

Asteroids and the origin of life—two steps of chemical evolution on the surface of these objects

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It is now well-known that carbonaceous chondrites contain large quantities of prebiotic molecules, including amino acids, carbohydrates, and heterocyclic bases of nucleic acids. It has become evident that the chemical evolution proceeds under conditions of open space, which serves as a huge chemical reactor. The extraterrestrial origin of these prebiotic molecules has been established on the basis of diversity, molecular structure, and isotopic composition. The molecular composition of a meteorite's organics resembles abiotic processes governed by physico-chemical processes that occurred on the parent bodies, including asteroids. The synthesis of soluble compounds in carbonaceous chondrites consists of a multi-step process in which organic precursors were formed in the interstellar cloud, incorporated with many volatiles into icy planetesimals and, upon aqueous processing produced the variety of compounds which can form complexes under space energy sources. We show experimentally that the solid mixtures of biologically significant compounds (nucleosides and amino acids) produce more complex compounds when they are exposed to either vacuum UV photons or ionizing radiation.

Key words: Chemical evolution, abiogenic synthesis, amino acids, nucleotides.

1. Introduction

It is well-known that carbonaceous chondrites contain large quantities of prebiotic molecules (Cronin *et al.*, 1988), including amino acids (Botta and Bada, 2002), carbohydrates (Cooper *et al.*, 2001), and heterocyclic bases of nucleic acids (Stocks and Schwartz, 1981). Chondrites contain a much wider variety of amino acids than is normally found in terrestrial organisms, and their isotopic composition suggests space origin. The amino acids share a deuterium enrichment found in other meteoritic organic extracts, such as kerogen, strongly hinting at synthesis by processes operating in the interstellar medium or the Solar nebula.

UV-radiation probably causes significant photochemistry within the mixed-molecular ices found in space. This process has been simulated in the laboratory using high-tech gadgetry. By simulating the photochemistry of interstellar and cometary ices in the laboratory, we were able to produce a host of organic compounds (i.e. compounds composed primarily of carbon, the kinds of molecules from which we and all living things are made). We suggest that this process may be responsible for the richness of the organics seen in the diffuse and dense interstellar medium, comets, and meteorites.

Simple organic compounds were formed originally as products of low temperature reactions that occurred in the interstellar molecular clouds, under radiation processing of astrophysical ices, and by gas-phase reactions in the primordial solar nebula (Fisher-Tropsch-type reactions), and

they entered the parent bodies at the time of their accretion. Such reactions may have been involved in the production of interstellar molecules, organic compounds in meteorites, and prebiotic organic matter on planets. The production of organic compounds on asteroids as parent bodies of the meteorites may have been catalyzed by the minerals found on the surface of these bodies.

There are many environments in space in which it is possible to find solid bodies subjected to UV-irradiation and particle bombardment. McDonald *et al.* (1996) reported the production of a large diversity of organic compounds by experimental simulation. Alkanes, ketones, esters, and other complex molecules have been detected by gas chromatography/mass spectrometry following the irradiation of the mixture $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}_2:\text{C}_6\text{H}_6$ (80:16:3.2:0.8) with helium plasma. A wide variety of the initial amino acids were also found following the irradiation of an ice mixture of propane (or methane, or carbon monoxide), ammonia, and water with 3 MeV protons. Dr. Kobayashi with co-workers identified such compounds as glycine (the most abundant), alanine and aminobutyric acid (Takahashi *et al.*, 1999). Amino acids were formed from carbon monoxide, nitrogen, and water, which are possible constituents of extraterrestrial atmospheres, following irradiation with high-energy particles (protons, helium nuclei, and electrons, all components of cosmic rays). Glycine, aspartic acid, serine, alanine, threonine, glutamic acid, aminobutyric acids, aminoisobutyric acid, valine, norvaline, sarcosine and proline were detected (Kobayashi *et al.*, 1998). These compounds were identified after irradiation of different gas mixtures ($\text{CH}_4\text{-N}_2\text{-H}_2\text{O}$; $\text{CO-NH}_3\text{-H}_2\text{O}$; $\text{CO-N}_2\text{-H}_2\text{O}$) by X-ray (Takahashi *et al.*, 1999) and visible-ultraviolet (VUV) irradiation (Takahashi *et al.*, 2005).

Among several energy sources available for abiogenic synthesis of biomolecules in space, UV-light with different wavelengths and cosmic rays are two of the most abundant. Some extraterrestrial material exhibits strong evidence that irradiation by H and He ions is an important process on solids throughout the interstellar and interplanetary medium (Bradley, 1994). Strazzulla and Johnson (1991) demonstrated the formation of non-volatile organic polymers from proton-irradiated simulated cometary ices. The synthesis of simple oligopeptides (Gly-Trp and Gly-Tyr) from a solid mixture of single amino acids under the action of vacuum UV-radiation ($\lambda < 200$ nm) was reported by Simakov *et al.* (1996). Kobayashi *et al.* (1995) showed that some amino acids, such as glycine and alanine, were detectable in hydrolysates when a mixture of simple inorganic compounds (CO, NH₃ and H₂O) was irradiated in a cryostat at 10 K (simulated cometary ices) with high-energy protons. Our experiment indicates that oligopeptides are also produced from mixtures of amino acids irradiated with high-energy charged particles.

