = 584 Å), the formation of methane, ethylene, and propane was observed. Saslaw and Wildey [13] also discussed theoretical chemical models of the upper Jupiter atmosphere postulating various chains of reactions between hydrocarbon molecules and ions. The equilibrium concentrations of a number of molecules in the upper layers of the Jupiter atmosphere, calculated on various assumptions concerning their temperature, are listed by Lippincott et al. [11]

Despite the enormous pressure, amounting to millions and tens of millions of atmospheres, in their interior, the giant planets have a low average density (0.7–2.2 g cm^{-3}). Calculations of the internal structure of these planets show that Jupiter contains about 80% of hydrogen and Saturn about 60%, the remainder of the mass of these planets being made up of helium, rocky materials, and also various light compounds such as methane, ammonia, carbon dioxide, water, and others. The average densities of Uranus and Neptune show that these planets contain little hydrogen and consist almost entirely of light compounds such as methane, ammonia, carbon dioxide, and others (with an admixture of rocky materials). When account is taken of the enormous mass of the giant planets, it is found that the overall mass of the light compounds which they contain, including organic compounds, is dozens of times greater than the mass of the earth. There is no doubt that these organic compounds are of a abiogenic origin.

† According to Owen's new determination [18], the amount of hydrogen is 85 ± 15 km.

Table 2. Upper limits to the contents of certain gases in Jupiter's atmosphere above the cloud level from spectroscopic data [6].

Gas	Upper limit to content, cm at s.t.p.
CH_3NH_2	800
C_2H_4	200
C_2H_6	250
SiH_4	2000
CH_3D	3000
HD	50000

The abundance of light compounds in the giant planets is associated with the abundance in the universe of the chemical elements which enter into the composition of these light substances. The most abundant element in the universe is hydrogen (60 wt.%, i.e. about 86% in terms of the number of atoms); the second place is occupied by the chemically inert helium (38 wt.% or about 14% in terms of the number of atoms). Next we have carbon, nitrogen, and oxygen, constituting altogether about 1.2 wt.% or 0.1% in terms of the number of atoms. The total number of atoms of all the remaining chemical elements taken together is only 0.8%. When gas with the cosmic composition (or a composition close to the latter) comes under the influence of fairly low temperatures permitting the formation of molecules, hydrogen molecules (H_2) are formed in the greatest amount, in the second place are compounds of hydrogen with C, N, and O atoms, such as methane, ammonia, and water, and finally in the third place there are compounds of carbon, nitrogen, and oxygen with one another, such as carbon monoxide, carbon dioxide, and CN. Thus the total cosmic abundance of chemical elements predetermines the abundance of carbon-containing and in particular organic compounds in cold cosmic bodies, whose matter has not been subjected to pronounced fractionation.

Organic compounds probably enter into the composition not only of the giant planets but also of their satellites. Unfortunately the average densities are known, if only approximately, for only five of the largest satellites of the giant planets (the four Galilean satellites of Jupiter and Titan—the largest satellite of Saturn), from which an indirect assessment of their composition may be made. The two satellites closest to Jupiter have a rocky composition and the two more distant ones (among the Galilean satellites) and Titan consist of 50% of rocky material and of 50% of light substances. These light substances probably include various organic compounds. An indirect indication

of this may be the presence on Titan of a methane atmosphere (possibly containing also ammonia) discovered by Kuiper in 1944.

We shall now consider the planets of the earth group. As early as the 1930's, the infrared spectrum of Venus revealed absorption bands which proved to belong to the carbon dioxide molecule. The amount of carbon dioxide present above the cloud layer forming the visible surface of Venus corresponds to a layer about 2 km thick (at s.t.p.). Kuiper, using spectroscopic data, found the upper limits to the possible contents of a number of other gases (Table 3).

Table 3. Composition of the atmosphere of Venus above the cloud level from spectroscopic data[1,14].

Gas	Amount, cm at s.t.p.
CO_2	200 000
CO	<3
N_2O	<100
CH_4	<20
C_2H_4	<3
C_2H_6	<1
NH_3	<4

Until recently the thickness and composition of the atmosphere under the cloud layer were unknown. In October 1967 the remarkable landing on Venus of the Soviet automatic station Venus-4 established that the carbon dioxide content is 90 ± 10%.[15]

Assuming a considerable concentration of water vapour in the atmosphere of Venus, Wildt put forward the hypothesis that the cloud layer of this planet consists of condensates of formaldehyde and its polymers. However, subsequently this hypothesis was abandoned. In the first place the attempts undertaken by Wildt himself to find the formaldehyde band in the ultraviolet part of the spectrum were unsuccessful. In the second place the water vapour content proved to be very small: in all several tens of grammes per cm^2. At present it is believed that the clouds most probably consist of crystals of ordinary ice.

At one time it was suggested that the entire surface of Venus is covered by a continuous ocean preventing the formation of carbonate rocks from the carbon dioxide atmosphere. Whipple and Menzell put forward the hypothesis of a soda water ocean, i.e. water saturated with carbon dioxide. Hoyle, believing that many organic compounds must have formed even in the protoplanetary gas–dust cloud under the action of various types of hard solar radiation, suggested the possibility of the existence of a petroleum ocean evolved from the inner parts of Venus. Both these hypotheses were rejected when several years ago radioastronomical measurements of the intrinsic thermal radio emission from Venus showed that its temperature is about 600°K. However certain investigators suggested that this temperature does not refer to the surface but the upper ionosphere of Venus. However, measurements by the automatic station Venus-4 showed that the temperature increases on going deeper into the atmosphere, reaching more than 500°K at the surface.

Since at the high temperature of the Venus atmosphere thermochemical equilibrium must be established rapidly, Mueller[16] estimated the possible content in this atmosphere of various hydrocarbons and found that it must be negligibly small. Recently this was confirmed by new more complete calculations‡ [11,17].

Studies of the spectrum of Mars for a long time failed to yield any information about the composition of its atmosphere. It was not until 1947 that weak carbon dioxide bands were observed in the infrared part of the spectrum. According to the latest data[18], the amount of carbon dioxide in the Mars atmosphere corresponds to a layer 75 ± 15 m thick (at s.t.p.). Spectroscopic estimates of the upper limits to the possible contents of other gases are listed in Table 4. Until recently it was believed that the atmosphere of Mars is thinner by a factor of 10 than the earth atmosphere and under such circumstances carbon dioxide would constitute less than 10 wt.%. The main component was believed to be molecular nitrogen, which is not revealed in the part of the spectrum accessible to observations. However, during recent years the application of new methods of observation resulted in a lower estimate of the density of the Martian atmosphere and a corresponding increase in the importance of carbon dioxide. Finally, in 1965 studies carried out with the aid of the American automatic station Mariner-4 showed that the Martian atmosphere is thinner than the earth atmosphere by a factor of 100 and therefore carbon dioxide constitutes not less than 50% and possibly the entire 100% of the atmosphere.

Table 4. Composition of the Martian atmosphere from spectroscopic data[19].

Gas	Amount, cm at s.t.p.	Gas	Amount, cm at s.t.p.
CO_2*	4500±2500	NH_3	$<0,1$
H_2O**	$(14\pm7)\cdot10^{-4}$	NO_2	$<1\cdot10^{-3}$
O_2	<2	N_2O	<0.08
O_3	$<4\cdot10^{-4}$	NO	<20
CH_3CHO	$<6\cdot10^{-3}$	H_2S	<7.5
CO	<1	H_2CO	<0.3
CH_4	<0.1	COS	<0.2

*According to Owen's new data[18], the amount of carbon dioxide is 7500 ± 1500 cm.
**Precipitated water. The amount varies both in space and in time.

