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# COSMIC RAYS INDUCED POLYCONDENSATE HYDROCARBONS IN THE GIANT MOLECULAR CLOUDS

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Astrophysical and cosmochemical data show that many kinds of hydrocarbons are widespreaded in space, including giant molecular clouds, diffuse interstellar medium, comets, interplanetary dust particles and carbonaceous meteorites. Here effort is made to show a close relation between high-molecular weight hydrocarbons, observed in space and existing on the Earth. Results of astrochemical modelling of dust grains in dense collapsing cores of giant molecular clouds also are presented. They show that about 10% of the total abundance of dust grains may be resulted as aliphatic hydrocarbons. This dust serves as initial material for comets, formed in protosolar nebula. A problem of survival of cometary organics during impact on to the Earth is discussed, and it is shown, that a so called 'soft-landing comet' hypothesis may explain an accumulation of complex hydrocarbons on the Earth's surface. We conclude that a significant fraction of terrestrial pre-biotic petroleum was delivered by extraterrestrial matter.

Key words: *ISM:dust - heavy hydrocarbons:radiation chemical transformations*

1. *Introduction*. It is generally accepted now that giant molecular clouds (GMC) are rich in carbon-bearing molecules. In general a gas-grain interaction during the collapse phase of GMC play an important role in the material evolution in space, particularly through the depletion of atoms and molecules, and through the formation and evaporation of ice mantles in star-forming regions. These icy mantles of dust particles are believed to contain water, carbon monoxide, methane, ammonia and other species. But gas-phase-only chemical models of these regions are incapable of reproducing the Infrared Space Observatory (ISO) observations of $CH_4$, CO, $CO_2$, $C_2H_6$, $CH_3OH$ etc. [1]. It appears that a rich chemistry occurs in the ice matrices frozen onto dust grains in the different stages of cloud collapse. Besides, many species (e.g. C, N and O) sticking to grain surface are processed in hydrogenation reactions to form saturated species ($CH_4$, etc.), which also enriches the chemistry. It seems that dust grains are possible sites for the formation and preservation of large organic species at low temperatures down to 10 K [1]. In addition to surface chemistry complex carbon-rich species could be produced by space irradiation of the ice mantles. Galactic cosmic rays (GCR) in the middle energetic regime of about 1-1000 MeV per nucleon, together with ultraviolet light, are among the most effective energy sources

for the formation of complex organic molecules in space [2].

Besides, they are some of the more abundant types of organic compounds present in cosmic dust: for example, the most prominent feature of interstellar extinction, a bump at a UV wavelength 217.5 nm, is traditionally attributed to carbon-containing structures [3]. Another well known example is that carbon-bearing macromolecules are believed to be responsible for emission feaures in the near infrared spectra of the interstellar medium (ISM) [4]. Finally, we recently have shown experimentally that some fractions of petroleum possessed aromatic and aliphatic hydrocarbons with 50 or more carbon atoms that may successfully explain not only emissions of unidentified infrared bands of the diffuse ISM but also the absorption "bump" at ~220 nm in UV [3,4]. Unsuccessful efforts of many investigators to attribute observed spectral features to a given carrier (e.g. to a given PAH molecule) pushed us to develop a new approach, namely to study a mixture of different groups of molecules, and operate with average characteristics of the spectral behaviour. It should be emphasized here that such interpretation, if true, is very attractive, because no convincing evidence has been published so far to really connect hydrocarbons to the interstellar absorption UV feature.

It has been observationally confirmed for some time that both aromatic and aliphatic hydrocarbons are present in the ISM [5]. Moreover, the "CIDA" detector on-board a space mission "STARDUST" has identified interstellar dust particles of unexpected complexity - probably polymeric heterocyclic aromatic and aliphatic hydrocarbons [6].