In order to simulate the process of chemical evolution that takes place in the interstellar and interplanetary medium, some experimental mixtures have been placed into the space environment onboard the BION-type sputnik. The full range of the solar light spectrum and the primary components of cosmic rays are available in space at high density. In contrast, the flux and energy range of light radiation are limited in laboratory exposure experiments on the ground. UV-light and cosmic rays can work together on organic molecules in space, but it is difficult to apply these two energy sources together in laboratory. The scientific aim of this experiment was to expose simulated organic films to interstellar dust and meteoritic (asteroid) surfaces. To this end, (1) the efficiency of abiotic synthesis of complex organic compounds, such as nucleotides and dipeptides, from nucleosides and simple amino acids deposited on grains was evaluated in a quantitative manner; (2) the role of each energy source in this synthesis was assessed; (3) the role of mineral surface on abiogenic synthesis was evaluated.

All young Solar system objects are subjected to energetic processing by photons and ions. As a result, the chemical and physical properties of the materials composing these objects will change significantly over time. Energetic processing of organic compounds into more complex species can be driven by a significantly enhanced UV-field in star-forming regions, high-energy particle bombardment, and UV-radiation from the T-Tauri phase in stellar birth; at the early stage of evolution and at the present, UV-radiation of different wavelengths, protons of the Solar wind, and flares can drive this process. The surviving remnants of the population of planetesimals which filled the inner early Solar system during the late stages of collapsing solar nebula had a tremendous total surface, and the reactions of complex organic compounds could have taken place on the solid surface of those bodies. It is therefore important to test experimentally how far the process of chemical evolution could have taken place on the surface of space bodies under the action of energy sources available during that period and how it could take place at the present time.

Meteorites and other small bodies which orbit the Sun are presently exposed to high-energy particles in quantities large enough to produce a measurable effect of abiogenic synthesis within a few million years. At the present time, the Sun is the largest source of protons which impinge upon meteorites or interplanetary dust grains (Sandstrom, 1965). Protons emanating from the Sun are divided into two principal groups: solar-wind protons, with energies of a few keV and fluxes of roughly 10^{16} particles/cm² per year, and solar-flare protons, with energies of more than 0.5 MeV and average fluxes of 10^{11} particles/cm² per year. The third group of protons is those which have their source within the galaxy but outside the Solar system; these have average energies of about 1 GeV and average fluxes of about 10^8 particles/cm² per year. These particles do not normally enter into chemical reactions themselves, but they can produce at least ten secondary protons which could react chemically. Estimated fluxes of energy for ice processing environments are given in Colangeli *et al.* (2004).

The chemical evolution of the simple molecules would continue on the surface of these bodies under the action of the energy sources available in open space. Simple oligopeptides can be formed on solid material not only by proton radiation as described here but also by vacuum UV-light, heat, and γ -radiation (Simakov *et al.*, 1996). Thus, it can be assumed that the chemical evolution would have taken place during the early stage of the Solar system origin and reached the stage of polymerization before the end of planet accretion. Such complex biomolecules as oligopeptides would have been brought onto the primordial Earth with comets, carbonaceous chondrites, and interplanetary dust particles (Chyba and Sagan, 1992). The next stage of evolution would be the origin of the first protoliving organisms.

Chondritic material would have been a common component of the inner Solar system shortly after its formation, and the biologically useful products of clay mineral-organic matter interactions would have also widespread and delivered to planetary surfaces through the accretion of carbonaceous asteroids. A large amount of meteoritic material has undoubtedly showered the Earth through time. The organic compounds which have been delivered to the primordial Earth would have had a very complex structure and reached the second stage of chemical evolution-polymerization.

Meteorites, being remnants of asteroids, may have imported prebiotic elements to the early Earth which, when mixed with liquid water, would have enabled the synthesis of all molecules thought to be necessary for the origin of life.

2. Experiments

In our experiments the solid mixtures of biologically significant compounds (nucleosides and amino acids) were exposed to either vacuum UV-photons or ionizing radiation (Kuzicheva *et al.*, 1996; Kuzicheva and Simakov, 1999; Simakov *et al.*, 2002). Both irradiation and photolysis may destroy molecules as well as allow the synthesis of new and more complex ones. Two types of reactions were investigated here: (1) the abiogenic synthesis of nucleotides from mixtures of nucleoside + inorganic phosphate; (2) the

abiogenic synthesis of dipeptides from mixtures of simple amino acids. The reaction mixture in the form of a solid film contains (1) nucleoside and dihydrogen phosphate; (2) two different amino acids. Seven different nucleosides (thymidine, cytidine, uracil, adenosine or deoxyadenosine, guanosine or deoxyguanosine) and four mixtures of aromatic (tyrosine or tryptophan) and aliphatic (glycine or alanine) amino acids were investigated. Mixtures were irradiated as solid films with different sources of energy: (1) VUV-light of 145 nm; (2) high-energy protons (2–6 MeV); (3) the action of all spectra of the open space energy sources during the entire time of flight (327 h; an outstanding container was installed on the surface of biosputnik).