The problem of the presence of an atmosphere on the planet Mercury, which is closest to the sun, remains to a large extent obscure. Polarimetric observations indicated the existence of an atmosphere with a mass of 3 g cm^{-2} (on earth about 1000 g cm^{-2}), but there was no spectroscopic confirmation of its existence. In 1963 V. I. Moroz observed a slight increase in the intensity of the carbon dioxide bands in the infrared spectrum of Mercury relative to that of the moon (in the latter case the carbon dioxide bands are due to the presence of carbon dioxide in the terrestrial atmosphere).

For a long time it was believed that one side of Mercury is always turned towards the sun and therefore it might have been supposed that in the night hemisphere of the

‡ In all these calculations models of the Venus atmosphere postulating an unduly high pressure at the surface and an unduly high nitrogen content were employed. However, the conclusion concerning the negligibly low concentration of hydrocarbons is almost independent of these initial data and remains valid also for the true atmosphere of this planet.

planet, under the conditions of a constant low temperature, there are frozen volatile substances. However, radar observations showed that Mercury rotates about its axis with a period amounting to two thirds of its period of rotation about the sun. In agreement with this finding, radio-astronomical observations, permitting an estimate of the surface temperature to a depth of several meters, do not reveal an appreciable difference between the day and night hemispheres. Thus the possibility of the existence of frozen volatile substances is completely excluded for the major part of the surface of Mercury, with the possible exception of the polar regions whose temperature remains unknown.

We have no information about the presence of organic compounds on the moon, which lacks an atmosphere. Only theoretical considerations concerning their possible presence have been put forward. Thus Sagan[20], believing that a reducing atmosphere consisting mainly of methane, ammonia, and water existed at one time on the moon, put forward the hypothesis that organic substances formed in this atmosphere under the action of solar ultraviolet radiation may have persisted in the upper layer of the moon. In an atmosphere with this composition fairly complex organic molecules with molecular weights up to 100 are formed under the action of ultraviolet radiation (and electric discharges): amino-acids and other organic acids, pyrroles, pyridines, and simple hydrocarbons and their polymers (see, for example, Miller[21] and Miller and Urey[22]). According to Sagan's estimate, the amount of amino-acids with a molecular weight of about 100 alone, formed during ten million years in an atmosphere opaque to ultraviolet rays, may be of the order of 5 g cm^{-2} (for a quantum yield of 10^{-6}). The heavy molecules produced must have sunk towards the surface and then on to the surface itself where they were protected by the atmosphere from the destructive short-wavelength radiation. As the atmosphere became dissipated, ultraviolet radiation must have partially decomposed the organic molecules, while some may have been converted into more complex compounds (for example, polypeptides may have been formed from the amino-acids). Sagan believes that organic compounds on the moon were protected from complete degradation under a layer of meteoritic material and have persisted up to the present time on the elevated "mainland" parts of the lunar surface, while in the sections corresponding to the "seas" they were destroyed by the lava flow.

However, the picture drawn by Sagan is probably incorrect for a number of reasons. Firstly, recently serious doubts have been expressed concerning the hypothesis that the primary atmospheres of earth type planets and the moon consisted mainly of methane, ammonia, and water. Data on the oxidation equilibrium between gases and silicate melts showed that, for the evolution of methane to occur, the melts must have contained metallic iron, which is in fact not the case. Gases of the same composition as those evolved from volcanos[23] must have been evolved from the basalt magmas. Consequently the lunar atmosphere must have consisted of water, carbon dioxide, sulphur dioxide, molecular hydrogen, and carbon monoxide. Secondly, the density of the atmosphere at the surface of the moon can have scarcely exceeded one millionth part of the density of the present day terrestrial atmosphere at the surface[24], i.e. was the same as the density of the terrestrial atmosphere at the height of about 150 km. This density is altogether too low both for the formation of a sufficient number of organic molecules and for their protection from solar ultraviolet radiation after they have sunk to the lunar surface. Thirdly, impacts of meteorites of various dimensions keep "ploughing up" the surface layer of the moon to a depth of several metres and therefore favourable conditions for the protection of organic matter do not exist there.

Gilvarry[25,26] goes much further than Sagan and suggests that biogenic organic substances may be present on the moon. He is the only astronomer who suggests that real seas, in which even life may have existed, were present at one time on the moon. Gilvarry starts from the unlikely hypothesis of extremely rapid evolution of water from the interior of the moon and greatly overestimates the possible duration of its persistence on the lunar surface. This hypothesis has not found any supporters.

There exists, however, another theoretical possibility of the presence on the moon of considerable amounts of organic compounds, including hydrocarbons. It is associated with the presence of these substances in meteorites (see section 4) and, judging from all available data, in the materials from which earth type planets and the moon aggregated. As noted by Wilson[27], if the average hydrocarbon content in meteorites (about 0.01%) is assumed for the primary material of the earth and the moon and account is taken of the fact that only part of these may have been converted into liquid hydrocarbons by cracking in the interior parts of these bodies, then the amount is still sufficient to account for the origin of all petroleum accumulations on earth. Wilson put forward the hypothesis that the lunar seas are covered by the asphalt remaining after the evaporation of lighter hydrocarbons which emerged in the form of petroleum from the interior of the moon. Wilson's hypothesis was objected to by Mueller, who is a supporter of the biogenic hypothesis of the origin of petroleum. However, Wilson's quantitative estimates are quite correct. Nevertheless there is a serious astronomical basis to doubts concerning the possibility of such large petroleum outflow on the surface of the moon.

As a result of the extremely low thermal conductivity of the surface layer of the moon, the daily temperature variation penetrates only to a depth of about 0.5 m; at greater depths the temperature remains always constant. In the equatorial zone this constant subsurface temperature is about −30°C and in the polar regions it is considerably lower. As a result of the constant increase of temperature with depth, a temperature of 0°C is attained at a depth of 2–4 km in the equatorial zone and at a depth of 15–20 km in the polar regions. The existence of a layer of subzero temperatures implies the great probability of the existence of a layer of permafrost. In the polar regions of the moon not only water vapour arising from the interior but also carbon dioxide can freeze in this layer. The permafrost layer must prevent the outflow on to the lunar surface of non-biogenic "petroleum" and in general the evolution and dissipation of volatile organic compounds; their presence in large amounts in the interior layers of the moon appears very likely. However, the properties of the lunar surface, its dielectric constant and low reflectivity, have been successfully explained by astronomers on the basis of the silicate nature of its composition without resorting, like Wilson[27], to the asphalt or petroleum coke hypothesis.

It should be added that under the layer of subzero temperatures there must exist a fairly thick layer in which water may exist in the liquid state. The permafrost layer (if it does exist on the moon) is self-sealing, i.e. all cracks in it are rapidly eliminated. A coating is obtained which does not permit the escape to the outside even of gases and therefore it allows the existence of a kind of "internal atmosphere"[28]. The only case of the evolution of gases from the interior of the moon was observed by Kozyrev in 1959. In one of the spectrograms of the moon which he obtained

there is an emission band extremely similar to the most intense C_2 band which is also observed in the spectra of comets.

All that has been said above concerning the possibility of the existence on the moon of a permafrost layer, containing and retaining organic compounds, applies to a considerable extent also to Mars.

3. ORGANIC COMPOUNDS IN COMETS

Apart from the giant planets, the solar system contains yet another type of bodies consisting mainly of volatile materials, namely comets. The solid nuclei of the comets are small, usually between several hundred metres and several tens of kilometres in diameter and consist of "ice" comprising different gases with an admixture of involatile rocky materials (10–30 wt.%). In their structure the comet nuclei must resemble enormous lumps of snow (however, these are black and not white) rather than blocks of ice. They move around the sun along extended orbits and most of the time they remain far from it. The temperature of the nucleus is then extremely low and therefore gases are not evolved from the latter. On approach to the sun, the surface layers of the nucleus are beginning to heat up and the evolved gases form an atmosphere which is continually dissipated—the head of the comet and the tail.

