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Microwave discharge in the lunar dust simulant with the addition of ammonium carbonate for studying prebiological synthesis

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Using a microwave discharge, plasma-dust clouds were obtained in an environment of gases and vapors that could have been present in the atmosphere of the early Earth. The source of H_2O, NH_3 and CO_2 molecules were decomposition processes under the action of a discharge of ammonium carbonate added to the main material under study — the LMS-1D lunar dust simulant. The discharge emission spectra showed the appearance of molecular bands OH, NH, CN, C_2 in the plasma-dust cloud. By comparing the experimental and calculated contours of the bands corresponding to the electronic-vibrational transitions CN ($B^2\Sigma \rightarrow X^2\Sigma$, $\Delta\nu = 0$), the vibrational ($T_v = 5000\,\mathrm{K}$) and rotational ($T_r = 2500\,\mathrm{K}$) temperatures of CN ($B^2\Sigma$) were found.

Keywords: prebiological synthesis, Earth's early atmosphere, microwave discharge, lunar dust simulant.

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Miller's experiments [1] have initiated a series of attempts to model the processes of prebiological synthesis of simple organic molecules in laboratory conditions. In most studies, the effects of gas discharges on mixtures simulating the early atmosphere of the Earth or the energetic influence on solid targets, which are in contact with the atmosphere and simulate the composition of hypothetical early Earth rocks, comets, and asteroids/meteoroids, are investigated. The impact of laser radiation with a high power density [2–4] or a high-speed mechanical impact [5] on the target simulate the conditions established in meteoroid impacts and are accompanied by the formation of a complex medium: plasma in a vapor-gas cloud containing dust particles and microdroplets of melts. Meteoroid tails and dusty plasma they contain may serve as a system suitable for prebiological synthesis, where dust particles act as crystallization nuclei or catalysts for synthesis reactions.

The aim of the experiments reported below was to recreate a plasma-dust cloud under the conditions of the hypothetical early Earth atmosphere using a microwave discharge in a lunar dust simulant powder. The feasibility of modeling of individual stages of prebiological chemical evolution with a microwave discharge in powder samples under the influence of radiation from a high-power gyrotron [6] is evidenced by the experimentally achieved levels of gas and solid temperature, plasma concentration, and heating rate of the initial substances and the possibility of rapid cooling of synthesized compounds leaving the discharge region (thermal quenching). The breakdown of a powder mixture results in the formation of a plasma-dust cloud consisting of both dust particles and vapors of elements found in the target [7].

In the present study, we examine the effect of microwave gyrotron radiation in the form of a sequence of three 2-ms-long pulses with 8.5-ms-long pauses between (Fig. 1). The radiation power was 400 kW; for a Gaussian beam with a diameter of 6 cm in the region of the irradiated sample, this corresponds to a power density averaged over the beam cross-section of 14 kW/cm^2 and a mean-square electric field strength of 2.3 kV/cm. The LMS-1D (1 g) [8] lunar dust simulant, which is produced from minerals and rocks (pyroxene, glass-containing basalt, anorthosite, olivine, ilmenite), served as an inorganic target. Since certain minerals found in this simulant are typical of meteoric bodies, the use of such a sample at the stage of optimizing the experimental design is justified. Ammonium carbonate $(NH_4)_2CO_3$ (0.2 g) was added to the powder as a source of gases present in the atmosphere of the early Earth. When heated to temperatures above 60°C, it decomposes into CO_2, NH_3, and H_2O. A sealed reactor chamber with the powder inside was filled with argon to a pressure of 1 atm.

Microwave radiation was directed vertically from below onto a powder sample layer positioned horizontally on a quartz substrate in the reactor. To facilitate the breakdown and formation of a plasma-dust cloud, a microwave subthreshold discharge initiator [9,10] in the form of a nickel wire was mounted 7 cm above the sample (Fig. 1). The initiated subthreshold discharge propagated towards the microwave radiation source and reached the powder surface. A discharge developed in the powder sample itself under the influence of plasma (the exact mechanism has not been