The thin solid films, which simulated the surface of such solar system bodies as comets, carbonaceous chondrites, and interplanetary dust particles, were irradiated with high-energy protons, which are the predominant components in cosmic ray, in order to verify the possibility of forming complex amino acids together with the formation oligopeptides.

2.1 Abiogenic synthesis of nucleotides

Nucleosides, nucleotides, phosphate, and methanol were used as received from commercial available sources. All compounds were of the highest purity commercially available. The investigated compounds were irradiated as solid thin films prepared by air drying an aqueous solution (300 mL) of an equimolar mixture of adenosine with inorganic phosphate (NaH_2PO_4). The area of the film was $\sim 1 \text{ cm}^2$. The films contained 1.3 mM nucleoside and 1.3 mM NaH_2PO_4 . The H_2PO_4^- ion was chosen as a source of phosphate based on the results of Kuzicheva *et al.* (1993), which showed that the ability to phosphorylate decreases in the order $\text{H}_2\text{PO}_4^- \gg \text{HPO}_4^{2-} \gg \text{PO}_4^{3-}$ but that the process takes place in all cases. When the effect of a substrate was being studied, an aqueous solution of the reagents was added to 3 mg of mineral component and the suspension was dried as above. The following minerals were used as a substrate: kaolinite ($\text{Al}_2(\text{Si}_2)\text{O}_5(\text{OH})_4$), montmorillonite ($\text{M}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_4)\text{O}_{10}(\text{OH})_2 \times n\text{H}_2\text{O}$), and ash from the Tyatya volcano. Homoionic Na^+ montmorillonite was prepared by titration (Banin *et al.*, 1985). The exchange capacity (CEC) of the cations Na^+ -montmorillonite used in this study was 92 meq/100 g clay.

2.2 Abiogenic synthesis of dipeptides

The investigated mixtures of amino acids were irradiated as solid thin films, which were prepared by air drying an aliquot of aqueous or acetic solution of single amino acids, dipeptides or a mixture of different amino acids on a specially cut microscopic cover-glass (area $\sim 1 \text{ cm}^2$) and set in a sample holder for irradiation. Such amino acids as glycine, alanine, tyrosine and tryptophan and dipeptides as glycyl-glycine (Gly-Gly), tyrosyl-glycine (Tyr-Gly), glycyl-tyrosine (Gly-Tyr), tyrosyl-tyrosine (Tyr-Tyr), tryptophyl-tryptophan (Trp-Trp), glycyl-tryptophan (Gly-Trp), tryptophyl-glycine (Trp-Gly), alanyl-tryptophan (Ala-Trp), tryptophyl-alanine (Trp-Ala) and alanyl-alanine (Ala-Ala) were investigated.

2.3 Irradiation

A lamp with a barrier discharge in Kr (145 nm), a MgF_2 window, and a radiation power of 10 mW was used as

a source of VUV radiation. The quantum efficiency was about 10^{15} quanta/ cm^2 per second. The irradiation time was 1–9 h. The total doses, the incident energy per area, and the absorbed doses were virtually the same— $1.5\text{--}14 \times 10^7 \text{ J/m}^2$.

A low-pressure mercury lamp LB-30 (254 nm) with a radiation capacity of 6 mW/cm^2 or 8×10^{14} quanta/ cm^2 per second being absorbed by the sample and measured by a radiometer (UVX Digital Radiometer, USA) was used as a source of UV-radiation.

The films were irradiated with protons from a cyclotron U-120 of the Institute of Physics, St. Petersburg University. The beam of protons, with an initial energy of 6.75 MeV, was directed into a dispersion chamber with diameter about 1 m and then dissipated on a gold target with a thickness of 11.2 mg/cm^2 . The irradiating samples were arranged in dissipated beam of protons under angle 6° . The energy of the protons acting on the reaction mixture was 6.6 MeV. In order to avoid a heat influence on the sample, the maximal flow did not exceed 3×10^7 protons/ cm^2 per second. Beam intensities were monitored with a semiconductor detector which has a small diaphragm. The doses were $2 \times 10^9\text{--}5 \times 10^{11}$ protons/ cm^2 .