Spectroscopic observations on the heads and tails of comets reveal the presence of C_2, C_3, CN, CH, OH, NH, NH_2, CO, and N_2. Until recently it was believed that all these chemically unstable radicals are generated as a result of the photodissociation of chemically unstable parent molecules evolved (desorbed) from the comet nuclei. Methane, ammonia, carbon dioxide, and water were postulated in the first place as parent molecules of this kind. However, the problem of the parent molecules is much more complex.

Donn and Urey[29] put forward the hypothesis of the presence in the comet nuclei of considerable amounts of frozen unsaturated radicals. However, subsequently they changed their view. Even under laboratory conditions radicals are frozen only with considerable difficulty and under natural conditions they could enter into the composition of comet nuclei only in a small amount. Donn[30] estimated this amount as approximately 1%.

Delsemme and Swings[31,32] believe that the wide variety of volatilities of the hypothetical parent molecules enumerated above is incompatible with the results of observations on comets, which indicate that the ratio of the amounts of different molecules varies little with the distance of the comet from the sun, i.e. with the temperature of the surface of the nucleus. Therefore they suggest that the molecules in the comet nuclei are present in a hydrated form (such as $CH_4.6H_2O$), which gives rise to similar volatilities of all the compounds. Although their initial evidence appears unsound (the differences in volatility will be rapidly compensated during evaporation by the generation of various concentration gradients in the surface layer of the nucleus), the idea of an abundance of water in comet nuclei is probably valid. In recent years it was established that the lines due to atomic oxygen observed in the spectra of comets do not originate from the superposition of the luminescence of the terrestrial atmosphere but are due to the comets themselves. Oxygen atoms are produced as a result of the photodissociation of water.

The comet nuclei were formed at extremely low temperatures and therefore it may be suggested that initially they consisted of amorphous matter with a disordered arrangement of a wide variety of molecules, radicals, and atoms[33]. Subsequently the radioactive elements entering into the composition of the involatile fraction must have heated the central part of the nucleus to a temperature of about 50°K or above and must have caused the evaporation (sublimation) of the most volatile components and their diffusion through the porous material of the nucleus and condensation in the cold outer layers[34]. During this process the initial composition and structure of the material of the nucleus might have changed significantly.

Observations on some of the radicals contained in the comet atmospheres make it possible to establish the lifetimes of the parent molecules from the instant of their evolution from the comet nucleus to their photodissociation. In particular the lifetimes of molecules giving rise to C_2 and CN do not exceed 1–3 h at a distance of one astronomical unit from the sun.

Potter and Del-Duca[35] made laboratory measurements of the ultraviolet absorption cross-sections (in the region 4000–1300 Å) for ethylene, acetylene, methane, acetonitrile, monocyanoacetylene, dicyanoethylene, dicyanogen, methylamine, hydrazine, ammonia, hydrogen peroxide, and water, and using data on the ultraviolet emission intensity of the sun, found the lifetimes of these molecules in the interplanetary space. It was found that the lifetimes of molecules whose decomposition can give rise to C_2 and CN amount to tens and hundreds of hours at a distance of one astronomical unit from the sun, which is inconsistent with the astronomical data. Consequently C_2 and CN are formed by the photodissociation of some other uninvestigated molecules (for example, molecules, which are stable only at low temperatures) or they are formed not by photodissociation but as a result of another process, for example molecular collisions in the immediate vicinity of the nucleus.

Laboratory studies of Stief and De-Carlo[36] showed that, from the purely spectroscopic point of view, the parent molecule of C_2 may be acetylene (C_2H_2) or an acetylene molecule, but not ethylene or ethane. However, according to Potter and Del-Duca[35], acetylene must be excluded because its lifetime in the radiation field of the sun is much too great.

Stief and De-Carlo also found that NH observed in comets cannot form as a result of the photodissociation of ammonia (NH_3), but can be produced by the dissociation of hydrazine (N_2H_4) or some other related molecule.

Thus, although the presence of organic molecules in the nuclei of comets is not subject to doubt, only the first steps have been taken so far in the determination of their exact nature. A fairly complete idea about the organic compounds in the nuclei of comets will probably be derived in the next few years by direct analysis of the matter from the nuclei by means of automatic apparatus mounted on a space rocket which will be sent to intercept the comet.

4. ORGANIC COMPOUNDS IN METEORITES

The meteorites falling on earth are fragments of asteroids, i.e. bodies located at the boundary between the zone of the earth type planets and that of the giant planets. In the regions of the planetary system remote from the sun there exist probably objects of meteorite dimensions consisting of "ice" comprising different gases, i.e. similar to the nuclei of comets. However, bodies moving in the region of the earth orbit, i.e. in the vicinity of the sun, consist of refractory substances—silicates and iron–nickel alloy.

All meteorites contain at least a small amount of carbon and carbon compounds, including organic compounds. In particular, gases evolved when meteorites are heated contain carbon dioxide, carbon monoxide, methane, and ethane (together with molecular hydrogen, hydrogen sulphide, and sulphur dioxide). However, there exist chondrites of a rare type (about 30 are known) containing several per cent of organic compounds. These are known as carbonaceous chondrites. Carbonaceous chondrites contain carbon, predominantly in the form of high-molecular aromatic compounds and also in the form of bitumen-like material. In addition they contain hydrated minerals and free sulphur. The material of carbonaceous chondrites was never heated to temperatures in excess of 200–300°C. Mason's review[37] is specially devoted to carbonaceous chondrites.

Wiik[38] showed that carbonaceous chondrites can be naturally divided into three types, differing in the content of volatile substances and structure. The average carbon and water contents (expressed as percentages) are as follows:

	type I	type II	type III
C	3.5	2.5	0.5
H_2O	20.1	13.4	1.0

(The maximum observed carbon content is 4.83%).

Carbonaceous chondrites of type I have a composition very similar to that expected for a solid condensed in the protoplanetary cloud. Even the content of widely distributed elements is almost identical with the "cosmic" abundance, while in meteorites of other types there is a smaller or greater deficit. Carbonaceous chondrites contain large amounts of primary inert gases, i.e. gases captured from the surrounding medium in the formation of the meteorite material (and not evolved in consequence of radioactive breakdown). It is now believed that, of all the substances at present available to us, carbonaceous chondrites of type I are closest to the primary matter from which the planets of the earth type are formed.

The presence of organic compounds in carbonaceous chondrites was established as early as 1834 by Berzelius, who, however, found it difficult to identify them because of the complexity of their structure and the small amount available for analysis. In the XIXth century investigations consisted mainly in the isolation of organic compounds by sublimation or by extraction with solvents such as alcohol or petrol. The amount of bituminous substance isolated rarely exceeded 1% of the total weight of the specimen. However, the major part of the carbonaceous substance consists of a black carbon-like material which is not acted upon by solvents. It has been frequently called graphite or amorphous carbon. As early as 1864, however, Cloëz, who studied the meteorite Orgueil showed that this black substance is an organic complex. He isolated it by dissolving the inorganic component and obtained 6.4% of an insoluble residue. He assumed that this residue is a complex mixture of compounds with a high molecular weight. It is now known from X-ray diffraction data that the black substance in all carbonaceous chondrites is amorphous and consists of an aromatic polymer[39].

