

Abiogenic photochemical synthesis on surface of meteorites and other small space bodies

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Abstract

The abiogenic photochemical synthesis of complex biochemical compounds on the surface of small bodies in our Solar system was examined. 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 present on parent meteoritic bodies. In order to verify the existence of a relationship between abiogenic synthesis of nucleotides and inorganic components of the meteorites, we have investigated possible abiogenic reactions associated with different clay (montmorillonite, kaolinite) and a basaltic one (Tyatya's volcanic ash) under action of open space energy sources as a model of different exobiological environments on the surface of small space bodies. The abiogenic synthesis of natural adenine nucleotides from a mixture of adenosine and inorganic phosphate has been observed following irradiation with VUV light in the presence of different mineral samples. The yields of the products (5'AMP, 2'AMP, 3'AMP, 2'3'cAMP and 3'5'cAMP) depended on irradiation time and kinds of minerals used. 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. Clay minerals may also have concentrated organic compounds thereby promoting polymerization reactions. 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 also could influence the course of the reaction. Clay immobilization of phosphate could play an important role in this reaction. Chondritic material could 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 could have also widespread, and delivered to planetary surfaces through the accretion of carbonaceous asteroids.

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1. Introduction

All Solar system objects, such as planets, satellites, rings, comets, asteroids, meteorites, and interplanetary dust particles (IDP) are subjected to energetic processing by different kinds of open space energy. Study of the role of charged particles, ultraviolet radiation of different wavelengths, and other energy sources in the abiogenic

synthesis of biologically significant compounds (BSC) is closely related to the 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 (Botta and Bada,

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2002; Cooper et al., 2001; Cottin et al., 1999). Evidently, the chemical evolution proceeds under conditions of open space, which serves as a huge chemical reactor.

The “simulated space ice conditions” experiments have shown the synthesis of simple BSC in the form of amino acid’s precursors (Bernstein et al., 2002; Munos Caro et al., 2002) and pyrimidine bases (uracil, cytosine and thymine) of the nucleic acids (Kobayashi et al., 2004). Our investigation dealt with further reaction of nucleic acid components to nucleotides – main components of RNA and DNA. We previously reported that abiogenic synthesis of nucleotides takes place as in conditions of space flight (Kuzicheva and Simakov, 1999) under action of different types of energy – protons beam (Simakov et al., 2002), VUV- (Kuzicheva et al., 1996; Simakov et al., 1997), UV- and γ -radiation (Kuzicheva et al., 1993).

The aim of this work is to study the influence of mineral substrates on the reaction of nucleoside phosphorylation by an inorganic phosphate under the action of vacuum ultraviolet (VUV) radiation with wavelengths <200 nm, one of the main energy sources of the Sun. Nucleoside phosphorylation by inorganic phosphate under the influence of various energy sources is very important for understanding the processes of chemical evolution.

2. Experimental

Adenine, adenosine, nucleotides, phosphate and methanol were used as received from commercial available sources. The investigated compounds were irradiated as solid thin films prepared by air drying of aqueous solution (300 μ L) of equimolar mixture of adenosine with inorganic phosphate (NaH_2PO_4). The films contained 1.3 mmol of nucleoside and 1.3 mmol of dihydrogenphosphate. The H_2PO_4^- ion has been chosen as a source of phosphate on the basis of our earlier work (Kuzicheva et al., 1993). We have shown that the ability of phosphorylating is decreasing in row $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-} \gg \text{PO}_4^{3-}$ but the process takes place in all cases. When studying the influence of a substrate an aqueous solution of the reagents was added to 3 mg of mineral component and 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 has been prepared by the titration (Banin et al., 1985). The cation exchange capacity (CEC) of Na^+ -montmorillonite used in this study was 92 meq/100 g clay.

A lamp with a barrier discharge in Kr (145 nm) and a radiation power of 4.25×10^5 J/m² was used as a source of VUV radiation. The quantum efficiency was about 10^{15} quanta/cm² s.

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

3. Results and discussion

Irradiation of dry adenosine and inorganic phosphate films in the presence or absence of mineral substrates (kaolinite, montmorillonite, ash) produced 5'-, 2'-, and 3'-adenosine phosphates along with the cyclic products, such as 2',3'- and 3',5'-cycloadenosinemonophosphates. Under the maximal used irradiation dose (4×10^5 J/m², 9 h), the total yields of nucleotides were 5.96%, 5.55%, and 3.88% in the presence of montmorillonite, Tyatya's ash, and kaolinite, respectively. In the absence of the mineral substrate the yield was 2.12%.

The results given in Table 1 clearly demonstrate that, depending on the mineral substrate used, increase in the yield of nucleotides can vary by from 1.8 to 2.8 times. Kaolinite and montmorillonite are clay minerals, whereas the Tyatya's ash is compositionally very similar to terrestrial and extraterrestrial basalts, e.g., the Martian soil.

The whole spectrum of natural nucleotides is present in the reaction products (Fig. 1). The maximal yield of the main product, 5'-adenosinemonophosphate (5'AMP), was 3.48% after irradiation of the mixture for 9 h in the presence of montmorillonite. The yield increases with increasing irradiation dose in the presence or absence of the mineral substrate. The dependence of the nucleotide yield on the irradiation period in the presence of the Tyatya ash is shown as example in Fig. 2.

The second major reaction product is represented by 2',3'-cycloadenosinemonophosphate (2',3'cAMP). The maximal yields were 0.33% without the mineral sub-

Table 1
Synthesis of adenine nucleotides in the presence of different mineral substrates under VUV irradiation (irradiation dose 4×10^5 J/m²)

Mineral	Yield of adenine nucleotide (%)				
	5'-	2'-	3'-	2'3'-	3'5'-
Control	1.26	0.25	0.22	0.33	0.05
Kaolinite	2.14	0.49	0.51	0.61	0.12
Montmorillonite	3.48	0.49	0.66	0.89	0.24
Tyatya's ash	3.13	0.65	0.62	0.82	0.14

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