As dust particles become part of a protoplanetary nebula, they are embedded in freshly originated cometary nuclei in the outer part of the forming planetary system, like in our own solar system 4.5 Gyr ago. Comets form in a more cold part of the protoplanetary disk and are an agglomeration of various dust grains, or, to be more correct, the volatily components ($H_2O$, $CH_4$, CO, $CO_2$, $NH_3$ etc.) contribute ~40% by mass plus roughly equal amounts of the refractory components in the form of silicates and complex organic material dominated by carbon [7]. Therefore a great deal of organic chemistry in dust grains has already taken place under conditions of the ISM and the protoplanetary disk before the formation of the cometary nucleus (e.g. [8,9]). It is generally accepted now that comets were scattered by giant planets and caused a "heavy bombardment" of the Earth between 4.5 and 3.8 Gyr before present [8]. A question, to what extent cometary matter is of interstellar or solar nebula origin, is still open, but what is now quite obvious that comets (and/or micron-sized particles [9]) have brought to the Earth a significant (if not all - see, e.g. [8]) amount of volatile compounds.

Sec.2 of this paper contains the results of fractional abundances of frozen methane in icy mantles of dust grains. In Sec.3 we discuss the known experimental results that can be put as the base for the formation of interstellar hydrocarbons in the grains and estimate their abundance in the GMC and corresponding chemical time-scale. In Sec.4 we discuss a pathway from interstellar grains to solar comets and give a possible scenario of the delivery of heavy hydrocarbons to the early Earth. The conclusions are given in Sec.5.

## 2. *How much methane is contained in dust grains of the GMC?*

Our model follows the chemical evolution of a modified free-fall collapsing cloud [10,11] in the process of forming a low-mass star. The formula used for this collapse includes a scaling parameter $B$ to allow for collapse in free-fall ($B = 1.0$), or somewhat slower ($B < 1.0$) if gas or magnetic pressure resists the collapse. All models are time and depth dependent: this implies that the abundance of each specie is derived by a non-steady state computation of the chemical evolution of the gas/dust interaction processes. The original molecular cloud is assumed to have an initial and final density of respectively $10^3$ and $10^6\,\mathrm{cm}^{-3}$. The temperature is held at 10 K throughout the collapse. We assume that at the above densities the gas temperature is equal to the dust temperature.

The elemental abundances adopted are as in [12], and the initial chemistry is all in the gas phase. Before the collapse starts, the gas-phase environment is purely atomic, apart from half of the hydrogen which is initially assumed to be molecular. At the densities considered it might well be that more than half of the hydrogen is in the form of $H_2$. This, however, should not be crucial for our models since, as long as some hydrogen is present and its abundance exceeds that of oxygen, carbon or nitrogen, hydrogenation will occur.

The gas is subjected to a flux of cosmic rays and to an external ambient radiation field, as described in [10-12]. The cosmic ray ionization rate was taken to be $1.3 \cdot 10^{-17} \cdot z\ \mathrm{s}^{-1}$ where $z$ is a free parameter which was assigned different values in various models. We took, for one exception, $z = 5$. It is assumed that initially the gas is exposed to a weakened interstellar radiation field, which in units of the canonical radiation field [12] is parametrized by the factor $R$. In all models a value of $R = 0.3$ was adopted.

The cloud is represented by a uniform slab subdivided by 50 depth points of increasing visual extinction from the edge of the cloud towards the centre. For other details of the collapsing cloud models see [10-12].

### 2.1. *The chemistry.*

We have included 121 gas-phase species and 41 surface species interacting in 1736 chemical reactions. The UMIST chemical database ([10-12] and references therein) was used. The initial gas-phase elemental abundances are given in Table 1.