After a break of more than half a century, studies on the organic material in carbonaceous chondrites were resumed in the 1950's. Mueller[40] irradiated with ultraviolet light 20 carbonaceous chondrites and found that 19 of them do not fluoresce. Hence he concluded that they do not contain free hydrocarbons with an atomic ratio $H:C > 1.4$. However, further studies showed that luminescent extracts can be obtained from all carbonaceous chondrites. Mueller extracted organic compounds from the Cold Bokkeveldt meteorite by means of organic solvents. The substance extracted after the removal of sulphur crystals (10–12%) proved to have the following composition: C 19.8%; H 6.7%; N 3.2%; S 7.2%; Cl 4.8%; O and other elements 40.0%; ash 18.3%; the presence of chlorine is interesting. In contrast to solutions of terrestrial minerals of biological origin, which are always optically active, the solution of the extracts from the Cold Bokkeveldt meteorite showed no optical rotation within the limits of accuracy of the apparatus (0.02°). Mueller concluded that the organic substance from the meteorite consists of complex organic acids with different solubilities. They were produced by non-biological polymerisation in a gaseous medium containing nitrogen, sulphur, and chlorine. Judging from the difficulty of the dissolution of silicates, this substance envelops the strong particles.

Boato[41] studied the isotope composition of carbon and hydrogen from 12 carbonaceous chondrites and found appreciable differences between individual meteorites and in certain cases also between different parts of the meteorite. This is the result of fractionation processes or chemical reactions in the early stages of the formation of the meteorite.

At the beginning of the 1960's Calvin[42] and Briggs[43] showed that organic substances can be extracted from carbonaceous chondrites not only with organic solvents but also with water. The infrared and ultraviolet spectra of the extracts from the Orgueil, Murray, and Alais meteorites investigated by Calvin showed that they contain a wide variety of organic compounds including hydrocarbons and heterocyclic bases. Cytosine was found in the extract from the Murray meteorite[42]. On the other hand, no amino-acids were found in the aqueous extracts. On the basis of the infrared and ultraviolet spectroscopic data and data obtained by paper chromatography, Briggs[44] suggested that the extracts from the Mokoia meteorite contain purine or the related imidazole compound and also conjugated cyclic systems. He attributed the solubility in water to the presence of polar groups, such as carboxy- and hydroxy-groups and amines. He also found no indication of the presence of amino-acids.

An enormous explosion of interests in carbonaceous chondrites was stimulated by the work of Nagy and coworkers published in 1961.[45,46] In the first of these Nagy, Meinschein, and Hennesy[45] present the results of mass-spectrometric analyses of the linear and cyclic hydrocarbons from the Orgueil meteorite. They investigated a number of fractions distilled at temperatures between 100° and 400°C. Having found a similarity in the positions of the maxima on the distribution curves with respect to the carbon number for various hydrocarbons from the meteorites and from substances of biological origin—oils and sea deposits—the authors regarded this as evidence for the occurrence of biological processes "outside the limits of the earth", i.e. in the parent bodies from which the meteorites were derived.

In the second paper Lakus and Nagy described the results of the microscopic study of the Orgueil and Ivuna meteorites. They assert that both meteorites contain an enormous amount of microscopic particles (about 10 μm) resembling fossil seaweed, pollen, or spores. They amount to thousands per milligramme. These particles, which have come to be called "organised elements", are dyed by biological stains. Referring to the previous paper, in which it was claimed that biochemical compounds were observed, the authors expressed the view that the "organised elements" are indeed petrified unicellular micro-organisms.

As pointed out correctly by Briggs[47], to establish the biological nature of the organic material from meteorites, "it is necessary to show that the composition of the mater-

ial is identical with that wihch can be obtained on breakdown of a terrestrial cellular life form. If the composition is different, it follows that the material is either of an abiogenic nature or that it originates from an extraterrestrial life form having a chemical composition different from that of the terrestrial life forms familiar to us. If this latter hypothesis is adopted, it is impossible to employ merely the presence of organic matter in meteorites as a criterion of extraterrestrial biogenic processes, since evidently one can say about any chemical substance that it is part of a completely unknown and hypothetically alien life form. The last consideration is important, since it is difficult to doubt that in many of their properties the meteoritic organic compounds do not resemble terrestrial biological residues".

As regards the "organised elements", the attempts to revive the micro-organisms from meteorites proved unsuccessful[48] and the investigations had to be based merely on their morphology which is a very indefinite and unreliable procedure.

The conclusions of Nagy, Meinschein, and Hennessy were objected to by Anders[49] on several counts, who emphasised that despite their captions, the mass spectra quoted by these workers for the range C_{15}–C_{30} do not refer to the pure hydrocarbons (straight-chain alkanes and mono-, di-, and tri-cycloalkanes), including also the degradation products of heavier molecules with masses up to 600. He noted that the curves for the oil and sea deposits differ appreciably from one another and therefore there is no standard curve characteristic of hydrocarbons of biological origin. Anders also pointed out a number of possibilities of contamination of the meteorite by terrestrial biogenic hydrocarbons: as a result of contact with the hands, the "respiration" of the porous meteorite during changes in atmospheric pressure, etc. He concluded his paper with the following words: "even if it should be possible to prove a close resemblance in the distribution of compounds, as opposed to cracking patterns, a logical difficulty remains: it must also be proved that a similar distribution could not have arisen in the solar nebula by purely inorganic reactions. Like all negative proof, this is impossible to obtain. A far more promising approach would be to look for optical activity in meteorite hydrocarbons. Optical activity is a universal and indispensable property of life as we know it and its discovery in meteorites would go a long way toward convincing sceptics such as myself of the onetime existence of life on the meteorite parent bodies".

It is therefore difficult to convince the investigators of meteorites of the possibility of the existence of life on their parent bodies, which would imply a complete revision of the modern hypotheses concerning the origin and history of these bodies. Nevertheless, as far as the astronomical and cosmochemical data are concerned, there is no justification for such revision.

The critical remarks of Anders were published together with the reply of Nagy, Meinschein, and Hennessy which they conclude with the hope that their further results would completely confirm their preliminary conclusions. In Urey's words[50], these authors were very surprised by the reaction to their paper from meteorite experts. They believed that they had made an interesting discovery which would be accepted without objection.

In 1962–1963 a vigorous controversy developed around the work of Nagy and coworkers. In March 1962 a series of articles were published in Nature (No. 4821) on this question (Urey; Briggs, and Kitto; Fitch, Schwarcz, and Anders; Bernal; Nagy, Klaus, and Hennessy). In May 1962 a special conference devoted to the "organised elements" was held in New York (for the conference report, see Urey[51]). A number of papers have been published both by the supporters of the biological origin of the particles discovered and by their opponents, who explain them away by the unusual forms of natural minerals or by contamination by terrestrial particles of biological origin—pollen, pores, etc.

Klaus and Nagy discovered several types of "organised elements". Fitch and Anders[52–54] divided these elements into two groups: particles with a very complex structure and particles with a much simpler structure. There is no doubt about the latter that they belong to the meteorite itself. However, Fitch and Anders and also Mueller[55,56] showed that the Orgueil and Ivuna meteorites contain microscopic hexagonal crystals of troilite (FeS), which resemble the hexagonal "organised elements" described by Klaus and Nagy. By centrifuging in heavy liquids the meteorites ground to a powder, as was also done by Klaus and Nagy to concentrate the "organised elements", Fitch and Anders also found spherical particles resembling the spherical "organised elements", but which they showed to be supercooled drops of sulphur and hydrocarbons. As regards the group of particles with complex morphology which resemble terrestrial micro-organisms both in structure and in the remaining properties, there are grounds for the belief that their presence in the Orgueil meteorite (probably only in a few individual lumps of the meteorite) is a result of contamination.