2.4 Space experiments

The system is an outstanding container (OC), which is a large pan with a deployable lid fixed to the exterior of a Russian BION satellite. Closed and sealed during launch and reentry operations, the system is opened upon command during the Earth orbit. Before flight and after integration of the experiments, the system was flushed with nitrogen in order to protect the samples from oxygen and humidity. The spacecraft was launched on December 24, 1996 and landed back on Earth on January 07. The duration of the flight was 13.5 days with a lid-opening time of 10 days. The orbit was not synchronous; it had a 225 km perigee altitude and a 401 km apogee altitude. The spacecraft eccentricity was 0.01239 and its inclination was 62.8° . The lid-bearing experiments were not thermally controlled during the flight. The temperature in the cavities oscillated between -31°C and $+26^\circ\text{C}$. The lid was programmed to close automatically at temperatures below -35°C . The UV flux was measured with a 260–400 nm spectral response UV-sensor (G36 14, Hamamatsu). After landing, vacuum was maintained in BIOPAN until the instrument was vented with nitrogen. The samples were recovered 4 days after landing. During pre- and post flight operations, the experiments were protected against light and humidity.

The reaction mixture in the form of a solid film contained 1.3 mM of nucleoside and 1.3 mM of NaH_2PO_4 . Four different mixture samples, consisting of equimolar quantities of nucleoside (thymidine, cytidine, adenosine, or deoxyadenosine) and inorganic phosphate, were investigated. Mixtures were prepared by air drying of aqueous solutions on a piece of glass. The area of the film was $\sim 1 \text{ cm}^2$. The glasses were installed on the surface of sputnik in OC, on Plate #3. Seven samples of each mixture investigated were exposed to the action of all spectra of the open space energy sources during the entire flight. One control sample of the each mixture was placed inside and sheltered from temperature variations, high-energy charged particles, and UV- and ionizing-radiation.

3. Analysis

3.1 Nucleotides

Following the irradiation of the solid films, the resulting products were dissolved in water and analyzed on a Varian-5000 high performance liquid chromatograph (HPLC). The sample volume was 10 mL. A reverse phase column (MZ-RP 18; 4×250 mm; particle size 10 mm) was used, and a buffer solution of 0.05 M KH_2PO_4 containing 5% of methanol was employed as the mobile phase. The elution rate was 1 mL/min, and the pressure in the column was approximately 160 atm. This method shows a good separation of different nucleotides. The products were identified by co-injection with authentic samples, and yields are expressed as a mole % relative to reactants.

3.2 Dipeptides

Following irradiation, the resulting products were dissolved in water and analyzed with Varian-5000 HPLC. A reverse phase column (MZ-RP 18; 4×250 mm; 10 mm) was used, and a 40% solution of methanol in 0.005 M ammonium acetate was employed. The elution rate was 1 ml/min, the pressure in the column was approximately 160 atm, and the chromatographic sample volume was 10 mL. For each run a solution of known concentration was used for calibration. Product yields were measured from elution profiles monitored at 275 nm.

4. Results and Discussion

4.1 Polymerization of amino acids

The reactions of the amino acids in solid films was the primary objective of this investigation—primarily, the abiogenic synthesis of dipeptides from mixtures of simple amino acids. Four mixtures of aromatic (tyrosine or tryptophan) and aliphatic (glycine or alanine) amino acids were investigated. These mixtures were prepared by air drying aqueous solutions and irradiating these with different sources of energy: (1) VUV-light of 145 nm; (2) UV-light of 254 nm; (3) high energy protons (2–6 MeV).

Films containing a mixture of amino acids have been shown to yield various oligopeptides after being exposed to VUV-radiation and protons (Simakov *et al.*, 1996, 1997a). Such dipeptides as Trp-Trp, Trp-Gly, Gly-Trp, Ala-Trp, Trp-Ala, Tyr-Tyr, Tyr-Gly, and Gly-Tyr were detected as products of irradiation with summary yields of ~2% in the case of VUV-irradiation (Table 1) and ~2.5% for proton irradiation (Table 2).

When thin solid films of single amino acids—tyrosine or tryptophan—were irradiated with protons, dipeptides, such as tryptophyl-tryptophan and tyrosil-tyrosine, were found. The yields of dipeptides were 2.43% for Trp-Trp and 2.38% for Tyr-Tyr under a maximal dose of irradiation (5×10^{11} protons/cm²). In the case of a mixture consisting of aromatic and aliphatic amino acids (tyrosine + glycine), the yields of synthetic reactions did not essential differ from those for single amino acid. Dipeptides Gly-Tyr and Tyr-Gly were formed with the equal probability, together with Tyr-Tyr and, possibly, Gly-Gly. This last dipeptide was not found with the method of analysis used in the present investigation. The control experiments without irradiation did not yield any trace of oligopeptides.

These values suggest that dipeptide formation does not

Table 1. The abiogenic synthesis of dipeptides under action of VUV-radiation (dose 3×10^6 J/m²).

Irradiated mixture	Products	Yields (%)
Gly + Trp	Gly-Trp	0.39
	Trp-Gly	0.37
	Trp-Trp	0.48
Gly + Tyr	Gly-Tyr	0.36
	Tyr-Gly	0.37
	Tyr-Tyr	0.52
Ala + Trp	Ala-Trp	0.45
	Trp-Ala	0.45
	Trp-Trp	0.51
Trp	Trp-Trp	1.87
Tyr	Tyr-Tyr	1.92

Table 2. The abiogenic synthesis of dipeptides under action of protons (6.6 MeV).