We start our chemical computation from a pure gas-phase chemistry, and allow freeze-out of gases to occur during the collapse phase. Dust grains accrete gas-phase species very effectively and quickly: loss of that by freeze-

*Table 1*

TOTAL INITIAL GAS-PHASE ELEMENTAL ABUNDANCES

| | |
|---|---|
| H | 1 |
| He | 0.14 |
| C | $2.0 \cdot 10^{-4}$ |
| N | $7.0 \cdot 10^{-5}$ |
| O | $4.0 \cdot 10^{-4}$ |
| Mg | $1.0 \cdot 10^{-7}$ |
| Si | $1.0 \cdot 10^{-8}$ |
| S | $1.0 \cdot 10^{-5}$ |

out from gas would occur on a time-scale $t_f = 3 \cdot 10^9\,\mathrm{yr}/n$, where $n$ is the concentration of H nuclei ($\mathrm{cm}^{-3}$) [12]. The mantle composition is therefore determined self-consistently with the gas-phase chemistry. To calculate the rate at which collisions between gas phase species and grain surfaces remove species from the gas phase we have used a free parameter $S$ (in the range 0 to 1) that incorporates uncertainties associated with the sticking probability per collision, and in the grain size distribution, $S = 1$ corresponds to the standard grain size distribution and 100% sticking efficiency ([12] and references therein). For one exception, we have normally taken $S$ to be 0.1.

A main chemical pathway to solid methane is the formation from atomic C and/or $C^+$ through grain surface reaction [11]. Methane is a natural consequence of hydrogenation, which seems more effective in the collapse phase, especially in the early, low density phase, during which less carbon (and oxygen) is tied up in CO. To the known chemical routs to frozen methane, we have added the formation of solid $CH_4$ from a reaction of H atoms with solid CO [13], which leads to the production of methane, formaldehyde and methanol. Because a yield of $CH_4$ due to this CO hydrogenation is larger than that of $CH_3OH$ [13] (0.024% and 0.003% respectively) we have used an eight times larger reaction rate for conversion of CO to icy $CH_4$, as compared with that of CO to icy $CH_3OH$, which has been used in [14].

2.2. *Results for frozen methane.* Table 2 gives the parameters defining each of the models for which we carry out calculations. We adopt a physical model of molecular clouds in which dense clumps are embedded in a relatively low-density interclump medium. Material in clouds is assumed to be recycled between these phases [11]. The clumps undergoing collapse from initial $10^3$ to final number density $10^6\,\mathrm{cm}^{-3}$.

Models 1,3-8 are for regions undergoing collapse, whereas a static model 2 is for an already dense cloud with cloud characteristics from model 1. In model 8 all carbon is initially in the form of CO.

*Table 2*

MODEL PARAMETERS

| Model | $S$ | $B$ | $z$ | C/H | O/H | $q$ ($CH_4$) |
|---|---|---|---|---|---|---|
| 1 | 0.1 | 1 | 5 | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.23 |
| 2 (static) | 0.1 | 1 | 5 | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.21 |
| 3 | 0.1 | 1 | 100 | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.24 |
| 4 | 1 | 1 | 5 | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.33 |
| 5 | 0.1 | 1 | 5 | $1 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.13 |
| 6 | 0.1 | 1 | 5 | $4 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.35 |
| 7 | 0.1 | 0.5 | 5 | $2 \cdot 10^{-4}$ | $4 \cdot 10^{-4}$ | 0.25 |
| 8 | 0.1 | 1 | 5 | $1 \cdot 10^{-9}$ | $4 \cdot 10^{-4}$ | 0.16 |