The experiments of Imshenetskii and Abyzov[57] showed that not only stone but also iron meteorites are completely permeable to soil micro-organisms. It is therefore not surprising that Roy found Johnstown achondrite to be contaminated with two types of terrestrial bacteria and Oro and Tornabene[58] isolated three types of terrestrial bacteria on the Murray and Mokoia carbonaceous meteorites. These meteorites were stored simply wrapped up in paper. A lump of the Orgueil meteorite, which these authors also investigated, was preserved in a museum in a sealed glass vessel and no contamination with micro-organisms could be observed. In all the remaining cases of the observation of bacteria in meteorites, it was asserted without sufficient evidence that bacteria brought by the meteorite from space had been revived. The contamination of meteorites by terrestrial bacteria results at the same time in contamination by terrestrial biogenic organic substances, which may be erroneously assumed to belong to the meteorites themselves§.

Both Briggs and Anders and Fitch noted that the attribution of a biological origin to the "organised elements" on the basis of morphological data is unconvincing, since it is based to a large extent on subjective assessments. Later Urey[50] in his review on the hypothetical presence of biogenic substances in meteorites¶ also wrote that "to a chem-

§ In one of the lumps of the Mokoia meteorite which was contaminated with pieces of wood, spores, and radiolaria after falling, Mueller[60] found a resinous substance which subsequent investigations showed to be identical in composition with the substance exuded from the root of the tree on which the meteorite had fallen.

¶ Urey's review has the unfortunate title "Biological Material in Meteorites", which creates the impression that the author firmly admits the biogenic nature of the organic compounds from meteorites. Recently Urey et al. published a special note[59], in which they emphasise that they do not regard the biogenic origin of these compounds as proved, but at the same time they find that there is no adequate proof for their abiogenic nature.

ist, morphological forms appear to be an unsatisfactory basis for identification of biological remains because so many artifacts of approximately the size of micro-organisms, can be made both from organic material and inorganic material". At the same time Urey noted that the evidence in favour of the presence of organic substances is such that if terrestrial objects and not meteorites were concerned there would be no question about their validity. In the case of meteorites, as pointed out both by himself and Anders and Fitch, further objective study of the factual data is essential.

It was indeed essential both because of the exceptional importance of the problem of the existence of extraterrestrial life and because it might reveal the weak points of the method used previously to establish the presence of life residues in terrestrial specimens. An extremely important step was taken in 1965 when Anders and coworkers succeeded in obtaining proof that the organic compounds found in meteorites might have arisen in the protoplanetary cloud without any participation of biological processes (see below). As regards the "organised elements", nowadays almost everyone admits that the part of these belonging to the meteorite itself is abiogenical in nature and consists of complex crystals and mineral grains or hydrocarbon droplets, while the remainder are a result of the contamination of the meteorite by earth spores, pollen, etc.

In 1962–1965 a series of studies on the organic material in carbonaceous chondrites was carried out by Vdovykin[61]. These investigations dealt both with the bitumen-like material extracted by solvents and with the high-molecular insoluble phase. Luminescence analysis of the extracts obtained by cold extraction with various solvents by Florovskaya's method revealed the presence in these materials of reducing, neutral, and acid organic compounds: oils, neutral and acid resins, and humic components. The content of oils was 45–75% and that of asphaltenes 9–20%. The study of the fluorescence band spectra established the presence of condensed aromatic hydrocarbons[62].

The high-molecular phase constituting more than 90% of the carbonaceous substance was investigated by X-ray diffraction, electron diffraction, and microdiffraction methods. This phase consists mainly of an amorphous organic substance in which crystalline polymers are encountered and also very small inclusions with some order in the arrangement of carbon atoms. A gradual transition of the high-molecular phase of the carbonaceous substance into carbon black, and subsequently to graphite was noted. This phase, consisting of highly condensed aromatic compounds, is present also in achondrites and in the graphite inclusions in iron meteorites.

During these years a large number of papers were also published abroad and their number continues to grow. These studies dealt with the aromatic and aliphatic compounds in the bitumen-like (extractable) and high-molecular phases of the carbonaceous substance and also with compounds containing sulphur, nitrogen, and the halogens. Hayes[63] reviewed systematically the work published in 1953–1966. Information about this work, including the bibliographical references, is also available in Vdovykin's book[61]. Many organic compounds have been observed with absolute certainty but for others there are discrepancies in the results.

An example of the pitfalls encountered in the analysis of organic compounds in meteorites is provided by the history of the detection of amino-acids in them. Thus Degens and coworkers reported the observation of sugars and amino-acids in a number of carbonaceous and ordinary chondrites[64,65]. On this basis, Degens[66] speaks of a genetic relation between the organic material from meteorites and from sea deposits.

However, Oro and Skews[67] soon detected the same amino-acids as those found in meteorites on the skin of human fingers and actually in similar relative amounts. It was found that the amounts of amino-acids detected in meteorites can be fully accounted for by the amino-acids present in the fingerprints remaining after the meteorites have been handled. Therefore Oro believes that his data support the results of Calvin[42] and Briggs[44], who failed to detect amino-acids in meteoritic organic materials (see also Ref. 68). Probably their detection in other investigations[64–66] can be accounted for by the contamination of the specimens studied.

A pitfall of another kind is clearly demonstrated by the study of the isotopic composition of hydrogen carbon, and sulphur from the organic material in four carbonaceous chondrites carried out by Briggs[68]. He observed enrichment in deuterium and sulphur-34 and depletion in carbon-13. As regards the enrichment in deuterium and depletion in carbon-13, this substance resembles terrestrial materials, but the enrichment in sulphur-34 is contrary to what is observed on earth. Therefore Briggs believes correctly that his results confirm the extraterrestrial origin of the substance which he investigated. However, if only hydrogen and carbon were studied, the opposite conclusion would probably have been arrived at!

The application of the ESR method led to the detection of free radicals in the carbonaceous material in meteorites[61,69,73]. It was found that the concentration of free radicals is 10^{16}–10^{17} per gramme of carbon. Repeated measurements after the irradiation of the meteorites with X-rays established that the free radicals are associated with aromatic structures. Soviet investigators attribute the formation of radicals to the effect of cosmic radiation. According to French scientists, the carbonaceous components of the meteorite material are at least partly of biological origin. However, Urey[50] in his discussion of this finding also pointed out that free radicals might have arisen in the abiogenic material of meteorites under the influence of the radiation to which they were subjected in the interplanetary space. Schulz and Elofson[73], who investigated the Orgueil meteorite, carbonised the carbonaceous material at different temperatures and concluded that this meteorite had never been subjected to a temperature in excess of 300°C. They note that the presence of free radicals can be explained in different ways and that an abiogenic origin is also possible.

The studies discussed above led to a significant advance of our knowledge about organic compounds in meteorites but did not and could not provide a definite answer to the question of their biogenic or abiogenic nature. At the same time experimental studies, begun even earlier, continued to reveal new possibilities in laboratory abiogenic synthesis[12,21,22,42,43,74–84].

Perhaps one of the main difficulties arises in connection with the explanation of the abiogenic origin of saturated hydrocarbons. In meteorites they are mainly of the unbranched type, although abiogenic synthesis usually yields a mixture of branched and unbranched compounds. At the same time saturated hydrocarbons in most terrestrial organisms are unbranched. Only Wilson[74] succeeded in obtaining by an abiogenic procedure similar high-molecular hydrocarbons on the surface of a salt solution by passing an electric discharge through a mixture of methane, ammonia, and hydrogen above the solution. It is also known that thin films of waxy material are formed in electron microscopes on surfaces subjected to the action of an electron beam.