Irradiated mixture	Products	Yield (%) at doses protons/cm ²		
		2×10^9	8×10^9	500×10^9
Trp	Trp-Trp	0.47	0.98	2.43
Tyr	Tyr-Tyr	0.54	1.08	2.38
Trp + Gly	Gly-Trp	0.09	0.31	0.71
	Tyr-Gly	0.10	0.31	0.67
	Tyr-Tyr	0.16	0.33	0.62

depend on the type of side chain residue. The super-excited state that is produced during the interaction of high-energy particles with amino acids may play a major role in these processes. Free radicals are formed due to the collision of protons with molecules, and these free radicals could react with each other.

The initial amino acids are able to undergo processes of destruction as well as the process of abiogenic synthesis of oligopeptides. Of the amino acids tested, glycine is the most resistant to decomposition by UV-photons. The rate of decomposition for aromatic amino acids (tyrosine, tryptophan and phenylalanine) is significantly accelerated under these conditions, mostly due to the strong UV-absorption of the aromatic group (Orzechowska *et al.*, 2007).

Polymerization is an essential step in prebiological evolution, and the results reported here show that this process probably could take place even at an early stage of the Solar system formation, before planet accretion, on the surface of small bodies.

4.2 Synthesis of nucleotides

VUV-irradiation of the mixture of nucleoside and inorganic phosphate resulted in the production of the natural monophosphates of the corresponding nucleosides. The main products were nucleoside-5'-monophosphates (5'NMP) and some small amount of by-products (2'- and 3'-monophosphates, 2'3'- and 3'5'-cyclomonophosphates) (Table 3). The yields of products were small, within a few percentages; however, the effectiveness of the abiogenic synthesis with VUV irradiation was higher than that with UV-radiation ($\lambda = 254$ nm) and heat. When the investigated films were irradiated with protons, the full mixture of nucleotides was also found (Table 4). The maximal summary yield was 9.43%. The main product was 5'AMP under the

Table 3. The abiogenic synthesis of nucleotides under action of VUV-radiation (dose: 3×10^6 J/m²).

Nucleoside	Nucleotide's yield (%)					Sum
	5'	2'	3'	2'3'c	3'5'c	
Ado	0.36	0.21	0.20	0.20	traces	0.97
Guo	0.30	0.21	0.22	0.27	0.05	1.05
dAdo	0.13	—	0.15	—	0.02	0.30
dGuo	0.23	—	0.13	—	traces	0.36
Urd	2.80	1.21	1.07	2.13	0.56	7.77
Cyt	3.75	1.32	1.67	2.46	0.86	9.46
dThd	2.59	—	2.00	—	0.84	5.43

Ado, adenosine; Guo, guanosine; dAdo, deoxyadenosine; dGuo, deoxyguanosine; Urd, uridine; Cyt, cytidine; dThy, deoxythymidine.

Table 4. The abiogenic synthesis of nucleotides under space conditions.

Nucleoside	Nucleotide yields (%)					Sum
	5'	2'	3'	2'3'c	3'5'c	
Ado	3.28	0.82	0.71	1.12	0.01	5.94
dAdo	1.87	—	0.48	—	traces	2.35
Cyt	2.68	0.61	0.55	0.94	traces	4.78
dThd	1.70	—	0.36	—	traces	2.06

driving action of VUV.

The dominant formation of 5'-adenosinemonophosphate (5'-AMP) indicates that the hydroxyl group in the 5'-position of the carbohydrate residue is most reactive under these conditions. A similar regularity was also observed under the integral influence of extraterrestrial energy sources on dry films of nucleoside and inorganic phosphate.

The solid films made of mixtures of different nucleosides and inorganic phosphate were exposed to space conditions during the space flight experiment onboard the BION-11 satellite. The abiogenic synthesis of the full set of the natural nucleotides was observed, with yields of up to 6%.

After returning back to Earth the experimental films were dissolved in water and analyzed by HPLC. The abiogenic synthesis of nucleotides was observed. Such nucleotides as 5'-, 3'-, and 2'-monophosphates of adenosine, deoxyadenosine, cytidine, and thymidine were detected together with cyclomonophosphates of these nucleosides.

In the case of purines and pyrimidines, the main products of the reactions were 5'-monophosphates of the corresponding nucleosides. The preference to 5'-monophosphate formation is indicative of the more advantageous spatial position of the 5'-hydroxyl group in the carbohydrate residue in comparison with the 2'- and 3'-hydroxyl groups. The summary nucleotides yields were: for adenosine, 5.8%; for cytidine, 4.7%; for deoxyadenosine, 2.3%; for thymidine, 2.0%. The yield of products was calculated in relation to the initial amount of nucleoside.