The last column in Table 2 contains the fractional abundance of frozen methane with respect to other icy species in the dust mantle, that is the ratio $q = m(CH_4)/m(\text{total})$ (where "$m$" is the number of molecules in mantles) for different initial conditions. The values of $q$ are an average over the final state of the cloud at the time of 1.3 Myr after collapse starts. The resulting ice mantles are mostly composed of simple saturated and stable species such as $H_2O$, $CH_4$, CO and more complex species such as $CH_3OH$ and so on. Our aim is, at first, to establish whether there is an enrichment of the solid-phase methane abundance in the ice mantles. We note, that the fractional abundance of frozen methane with respect to hydrogen, $X$, varies with time (that is with density) and achieves it maximum final value about $X(CH_4) \sim 10^{-4}$ and then remains constant (being in chemical equilibrium). At the same time it decreases towards internal parts of the cloud by less than a factor of two. It should be stressed here that icy methane forms first, so is a large fraction of the mantling material, whereas it becomes a smaller fraction because water ice condenses later in the models. We find an excess for $X(CH_4)$ with respect to that of for icy water which occurs in all models of early time formation, for a period of 1 Myr. Thus, icy methane molecules are dominant early-time ones in the mantle. The result is common for all models, including the values of initial and final densities $10^2$ and $10^7$ cm$^{-3}$, respectively. When the gas reaches its final density, the relative abundance of frozen methane abruptly decreases, down to values $q = 0.1$, 0.2, due to fast growth of the fraction of icy water and other species in the mantle.

One of the highest computed values of $q$ (about and even over 0.3) arises in the Model 6, which is one that has the largest adopted value of C/H = $4 \cdot 10^{-4}$. It is interesting to note, that the same ($q > 0.3$) is true and for the Model 4 with the largest adopted value of $S = 1$ and in which atomic carbon sticking the grain surface is assumed to be processed to form $CH_4$. As is known [10], at relatively high temperature of the dust grains (of about and over 100 K) methane is unlikely to remains bound to the grains: its binding energy to the surface is relatively small, but the energy released in the final stage of hydrogenation is relatively large. On the other hand, the evaporation rate behaves almost like a step function versus temperature [12]: it is either close to zero, or extremely high with a strong dependence on the dust temperatures. It means, that unlike the models of "hot cores" with $T$(dust) $\sim 100$ K, which predict the fractional abundance of frozen methane be no larger than of $10^{-5}$ [14], our models with dust temperature $T$(dust) $\sim$ 10-50 K even at late time of evolution would predict one order of magnitude larger values for methane, that is of about $10^{-4}$. This may be also supported by the experimental data that a desorption of methane trapped in solid $H_2O$ or $CH_3OH$ is greatly suppressed by the matrix effect, that is a corresponding critical temperature changes from ~50 K for neat $CH_4$ to ~100 K for $CH_4$ in the $CH_3OH$ matrix and to ~150 K for $CH_4$ in the $H_2O$ matrix [13]. In other words, methane may well be preserved in the "dirty" ice at low temperatures.

It should be stressed here, that in all models q is never less than 0.1. Moreover, the value of 0.1 is the lowest one, which at final time corresponds to the carbon-deficient model 5 ($C/H = 1 \cdot 10^{-4}$) or model 8 (carbon is initially in the form of CO). Usually, in all models, $q$ is no less than 0.2 for the period near and after final time of the cloud collapse. Such a result is very common and does not depend on model conditions presented in the Table 2.

The most important conclusion to draw from these results is that the fractional abundance of icy methane during all cold period of clouds evolution is no less than 20% of total of other ice mantle components, that is $H_2O$, CO, $CH_3OH$, etc. (at the usual interstellar carbon abundance $C/H \sim 2 \cdot 10^{-4}$).

Heretofore interstellar solid $CH_4$ has been detected only toward the deeply embedded so called Young Stellar Objects (YSO): massive protostellar objects W 33A, NGC 7538:IRS1 and NGC 7538:IRS9 [15]. These observations have interpreted in [1,15]. The authors have concluded (with some reservation due to gradients in the abundances and in the temperature, which may exist along the line of sight) that the presence of $CH_4$ in a water-rich polar ice mantle and the low gas/solid ratio are the natural consequences of the formation of methane from atomic C through grain surface reactions as well as that a high CO/C ratio would be needed to explain the low observed $CH_4$ abundance $X$(gas+ice) $\sim 10^{-6}$.