Similar waxy coatings were observed on the surface of cosmic dust[85]; they probably consist of a hydrocarbon polymer formed in the interplanetary space under the action of radiation.

Vigorous controversy has developed on the question of the optical activity of the organic compounds from meteorites[86-90] (see also Refs. 61 and 63). The rotation of the plane of polarisation is extremely rarely observed in the products of non-biological laboratory processes, but is a characteristic feature of all substances of biological origin and therefore the detection of rotation in extracts from carbonaceous chondrites would be important evidence in favour of the biogenic nature of these extracts, but would still not constitute incontrovertible proof of this. Since the time when Mueller's work was carried out, the precision of measurements increased, but later observations also led to the conclusion that the extracts have no optical activity. The reported low optical activity in certain meteoritic extracts is probably associated with the surface contamination of the specimens by fingerprints.

An important stage in the investigation of the nature of the organic material in meteorites was reached with the work of Anders and his coworkers. These investigators succeeded in obtaining data on the composition of the organic compounds which were contained within the mineral grains and therefore had not lost their volatile components, in contrast to the remaining larger portion of organic material in the meteorite. The composition of this substance is similar to that observed for the equilibrium distribution in carbon-rich carbon–hydrogen–oxygen mixtures. Therefore Studier et al.[91] suggested that the organic substances present in meteorites were formed in the interplanetary cloud and were then captured on formation of the parent bodies from which the meteorites originated. Initially this concept was based on theoretical calculations of the equilibrium concentrations of various compounds in the system carbon–hydrogen–oxygen and was then supported by experiments.

The basic idea of their investigation was as follows. During the course of the last few millions of years of their existence, the meteorites were heated to 250–300°K each time they passed through the perihelion. Therefore the most volatile substances could persist only in a few "secluded" corners within the mineral grains, while the less volatile substances persisted also in the form of surface coatings and in the interstices between the grains. Carbonaceous chondrites contain traces of primary inert gases firmly retained within the mineral grains. These gases were captured from the primary gas phase (from the protoplanetary cloud or, in the view of certain investigators, from some atmosphere) during the formation of the carbonaceous chondrites or the minerals included in them. The above investigators made an attempt to elucidate whether other volatile substances were captured at the same time.

Volatile substances were evolved in a vacuum at low temperatures from freshly ground specimens of three carbonaceous chondrites. The fractions evolved at different temperatures (up to 140°C) were investigated using a mass-spectrometer, whereby mass spectra up to a mass number of 500 could be studied. The substances which could be identified on the basis of 28 individual analyses are listed in Table 5†.

The new measurements emphasised the predominance of aromatic hydrocarbons compared with aliphatic hydrocarbons. An important discovery was that the amount of ethane is smaller by a factor of at least 1000 than of methane. From the analysis of these results, the authors concluded that the volatile compounds which they detected do indeed represent little changed residues of the primary gaseous medium in which the carbonaceous chondrites were formed and on this basis they endeavoured to elucidate the origin of the organic compounds. Two alternative hypotheses are possible: (a) a non-equilibrium process associated with some high-energy source (for example Mueller–Urey reactions presupposing irradiation with ultraviolet light or charged particles), or (b) an equilibrium process presupposing reactions in the gaseous medium under conditions of thermodynamic equilibrium.

Table 5.*

Compound	Orgueil	Cold Bokkeveldt	Murray	Compound	Orgueil	Cold Bokkeveldt	Murray
H_2	++	+	++	$C_6H_4(CH_3)_2$	+*E*		
He			+	C_6H_5Cl	+		
CH_4	++	++	++	$C_6H_5C_2H_7$	+		
NH_3	–	–	–	$C_6H_5CH(CH_3)_2$	+		
H_2O	++	++	++	$C_6H_3(CH_3)_2(C_2H_5)$		++	
CO	++		++	$C_6H_4Cl_2$		+	
N_2	++	++	++	Xe	++		
NO	++	++	+	$C_{10}H_8$	+*E*		
C_2H_6	–	–	–	$C_6H_4(C_2H_5)_2$	+*E*		
Ar^{40}		++		anthracene	} *E*		
C_3H_8	–	–	–	phenanthrene			
CO_2	++	+		$C_nH_{2n+1}Cl$ (n = 12–18)	+	+	
C_4H_8	++	++	++	R—SO_3—CH_3	+*E*		
COS	++	++		trimethylanthracene or trimethylphenanthrene	*E*		
SO_2	++						
CS_2	++		++	alcohols	?	?	+
C_2H_6	++	++	++	aliphatic and alicyclic hydrocarbons	?	?	
Kr	++						
$C_6H_5CH_3$	++	+					
$C_6H_5C_2H_5$	+						

*The approximate abundances are denoted by one or two plus signs. The compounds which were looked for but not found are denoted by the minus sign and those detected on extraction with solvents are denoted by the letter *E*. The question mark denotes tentative compounds.

The non-equilibrium process is to a high degree non-selective with respect to the formation of particular compounds. In all the numerous experiments on this process it was found that methane is always accompanied by light alkanes, aliphatic compounds predominate over aromatic compounds, complex aromatic compounds, for example coronene, could not be detected at all, and the amount of branched alkanes obtained was considerably greater than that of the straight-chain isomers. Thus this process cannot explain the data obtained for the meteorites: neither the high methane : ethane ratio nor the absence of propane, butane, and pentane, nor the predominance or aromatic compounds, nor the high straight-chain alkane : branched-chain alkane ratio.

In recent years the equilibrium process did not attract attention, since thermodynamic calculations for the gas having the cosmic composition, i.e. with a very high hydrogen content, showed that in this way it is possible to obtain only traces of complex organic compounds. The first step in the demonstration of the possibilities of this process were taken by Suess[92], who pointed out that, in a gas depleted in hydrogen by a factor of 100 compared with the

† Studier et al.[91] quote the values of m/e for several dozen peaks in the mass spectra which were not identified.

cosmic abundance, complex organic compounds can form by equilibrium reactions. Subsequently this was fully confirmed by computer calculations[93,94] of the equilibrium concentrations of all the main components produced in the system carbon–hydrogen–oxygen and also of a representative group of more than 100 compounds present in small amounts. The concentrations of compounds containing nitrogen, sulphur, and chlorine in addition to carbon, hydrogen, and oxygen were also calculated. A wide range of temperatures and pressures was considered: from 300° to 1000°K and from 10^{-6} to 300 atm. The results for the carbon–hydrogen–oxygen mixture are presented in the form of a ternary diagram in Fig. 1. The straight lines separate the regions in which particular compounds predominate. The straight line in the centre of the diagram indicates the position of the "asphalt threshold", above which the concentration of aromatic compounds increases by a factor of 10^{20}–10^{30}, until finally these compounds become the main components of the system (Fig. 2). The curved lines in the lower part of the diagram correspond to the equality of the free energies of carbon in the gaseous mixture and the free energy of graphite (dashed line for 500°K and continuous line for 700°K). Above this line, complete thermodynamic equilibrium requires the formation of graphite. However, since the activation energy required for its formation is very high, considerable amounts of resins and asphalts accumulate before this happens. The points *A*, *B*, *C*, and *D* in Fig. 1 indicate the compositions of the mixtures for which the concentrations of a number of compounds have been published[93,94] (500°K and 1 atm). With these four compositions, it was found that many compounds which are biologically important, such as ribose, glycerol, and derivatives of adenine, cytosine, glycylglycine, and serine, are present at concentrations less than 10^{-35}.