The yield of phosphorylated nucleoside is dependent on the kind of sugar moiety. Compounds which have ribose in its structure form 5'-nucleotides twofold more frequently than those with deoxyribose. For example, the yield of 5'AMP was 3.23%, while for that 5'dAMP was 1.87%. This result is related to the higher reaction capability of the ribose in the ribonucleosides. Purine nucleosides react slightly more easily than the pyrimidine ones. Thus, the

yield of 3'AMP was 0.71% while that of 3'CMP was 0.55%. In general, however, it can be concluded that the formation of nucleotides in the space environment does not depend significantly on the nature of the nucleic acid base.

The 2', 3'-cyclomonophosphates were formed on the solid films under open space energy sources as well (if it was possible based on the structure of nucleosides). It is interesting to note that the yield of 2', 3'-cyclomonophosphates is more than those of 2'- and 3'-monophosphates. There have been previous reports of an interaction between all three nucleotides under VUV-radiation (Kuzicheva *et al.*, 1996; Simakov *et al.*, 1997b) and γ -radiation (Kuzicheva *et al.*, 1993). This possibility can be extended to the open space condition as well.

It is possible that the temperature variations (which were about 130°C) on the satellite surface during its rotation also contribute noticeably to abiogenic synthesis. Despite the fact that UV-radiation is the most abundant energy source in space, the heat used in the ground experiments (Kuzicheva *et al.*, 1992), is the most soft and plausible factor for the abiogenic synthesis of biochemical compounds. The radiation level was as much as 6 Gy (600 rad) per day and up to 80 Gy (8000 rad) per 15-day mission (depending on solar activity), and solar electromagnetic radiation was on the order of 40 solar constant hours per mission. The total dose of solar light (including UV) radiation during the space mission was 1.83 (10^9 J/m² at a UV-photon flow of 1.03×10^{21} photons/cm²).

Both the destruction of the initial compounds as well as the synthesis of products were observed. The ribose residue was more resistant to the action of destructive influences than the deoxyribose residue. This was observed for both the purine as well as the pyrimidine nucleotides. This is confirmed by earlier received data for adenosine and deoxyadenosine (Kuzicheva *et al.*, 1996). On the other hand, the double ring of purine nucleotides is more stable than the pyrimidine ring. During the flight time, 66% of the cytidine was destroyed, which is the maximal value of decomposition of all nucleosides. Adenosine was the most stable nucleotide in the open space environment, with 54% of the initial nucleoside surviving the flight time. Reactions involving the decomposition of the heterocyclic rings, cleavage of the N-glycoside bond, and destruction of the sugar moiety were observed in the investigated mixtures. About 20% of each nucleoside was decomposed with a cleavage of the glycoside bond and the elimination of a free nucleic acid base. In such reactions, VUV-radiation at wavelengths below 200 nm has the greatest effect (Kuzicheva *et al.*, 1996). UV-light at wavelengths of about 254 nm could be observed to be a factor in the destruction of the heterocyclic rings. Broad spectrum UV-light from the Sun is the principal source of energy for the destruction of organic molecules. In the ground experiments, quanta yields of nucleosides as a result of photochemical destruction have been found. For cytidine, these are 4×10^{-3} for VUV-radiation and 4×10^{-5} for UV (254 nm)-radiation.

The 5'-nucleotides are the dominant products of the nucleoside reaction with inorganic phosphate with all sources of energy, both in the lab (Simakov *et al.*, 2002) and in flight (Kuzicheva and Simakov, 1999). In addition to nucleotide

formation, the destruction of the initial adenosine, such as depurination (base release) and decomposition of the base moiety, also may take place.

The results of our laboratory experiments and experiments in open space show that many kinds of energy were effective in the chemical evolution on the surface of asteroids. Hydrated minerals are found within a chondrite matrix of meteorites together with significant amounts of organic matter. Clays are likely to have formed when water was presented on the parent meteoritic bodies. In order to verify the existence of a relationship between the abiogenic synthesis of nucleotides and the inorganic components of the meteorites, possible abiogenic reactions in the presence of different clay minerals (montmorillonite, kaolinite) and the basaltic sample (Tjatja's volcanic ash) were investigated in the presence of open space energy sources for modeling of different exobiological environments on the surface of small space bodies (Simakov and Kuzicheva, 2005). Clay minerals may have concentrated organic compounds, thereby also promoting polymerization reactions. An adsorption/binding of nucleic acid components by clay crystals could change the electron distribution and/or the conformation of the molecules.

The irradiation of dry adenosine and inorganic phosphate films with VUV in the presence of mineral substrates (kaolinite, montmorillonite, volcanic ash) produced 5'-, 2'-, and 3'-adenosine phosphates along with cyclic products, such as 2', 3'- and 3', 5'-cycloadenosinemonophosphates. Under the maximal used irradiation dose (4×10^5 J/m²), the total yields of nucleotides were 5.96%, 5.55%, and 3.88% in the presence of montmorillonite, Tjatja's ash, and kaolinite, respectively. In the absence of the mineral substrate, the yield was 2.12%. The results clearly demonstrate that, depending on the mineral substrate used, increases in the yield of nucleotides can vary by 1.8–2.8 times. Kaolinite and montmorillonite are clay minerals, whereas the Tjatja's ash is compositionally very similar to terrestrial and extraterrestrial basalts (e.g. Martian soil).