It should be noted here, that none of our models is specific to these warm sources with a grain temperature of the order of 80-90 K [1,15]. For example, our model 8 shows that even at all initial carbon locked in CO, frozen methane reaches the fractional abundances $X(CH_4) \sim 10^{-6}$ and $10^{-4}$ in time of ~0.01 Myr and ~1 Myr, respectively. Our models rather are intended to reveal a situation, when gas phase molecules are frozen out completely and there is no massive YSO to provide a bright IR continuum against which to detect absorption. Once massive star formation occurs, it will cause thermal heating followed by releasing the volatile ices into gas. Eventually parent species, including methane, evaporated from grain ices, are decomposed producing reactive intermediates which can drive a quite different chemistry.

We conclude that icy methane rich dust particles with $q$ of about 0.2 may survive in some molecular clouds and be a non-negligible suppliers of hydrocarbons for the ISM.

Improved IR spectroscopy of dark cold clouds and low-mass protostellar sources is necessary to see whether there is a persistent enrichment of icy methane rich mantles.

3. *Chemical processing of solid methane by energetic particles.* Complex species such as heavy hydrocarbons could be produced by cosmic rays irradiation of the ice mantles containing methane. These ice mantles are processed by the particles of the GCR leading to new molecules synthesized in the solid state. The particle component of GCR consist of 97-98% protons and 2-3% helium nuclei with a flux $F(\mathrm{GCR}) = 10\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$ in the energy range of 1 MeV - 1 GeV ([2] and references therein]). Because, however, usual C-H and C-C bond strengths in hydrocarbon molecules range between 3 and 10 eV, the GCR particles are too energetic to form stable chemical bonds when they interact with the dust grain. However, during interaction with the solid species, each GCR particle transfers its excess energy to the target atoms, with the result of ion-induced collision cascades in irradiated ice. Moderated to about 1-10 eV, these atoms are not in thermal equilibrium with the surrounding very cold, frozen methane and other species and can react finally with the molecules via insertion, abstraction and addition to chemical bonds. The efficiency of these suprathermal reactions to produce new complex molecules at temperatures even down to 10 K is based in their ability to overcome reaction barriers in the entrance channel easily, since suprathermal species can impart their excess kinetic energy into the transition state of the reaction [2].

Irradiating solid $CH_4$ samples with above MeV particles produce a broad spectrum of synthesized species, including heavy alkanes and alkenes with up to 28 carbon atoms, as well as PAHs up to coronene [2,16-18].

The radiation-chemical output of transformation of solid methane during proton bombardment to an oligomer of aliphatic hydrocarbons with up to 28 carbon atoms in the molecules on the basis of the experiments [2,16-18] has been estimated as [11]

$$G(\text{aliph.}) = 1.3 \text{ aliphatic molecules/100 eV} \qquad (1)$$

Similarly, one can obtain the radiation chemical yield of methane molecules destruction under proton ($G(\text{destr.}, p) = 0.69$ molecules/100 eV) and

$\alpha$-particle ($G$(destr., $\alpha$) = 0.83 molecules/100 eV) irradiation (see, for analogy [2,11]).

PAHs were formed only at the highest linear energy transfer, i.e. by $\alpha$-particles, using a "multicenter mechanism" [2] (protons form only benzene and substituted benzenes). It is straightforward to estimate the $G$ value for the transformation to PAH (up to coronene) during $\alpha$-irradiation, using the available description of the experiments [2,18,19]:

$$G(\text{arom.}) = 6.4 \cdot 10^{-8} - 8.1 \cdot 10^{-7} \text{ aromatic molecules/100 eV} \qquad (2)$$