Unfortunately only one of these four mixtures, mixture *O* (Fig. 1) with the ratios C : H : O = 1 : 1 : 1.33, lies above the "asphalt threshold". Studier, Hayatsu, and Anders[91] selected the compounds for which concentrations in excess of 10^{-10} had been calculated and, having arranged them in descending order, compared them with their own results (Table 6). It was found that all nine compounds which are the most abundant in mixture *C* are present in carbonaceous chondrites. The next two compounds, ethane and ammonia, were not found despite a thorough search. The upper limit of the ethane content thus found, 10^{-2} of the methane content, is higher by a power of ten than the calculated concentration. Of the remaining five compounds, only xylene was detected. Its detection is probably due to the characteristics of the sensitivity range of the mass spectrometer. In general there is a remarkable qualitative agreement between the theoretical distribution and the results of the experimental study of the volatile compounds from meteorites.

Having established that at least the major part of organic compounds in meteorites were formed in an equilibrium process, Studier, Hayatsu, and Anders posed the question of the time and place of their formation. Since meteorites are fragments of asteroids, there are three possibilities:

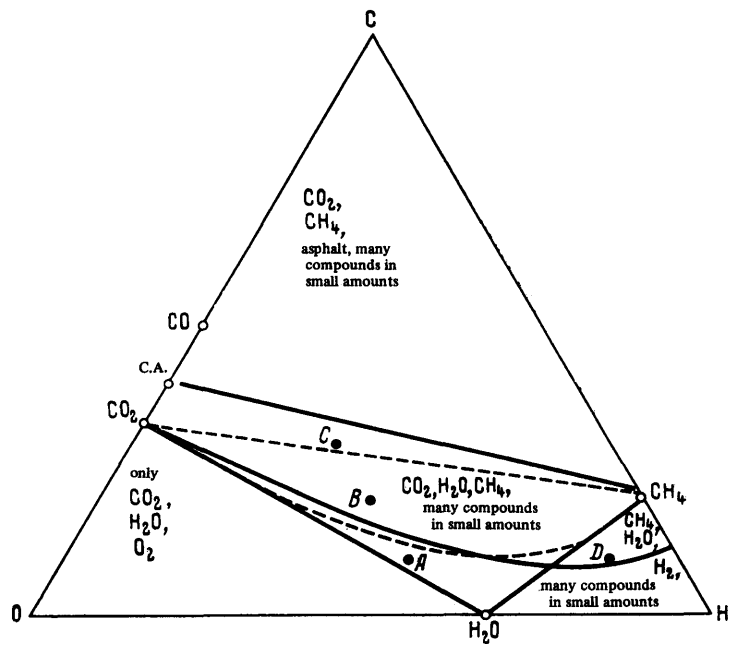


Figure 1. Ternary diagram for the system carbon–hydrogen–oxygen with the indication of the "asphalt threshold" (straight lines in the centre of the diagram) and the lines corresponding to the equality of the free energy of carbon in the gas mixture and the free energy of graphite (curved lines in the lower part of the diagram) at 500°K (dashed line) and 700°K (continuous line). The point C.A. on the O–C line indicates the ratio of the cosmic abundances of these elements.

(1) the transient atmosphere of asteroids (because of their low mass, asteroids do not have a permanent atmosphere); (2) the "internal atmosphere" (see p. 67); (3) the protoplanetary cloud. The first two possibilities must be rejected, since, in order to explain the amount of organic compounds present in meteorites, an impossibly large mass of the atmosphere is necessary—between 100 and 1000 kg of carbon dioxide and methane per cm^2. At the same time the formation of the organic compounds in the protoplanetary cloud is quite possible. The cloud having the cosmic composition coincides almost completely with the point H in Fig. 1, i.e. its composition occurs in the region where hydrogen, carbon, and oxygen are almost entirely present as H_2, CH_4, and H_2O. Along the C–O line the cosmic ratio of the abundances of these elements is represented by the point C.A. The selective loss of hydrogen alters the composition of the mixture along the C.A. line (not shown in Fig. 1) and at about 500°K the "asphalt threshold" is crossed by the mixture.

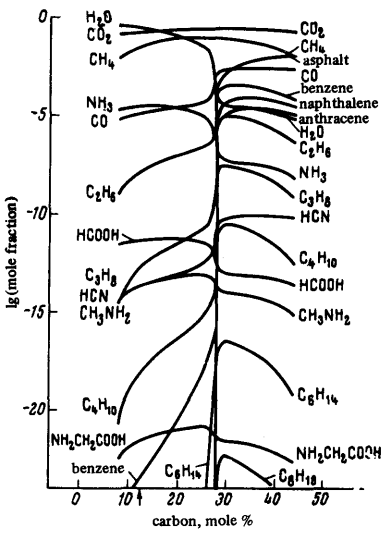


Figure 2. Variation of the concentrations of a number of organic compounds on crossing the "asphalt threshold".

The paper of Studier, Hayatsu, and Anders was very sharply critisised by Urey and Lewis and by Burlingame and Schnoes, but the criticism received an entirely convincing answer[95–97]. Urey and Lewis rejected the possibility of using the results of the calculation of equilibrium concentrations on the assumption that there is no graphite. However, in their reply Studier, Hayatsu, and Anders were already able to confirm the absence of free carbon by their experimental results obtained in the study of the attainment of equilibrium in the system carbon–hydrogen–oxygen[98]. They employed CO–H_2 mixtures, since in the temperature range 1000–200° and at moderate pressures carbon monoxide is the dominant form of carbon in the cosmic gas. In the first 15 experiments molecular hydrogen was employed but subsequently 38 experiments were carried out using molecular deuterium (D_2) to avoid the risk of contamination. The mixture compositions ranged from the atomic ratios C : H : O = 1 : 1 : 1, which corresponds to the "asphalt" region in the ternary diagram, to C : H : O = 1 : 500 : 1, which is close to the cosmic value. The principal aim of these experiments was to test the hypothesis that the formation of free carbon is inhibited kinetically, so that there arises a metastable distribution of compounds with a high proportion of aromatic components. In some series of experiments pure gas mixtures were employed and in others the catalytic effects of powders consisting of iron and stone meteorites were examined. The temperature of the gas mixture, which was usually under a pressure of 1–2 atm, was increased in steps and the compounds formed were investigated mass-spectrometrically.

Table 6.

Compound	Calc. concns. for mixture C	Presence in carbonaceous chondrites	Compound	Calc. concns. for mixture C	Presence in carbonaceous chondrites
Carbon dioxide	0.66	+	Anthracene	$2.9 \cdot 10^{-5}$	+
Nitrogen	0.50	+	Ethane	$2.3 \cdot 10^{-5}$	—
Methane	0.24	+	Ammonia	$1.1 \cdot 10^{-6}$	—
Carbon monoxide	$5.3 \cdot 10^{-3}$	+	Xylene	$9.4 \cdot 10^{-8}$	+
Benzene	$6.6 \cdot 10^{-4}$	+	Ethylene	$5.7 \cdot 10^{-9}$	
Naphthalene	$1.4 \cdot 10^{-4}$	+	Acetic acid	$1.2 \cdot 10^{-9}$	
Hydrogen	$1.3 \cdot 10^{-4}$	+	Hydrogen cyanide	$1.4 \cdot 10^{-10}$	
Water	$7.9 \cdot 10^{-5}$	+	Benzoic acid	$1.3 \cdot 10^{-10}$	

The experiments showed that the familiar Fischer–Tropsch reaction:

$$n\,CO + \left(n + \frac{1}{2}x\right) H_2 \rightarrow C_nH_x + n\,H_2O$$

took place. When this reaction is carried out under industrial conditions, the catalysts used are iron, nickel, and cobalt, i.e. precisely the elements which enter into the composition of iron meteorites. Therefore it is not surprising that the meteorite powder has a powerful catalytic effect. Without it a scarcely detectable amount of organic compounds is formed only after prolonged heating, whereas in the presence of the iron meteorite powder a wide variety of complex hydrocarbons are rapidly produced, but not even traces of free carbon were detected.