The whole spectrum of natural nucleotides is present in the reaction products. The maximal yield of the main product, 5'AMP, was 3.48% after irradiation in the presence of montmorillonite. The yield increased with increasing irradiation dose in the presence or absence of the mineral substrate. The second major reaction product was 2', 3'-cycloadenosinemonophosphate (2', 3'cAMP). The maximal yields were 0.33% without the mineral substrate and 0.89% with montmorillonite; i.e., the mineral component increases the nucleotide yield as in the case of 5'AMP synthesis. It is interesting to note the yield of 2', 3'cAMP is greater than those of the 2'- and 3'-monophosphates, respectively.

The yields from nucleoside decay are 11% (Tjatja), 13% (kaolinite), 15% (without the mineral), and 18% (montmorillonite). Here we can see a shielding effect of the volcanic ash and catalytic effect of the montmorillonite. The clay facilitates the destruction of the initial adenosine.

In the case of using the mineral substrate, a maximal influence on the reaction yield is typical of the montmorillonite. This clay gave the highest yields, both in terms of nucleotide formation and adenosine destruction. The mineral is composed of units made up of two silica tetra-

hedral sheets and an alumina octahedral sheet. There are isomorphous substitutions in both tetrahedral and octahedral sheets, which result in charge deficiency. This charge deficiency is counterbalanced by the metal ions, called interlayer cations or exchangeable metal ions, held between the layers. In contemporary clays these are mainly Na⁺ and Ca²⁺. The hydration or dissolving of these metal ions result in the expansion of the layers (increase of the interlayer distance), thereby permitting the entrance of organic molecules into the interlayer. The isomorphous substitutions are much less in kaolinite than in montmorillonite, resulting in fewer numbers of interlayer cations and, therefore, less expansion and a shorter interlayer distance. This structure can adsorb not only inorganic ions, but also organic material. For example, 1 g of this mineral can absorb up to 5×10^{10} mol of adenine (El Amri *et al.*, 2002). It is precisely this property that makes montmorillonite different from kaolinite, another clay mineral used in our experiment. Kaolinite possesses layers consisting of a 1:1 pair of octahedral and tetrahedral sheets. The shorter distance between the layers prevents any accumulation of organic molecules into the kaolinite. Consequently, nucleoside molecules can be adsorbed only by its surface. The specific surface area of both clays is also different: montmorillonite has 78 m²/g and kaolinite, 8 m²/g. The higher catalytic activity of montmorillonite, relative to kaolinite, has also been established by several other researchers studying the synthesis of abiogenic BSCs such as amino acids (Yushkin, 1999). Ash from the Tjatja volcano represents an erupted silicate product with an extremely porous texture and various oxides of different elements. The abiogenic synthesis of many organic compounds occurs precisely at the surface of ash particles in the ash-gas volcanic channels (Markhinin, 1980; Basiuk and Navarro-Gonzalez, 1996). On the other hand, this material could serve as an analogue of Martian soil, and ash from Hawaiian volcanoes is often used for such purpose (ten Kate *et al.*, 2006).

When adenosine associates with the mineral substrate, its behavior depends on the properties of this material. Ash particles are almost nontransparent to VUV-radiation, whereas clay minerals are sufficiently permeable to VUV radiation (Boillot *et al.*, 2002). The influence of mineral substrates on the abiogenic synthesis may depend on the following mechanisms: (1) the protective function of the mineral, which prevents the decay of both the initial components and newly formed reaction products; the screening effect of clays has been studied earlier (Bonner *et al.*, 1984), and it has been found that the clays provided a significant protection against photolysis; (2) catalytic properties of the mineral in heterogeneous photochemical phosphorylation reactions (Otroshchenko *et al.*, 2002); (3) the presence of residual water molecules, which can generate radicals under the influence of VUV radiation, in the interlayer space of clays; (4) the dependence of the reactivity of both adenosine and inorganic phosphate molecules on their absorption by mineral substrates. The results obtained suggest that the action of the VUV-radiation on films of BSCs makes them more complex and produces important natural compounds. One can assume that the abiogenic synthesis of relatively complex compounds can proceed under conditions of open