It is interesting to estimate necessary time $t(Q, j)$ of transformation of a some fraction $Q$ of initial methane to the both kinds of complex hydrocarbons ($j$ corresponds to *aliphatic alkanes* or *aromatic* PAH). The dose $D$ (an energy deposited on the grain during the irradiation time $t$, per equivalent 16 amu atom, in eV/atom), is given by [20]

$$D = S(i) \cdot F(GCR) \cdot t, \qquad (3)$$

where a specific energy loss due to interactions of energetic particles with atoms of the grain, $S(i)$ ($i = p$ or $\alpha$), is equal to $S(p) = 2.1 \cdot 10^{-15}$ and $S(\alpha) = 1.1 \cdot 10^{-13}$ eV $\cdot$ cm$^2$/atom, respectively, because in the experiments 1 s of the irradiation corresponds to $3 \cdot 10^{10}$ s in space and the dose ~30 eV per target molecule in the both cases has been exposed [2]. Introducing a fraction Q(j) of synthesized molecules of complex hydrocarbons, under the hypothesis of a first-order kinetic process of monomer destruction and polymer synthesis, we immediately have

$$Q(\text{aliph.}) = G(\text{aliph.})\left[1 - \exp\left(-t/t_p\right)\right]/G(\text{destr.}, p), \qquad (4)$$

$$Q(\text{arom.}) = G(\text{arom.})\left[1 - \exp\left(-t/t_\alpha\right)\right]/G(\text{destr.}, \alpha), \qquad (5)$$

where $G$(destr., $i$) is the mentioned radiation chemical yield of the methane molecules decomposition under protons ($i$ = p) and $\alpha$-particles ($i = \alpha$) irradiation and $t_i$ is a characteristic time of corresponding process

$$t_i = 1/[S(i) \cdot F(GCR) \cdot G(\text{destr.}, i)]. \qquad (6)$$

The value of $G$(arom.) is by 6-7 orders of magnitude less than that of $G$(aliph.) and can not arrange any appreciable fraction of PAH during a lifetime of the cloud of 10-100 Myr. It evidently means that the cosmic ray induced transformation of solid methane is not responsible for the origin of PAH in dust grains under conditions of the GMCs.

The characteristic time of the formation of the aliphatic molecules is $t_p = 219$ Myr/z, assuming a cosmic ray flux enhanced by a factor $z$. For time intervals $t \ll t_p$ one easily obtains necessary time needed:

$$t(Q, \text{aliph.}) = 116\,Q/z \text{ Myr}. \qquad (7)$$

Resulting values of conversion times $t(Q$, aliph.) are presented in Table 3.

*Table 3*

### CONVERSION TIMES *t*(Myr) OF FROZEN METHANE TO COMPLEX HYDROCARBONS

| z | Q=0.01 | Q=0.1 | Q=0.5 | Q=1.0 |
|---|---|---|---|---|
| 5 | 0.23 | 2.3 | 11.6 | 23.2 |
| 10 | 0.12 | 1.2 | 5.8 | 11.6 |
| 50 | 0.02 | 0.23 | 1.16 | 2.32 |

It stands to reason that in dense cold interior of molecular clouds, mentioned in previous section, the fractional abundance of icy heavy alkanes may reaches a value not less than 10% of dust grain components in time of about 2 Myr.

Indeed, to get the necessary dose for energetic particles induced solid phase radiation chemical transformation one needs either long time or comparatively high particles flux. There are a lot of observational constraints that the cosmic ray ionization rate in low mass cores of GMC is varied around the canonical value by a factor 0.1-10 [21]. It means that the enhancement of cosmic ray flux z may be essential, by the factor 10, on the assumption that collapse may enhance local magnetic field strengths and focus the cosmic rays into the clump. Moreover, if the pre-solar nebula was initially located in a spiral arm of the Galaxy ("exceptional position of the Sun in the Galaxy" [22]) then another factor of 5-10 can be placed for the cosmic ray increased flux [21]. An independent estimation of the $z$-factor under conditions of the pre-solar cloud is absent that is why its values of 5, 10 and 50 in Table 3 are presented.