The distribution of reaction products strongly depended on time and temperature. At low temperatures the reaction did not reach equilibrium. This was shown by the fact that, for the mixture whose composition lies within the "asphalt" region, aliphatic hydrocarbons predominated over the aromatic compounds. At high temperatures and for prolonged reactions the results are closer to equilibrium, when only traces of aliphatic compounds should be detected.

On the basis of their experiments, Studier, Hayatsu, and Anders concluded that the organic compounds present in meteorites can be obtained in two stages: initially the Fischer–Tropsch reaction yields as metastable products straight-chain alkanes, methyl- and dimethyl-alkanes, alkenes, and light aromatic compounds and then equilibrium is partially attained, whereupon the amount of light alkanes falls and that of aromatic compounds and methane increases, with formation of condensed aromatic compounds (but carbon is not formed!).

This two-stage process might have occurred in the protoplanetary cloud having the cosmic composition and there is no need for its depletion in hydrogen, which initially appeared to be essential for the carbon–hydrogen–oxygen

mixture to fall within the "asphalt" region of the ternary diagram. Experiments showed that the first stage (the Fischer–Tropsch reaction) takes place satisfactorily with H : C = 500, which is close to the cosmic value of this ratio. Only during the second stage is it necessary that the composition should be in the "asphalt" region, i.e. in the region where H : C < 4. However, the organic compounds formed in the first stage correspond to H : C ≤ 2; when they condense and are thereby virtually isolated from the hydrogen-rich gas phase, they automatically fall within the "asphalt" region. The organic compounds formed condensed on the surface of dust particles, where the second stage of the process took place.

The experiments of Hayatsu et al.[99] showed that nitrogen-containing organic compounds might have formed in the same two-stage process if the latter took place in the presence of ammonia.

Modern hypotheses concerning the formation of the protoplanetary cloud by separation from the protosun in the final stage of its contraction entail a hot brief initial stage during which carbon must have existed in the form of carbon monoxide. When the cloud cooled, the condensation of metallic and silicate dust particles created catalytic centres for the Fischer–Tropsch reaction between carbon monoxide and molecular hydrogen. Because of the presence in the protoplanetary cloud of nitrogen, sulphur, and chlorine, not only hydrocarbons but a wide variety of organic compounds might have formed. These compounds condensed on the surface of the dust particles and together with them entered into the composition of the parent bodies of the meteorites formed by accretion from the dust component of the protoplanetary cloud. The second stage of the process—the partial attainment of equilibrium—probably occurred within the interior of these parent bodies—in that part of their material which was subjected to even slight heating and which gave rise to carbonaceous chondrites.

Investigators adhering to the idea of the biological origin of organic compounds present in meteorites for some reason do not discuss the question of what were the involatile carbon compounds which entered into the composition of the parent bodies of the meteorites and served, from their point of view, as the raw materials for further biological synthesis. The work of Anders and coworkers shows that the principal features of meteoritic hydrocarbons are characteristic of the abiogenic material synthesised from carbon monoxide and molecular hydrogen.

Studier, Hayatsu, and Anders note that the similarity between meteoritic and terrestrial hydrocarbons, including biogenic hydrocarbons, is frequently exaggerated and also that the importance of this similarity is overestimated. In this connection they point to the work of Friedel and Sharkey[100,101], who showed that the abundance of different isomers in crude petroleum from Saudi Arabia is expressed by the same formula as their abundance in the products of the Fischer–Tropsch reaction. This formula involves only two adjustable parameters, namely the probability of increase in chain length and the probability of chain branching. This shows that the distribution of isomers in crude petroleum is not due to biosynthesis but to catalytic processes and therefore the similarity between terrestrial and meteoritic hydrocarbons does not constitute evidence for the biological origin of the latter. On the contrary, this may be regarded as evidence for a non-biological origin of a considerable proportion of terrestrial petroleum.

Thus considerable advances have now been achieved in the study of organic compounds present in meteorites and the principal features of their abiogenic synthesis in the protoplanetary cloud have been elucidated.

5. ORGANIC COMPOUNDS ON EARTH

The presence of abiogenic organic compounds in meteorites and consequently in the parent bodies of the meteorites (asteroids) makes it virtually certain that these compounds were also present in the material from which the earth accumulated. Judging from type I carbonaceous chondrites, the total mass of the "primary" organic compounds brought to the earth might have exceeded severalfold the mass of water in the oceans[27,102].

However, only a small fraction of the "primary" organic compounds could persist in the course of the formation of the earth and its subsequent evolution. In the first place the "primary" organic material broke down to a considerable extent as a result of the temperature rise accompanying the impact of planetismals against the surface of the growing earth. However, Studier, Hayatsu, and Anders believe that, during the dispersion and cooling of the products of the "explosion" accompanying the impact, new hydrocarbons and other organic compounds might have formed rapidly (as a result of the Fischer–Tropsch reaction and other processes occurring simultaneously). Nevertheless the newly formed compounds and the persisting portion of the "primary" compounds from the protoplanetary cloud were buried in the course of the further growth of the earth underneath the growing outer layers. At the same time the interior of the earth, starting with a depth of the order of 100 km, became hot, initially as a result of the evolution of the energy associated with the accretion process itself and then as a result of the accumulation of heat due to radioactivity. At the present time the temperature of the interior is 2000–4000°C and this should probably result in an almost complete breakdown of organic compounds. The material of meteorites of most types was heated to 500–1000°C and organic compounds are present in the latter in amounts corresponding to hundredths and thousandths of a per cent. (However, it should be noted that, although this content is smaller by 2–3 powers of ten than in carbonaceous chondrites, it is nevertheless of the same order of magnitude as the content of organic compounds in terrestrial rocks, frequently regarded as petroleum bearing.)

The "primary" organic compounds and the compounds formed during the dispersion of material after the impacts of planetismals might have partially persisted only in outer relatively cold layers of the earth. Furthermore new compounds might have been synthesised in these layers from the decomposition products diffusing from the hot interior to the surface. It has been shown experimentally that clays are good catalysts for the Fischer–Tropsch reaction[103].

Thus it appears very probable that a considerable proportion of the pre-biological organic matter on earth was not formed by the Mueller–Urey reaction in the terrestrial atmosphere but by Fischer–Tropsch reactions both in the protoplanetary cloud and during further stages in the evolution of the main bulk of terrestrial material. As early as a few years ago, a number of authors pointed out that the formation of organic compounds must have begun in the protoplanetary cloud[43,47,104–108].

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The studies carried out in recent years have significantly extended and deepened our knowledge concerning the presence of organic compounds, ranging from the simplest to the most complex, in various bodies in the solar system. The studies of the organic material from meteorites,

which demonstrate the presence in the latter of very complex organic compounds, frequently encountered in terrestrial biogenic organic materials, are particularly important.

Modern astronomical data quite definitely indicate that meteorites are fragments of parent bodies on which conditions necessary for the occurrence of life did not exist and therefore the organic material of the meteorites has an abiogenic origin. Thus the presence of complex organic compounds in meteorites demonstrates the wide possibilities of abiogenic synthesis of organic compounds under natural conditions.

The data on the organic compounds in meteorites together with the advances in the laboratory synthesis of organic compounds, and in planetary cosmogony as regards the formation of the earth, provide a basis for the revision of our hypotheses concerning the complexity attained by the abiogenic synthesis of organic compounds on earth before the generation of life led to the occurrence of biological synthesis, and also concerning the role of natural abiogenic syntheses at the present time.

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