space. The discovery that meteoritic organic compounds may be trapped and protected within a clay mineral matrix has implications for our understanding of prebiotic molecular evolution in the early Solar system (Pearson *et al.*, 2002). Clay minerals may have concentrated organic compounds, thereby also promoting polymerization reactions. This idea was first proposed by Bernal (1949). Organic molecules can then enter the interlayer region and interact with the negatively charged basal surfaces of montmorillonite. The interaction between the adsorbed molecules and the clay surface may be via simple electrostatic attraction, van der Waals forces, the formation of hydrogen bonding, or a combination of any two or three of the above. Adsorption of the compounds in the interlayer brings the molecules into close proximity of each other. Furthermore, it may orient them into a favorable position, thereby enabling intermolecular interactions. An adsorption/binding of nucleic acids components by clay crystals could change the electron distribution and/or the conformation of the molecules. The remnant water molecules in the clay sheets could also influence the course of the reaction. In addition, an immobilization of phosphate on clay also could play an important role in our reaction (Goldberg and Sposito, 1985). Chondritic material would have been a common component of the inner Solar system shortly after its formation and the biologically useful products of clay mineral-organic matter interactions would have also been widespread and ultimately delivered to planetary surfaces through the accretion of carbonaceous asteroids. The mineral components selected for substrates can serve as a model for the surface of minor bodies in the Solar.

5. Exobiological Implications

The problem of the origins of life is a very intriguing question of contemporary science. Geological data indicate that complex photosynthetic organisms possibly related to cyanobacteria existed 3.5 billion years (Gyr) ago (Schopf, 1993). There is also evidence of biologically mediated carbon isotope fractionation in the 3.85 Gyr old Isua metasediments, which indicate that the photoautotrophy biochemical processes must have existed at that time (Mojzsis *et al.*, 1996).

All Solar system objects, such as planets, satellites, rings, comets, asteroids, meteorites, and interplanetary dust particles (IDPs), are subjected to energetic processing by different kinds of open space energy. The study of the role of charged particles, UV-radiation of different wavelengths, and other energy sources in the abiogenic synthesis of biologically significant compounds (BSCs) is closely related to exobiological investigations in the Earth's orbit related to chemical evolution and the issue of the origin of life on Earth and throughout the Universe.

According to recent views, the majority of biologically significant compounds may have been introduced to the primeval Earth by micrometeorites, meteorites, and comets (Chyba and Sagan, 1992). These cosmic objects contain large quantities of complex organic compounds, including carbohydrates, amino acids, and heterocyclic bases of nucleic acids (Cottin *et al.*, 1999; Cooper *et al.*, 2001; Botta and Bada, 2002). Evidently, the chemical evolu-

tion proceeds under conditions of open space, which serves as a huge chemical reactor. "Simulated space ice conditions" experiments have shown the synthesis of simple BSC in the form of the precursors of amino acids (Bernstein *et al.*, 2002; Munos Caro *et al.*, 2002) and pyrimidine bases (uracil, cytosine and thymine) of the nucleic acids (Kobayashi *et al.*, 2004). The present investigation dealt with the subsequent reaction of the nucleic acid components to nucleotides, which are the main components of RNA and DNA. Abiogenic synthesis of nucleotides has been reported to take place under conditions of space flight (Kuzicheva and Simakov, 1999) in the presence of different types of energy-proton beams (Simakov *et al.*, 2002), VUV- (Kuzicheva *et al.*, 1996; Simakov *et al.*, 1997b), UV- and γ -radiation (Kuzicheva *et al.*, 1993).

In contrast, just before that period the surface of Earth may have been melted by high intensive comet and meteoritic bombardment, and any structures related to life may have been killed off by such catastrophic events (Sleep *et al.*, 1989). Life would therefore arise rapidly on Earth once conditions became clement, and this process could have been very rapid, almost instantaneous on the geological time scale. Only 300 million years (from the end of the late-heavy bombardment, 4–3.8 billion years ago, up to the first well-evolved living organisms at 3.5 billion years ago) appear to be left for terrestrial chemical evolution to lead to primitive, yet fully developed organisms. There is a very short time interval for producing the biochemical compounds in the atmosphere and on the surface of planet, but this type of matter evolution had to occur before the biological one.

It can be suggested that the chemical evolution which had proceeded at the early stages of the Solar system origin would lead to the appearance of very complex organic compounds. The compounds synthesized under these conditions could have survived inside comets and meteorites, the last witnesses of the formation of our Solar system, and have been delivered to early Earth at the stage of the "late heavy bombardment" and later. The comets, carbonaceous chondrites, and other primitive bodies of the Solar system, including interplanetary and interstellar dust particles, are responsible for essentially all carbon compounds and water currently present in our planet. Therefore, these highly complex organic molecules have been proposed as the starting material for early biological activity on Earth and on other planets in the Universe (Oro *et al.*, 1992; Flynn, 1996).

Anders (1989) estimated the flux of intact organic matter reaching the contemporary Earth in IDPs. Our planet is currently accreting $\sim 3.2 \times 10^5$ kg/year of intact organics. An additional source of exogenous organics on early Earth would have been the terrestrial accretion of dust as the Solar system passed through interstellar clouds. Greenberg (2002) that during its first 7×10^8 years, Earth should have passed through approximately four to five such clouds, thereby accreting organic molecules during each approximately 6×10^5 year passage at a rate 10^6 – 10^7 kg/year.

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