The time-scale available for icy mantles in the dense clump to be processed is of 1.2-1.4 Myr [11]. By means of the data presented in the Table 3 we conclude that if only about 1.4 Myr is available for ice processing (assuming a cosmic ray flux enhanced by a factor of 50), then about 50% of the icy methane mantles can be converted to aliphatic hydrocarbons, during the formation and lifetime of the clump. If the mantle contains initially about 20% of methane (see Table 2), then probably ~10% of the total abundance of dust grains may be resulted as aliphatic organics during one cycle of material between dense clumps and a relatively low-density interclump medium.

Thus aliphatic hydrocarbons must be wide-spreaded not only in dense molecular clouds but also everywhere in the ISM, in good accordance with the observational data [5]. At the same time the question of the origin of PAHs is still open, while a re-cycle of these compounds between them as well as between dense and rare phases of the ISM is questionable under conditions of existing astrochemical picture of the ISM evolution [1,5]. Discussion about following evolution of such organics in the ISM is beyond the scope of this presentation (see [5,23,24] and references therein). We rather are interested in a situation in the protosolar nebula.

4. *A possible links between interstellar organics and terrestrial prebiotic petroleum.* As the pre-solar nebula collapsed, solid particles settled to the midplane [8]. They may have undergone various processing of their icy mantles as they fell, nevertheless a generally accepted point of view is that much of the interstellar material is incorporated unaltered into comets. The planetesimals (cometesimals) grew by collisional coagulation until they were big enough to decouple from the turbulence between the dust layer and the gas. Also because collisions were caused by differential radial velocities induced by gas drag, a single comet nucleus may have incorporated cometesimals from different heliocentric distances [7]. At the same time there are many evidences that planetesimals at Earth's heliocentric distance would have accreted from dust particles too hot to have retained volatile elements [8]. Thus on the one hand the proto-Earth was completely out gassed up to its final formation, and on the other hand examination of the lunar cratering record suggests that the terrestrial water and other volatiles could have a cometary origin [8]. The case is that during the process of formation, vast numbers of comet-like objects were scattered by giant planets into interstellar space, and the inner Solar System, with the result of a so called "heavy bombardment" period of the Earth 4-4.5 Gyr ago.

It is generally accepted now that the Earth's mantle out gassing was the major source of water and the early atmosphere, while some authors in the recent works have argued that ocean's water, primary atmosphere's components and carbon-bearing molecules volatiles were delivered into the Earth by comets [8] and/or interstellar dust particles sized within the range of 10-100 micron [9].

The *n*-alkanes and isoprenoid hydrocarbons are found in sedimentary rocks dating back to 3.2 Gyr before present and are believed to constitute chemical evidence for earliest biosynthesis [25]. What are these hydrocarbons with a very stable molecular architecture, a "chemical fossil" whose carbon skeleton suggests an unambiguous link with a known natural bioproduct, or a potential building-blocks for future primitive cells - this is a question outside the scope of this work. But what is now quite obvious that comets have brought to the Earth a significant amount of complex organics.

Indeed, Blank and Miller [26] and, independently, Svetsov [27] have recently shown that under conditions of low angle impact a few percent of the comet's organic matter might be survived due to jetting in opposite direction. Under reduced atmosphere conditions [28] this material was readily preserved, buried and transformed to petroleum [29]. Later bioorganics also may be added.

A comet 10 km in diameter (1000 milliard tons) may deliver 1-10 milliard tons of heavy hydrocarbons, bitumens and so on to a limited rocky Earth surface (10-100 $km^2$) with a thickness of a uniform layer 0.01-1 km. In this case one simply gets the ready-made giant-oil field. One needs only no more than 100 "soft landing" events (one per million). It should be reminded here that during the heavy bombardment period over 100 million comets impacted the Earth ~4-4.5 Gyr ago [8] and it is straightforward to estimated that about 1 per cent of impactors would have had the low angle (less than 5-10 degrees) impact [30].

5. *Conclusion.* We have modelled the time-dependent chemical evolution of icy mantles of dusty grains to reveal methane-rich ices under conditions of dense, contracting cold molecular clouds. We found that the highest computed values of the fractional abundance of frozen methane $X(CH_4) \sim 10^{-4}$ arise at $t \sim 1.2$ Myr and then remain constant (being in chemical equilibrium) in static clouds which input data from model 1 of the cloud have been used. Under such conditions the relative abundance of frozen methane with respect to other icy species of the dusty mantle $q$ is kept no less than 0.1-0.2 in all models, even if all initial carbon is locked in CO.

According to published experimental data heavy hydrocarbon molecules, up to the oligomer on the base of larger alkanes and alkenes with up to 28 carbon atoms in the molecules, as well as PAH up to coronene can arise in neat icy methane due to MeV proton and $\alpha$-particle bombardment. These radiation-chemical reactions, known as solid-phase radiation polycondensation, have been assumed to proceed within icy methane monolayers of the interstellar dust particles under irradiation by GCR. With values of radiation chemical yield of polycondensation of solid methane to alkanes (~1.3 synth.mol/100 eV) and PAH (~$10^{-6}$ and less), assumed the mean galactic flux of the GCR to be enhanced by the factor 50, the necessary time to transform, say 50% of initial methane molecules to heavy hydrocarbon would be of 1.2-1.4 Myr. In such a case about 10% of the icy mantles can be converted to complex aliphatic hydrocarbons, during the formation and lifetime of the clump. To explain the observed abundance of PAHs, an alternative scenario involving aromatization of the aliphatic constituents of cosmic grain mantles, followed by their destruction and re-distribution of the resulting PAHs molecules in the ISM may be proposed [5,23].

Thus, if the mantle contains initially about 20% of methane, then about 10% of the total abundance of dust grains may be resulted as aliphatic organics, during one cycle of material between dense clumps and a relatively low-density interclump medium.

These results clearly demonstrate the urgency to include GCR triggered formation of complex organic molecules as an additional pathway in models simulating interstellar grain chemistry.

Further laboratory work on the investigations of laboratory spectra of ion irradiated icy alkane mixtures in relevant ice matrices also is needed to interpret observational data.

We have also discussed a possible link between the extraterrestrial larger hydrocarbons and terrestrial prebiotic petroleum and have shown that inevitable consequence of the existing scenario of the origin of the Earth is the extraterrestrial delivery and accumulation of complex hydrocarbons in countable amount prior to the origin of life (see also [29,31]. It is worthy of note that the role of polyisoprenoid compounds in the transition from chemical evolution to biological one may have been especially significant [32].

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# ОБ ИНДУЦИРОВАННОЙ КОСМИЧЕСКИМИ ЛУЧАМИ ПОЛИКОНДЕНСАЦИИ УГЛЕВОДОРОДОВ В ГИГАНТСКИХ МОЛЕКУЛЯРНЫХ ОБЛАКАХ

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Астрофизические и космохимические данные свидетельствуют о том, что углеводороды широко распространены в космосе, в том числе в гигантских молекулярных облаках, в диффузной межзвездной среде, в кометах, в межпланетных пылевых частицах и в углистых метеоритах.

Возможно, существует тесная связь между высокомолекулярными углеводородами, наблюдаемыми в космосе и существующими в земных условиях. Представлены результаты астрохимического моделирования пылевых частиц в плотных сжимающихся ядрах гигантских молекулярных облаков. Они показывают, что порядка 10% молекул пылинок являются алифатическими углеводородами. Эта пыль служит в качестве исходного материала для комет, формирующихся в протосолнечной туманности. Кратко обсуждается проблема выживания кометного органического вещества при падении на Землю, и показываеся, что так называемая гипотеза о "совершающих мягкую посадку кометах" в состоянии объяснить накопление сложных углеводородов на Земле. Таким образом, значительная доля земной предбиогенной нефти была привнесена внеземным веществом.

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