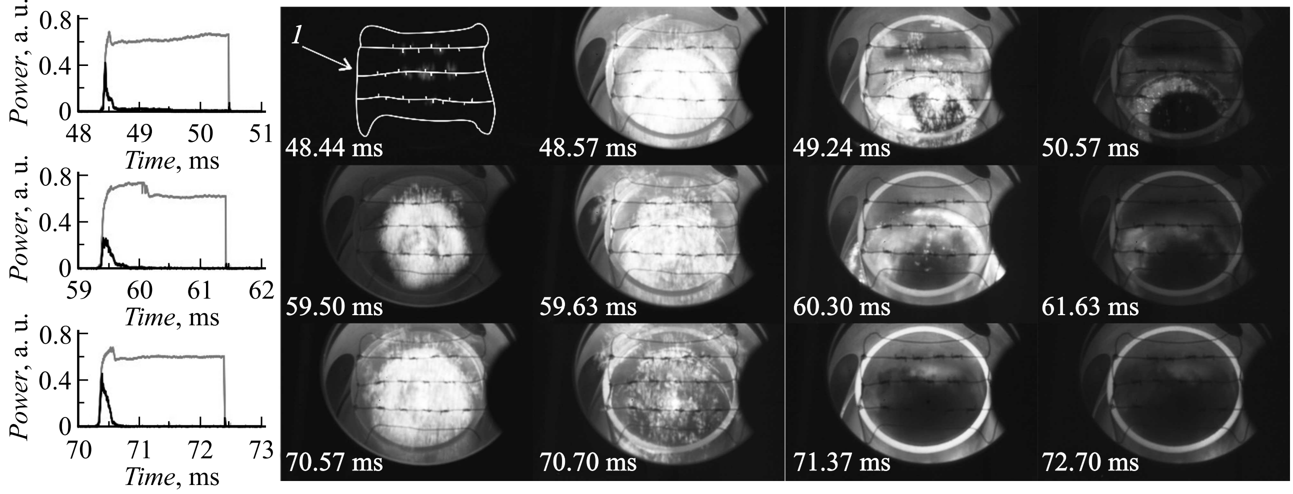

Figure 1. Frames (the exposure time is $130\,\mu$s) illustrating the evolution of a microwave discharge. The top, middle, and bottom rows correspond to the first, second, and third pulses in a sequence. *1* — Outline of the initiator of the microwave subthreshold discharge in the form of a nickel wire. The insets present the temporal variation of gyrotron radiation power (gray curve) and power transmitted through the powder sample and the plasma-dust cloud (black curve).

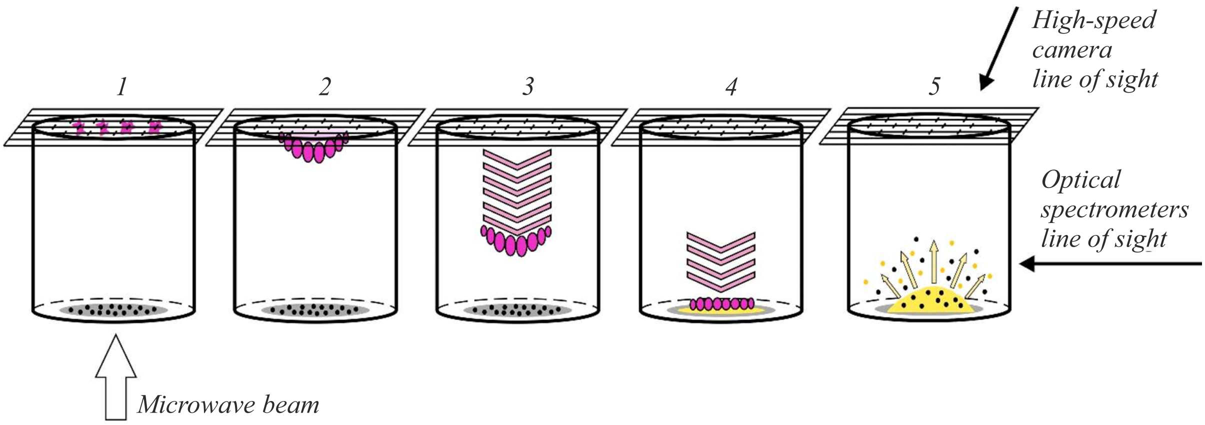

Figure 2. Stages of discharge development in the experiment. *1* — Formation of a self-sustained discharge at the nickel wire initiator, *2* — formation of a subthreshold microwave discharge front near the self-sustained discharge regions, *3* — propagation of the subthreshold discharge downwards to the powder sample, *4* — contact between the subthreshold discharge front and the powder sample and onset of development of a microwave discharge in the sample, and *5* — development of the discharge in the powder sample with the formation of a plasma-dust cloud and dispersion of particles.

established yet; possible factors: heating, UV and visible radiation, charged particle fluxes). This discharge induced an increase in the absorption of microwave energy, evaporation of the sample, dispersion of particles, and formation of a plasma-dust cloud (Fig. 1). A simplified diagram of the successive stages of development of the initiated subthreshold discharge and the microwave discharge in the powder sample is presented in Fig. 2.

The qualitative composition of the gaseous medium was determined from the plasma emission spectra (Fig. 3). The following two spectrometers were used: AvaSpec-ULS4096-CL-2-EVO with channel 2109527U2 operating within the 219–381 nm range with a resolution of ~ 0.1 nm (Fig. 3, *a*) and channel 2109528U2 operating within the 379–521 nm range with a resolution of ~ 0.1 nm (Figs. 3, *b* and *c*) and a single-channel AvaSpec-ULS2048CL-EVO spectrometer operating within the 520–739 nm range with a resolution of ~ 0.25 nm (Fig. 3, *d*). The line of sight of these spectrometers was directed horizontally and passed 2–3 cm above the powder surface. The first gyrotron pulse induced rapid development of the initiated subthreshold discharge and heating of the powder surface, but no discharge was developed in the powder and no significant dispersion of particles or formation of a plasma-dust cloud was observed (see the upper row of frames in Fig. 1). However, the heating level was sufficient to decompose ammonium carbonate. In addition to argon Ar I and hydrogen H_α lines, the

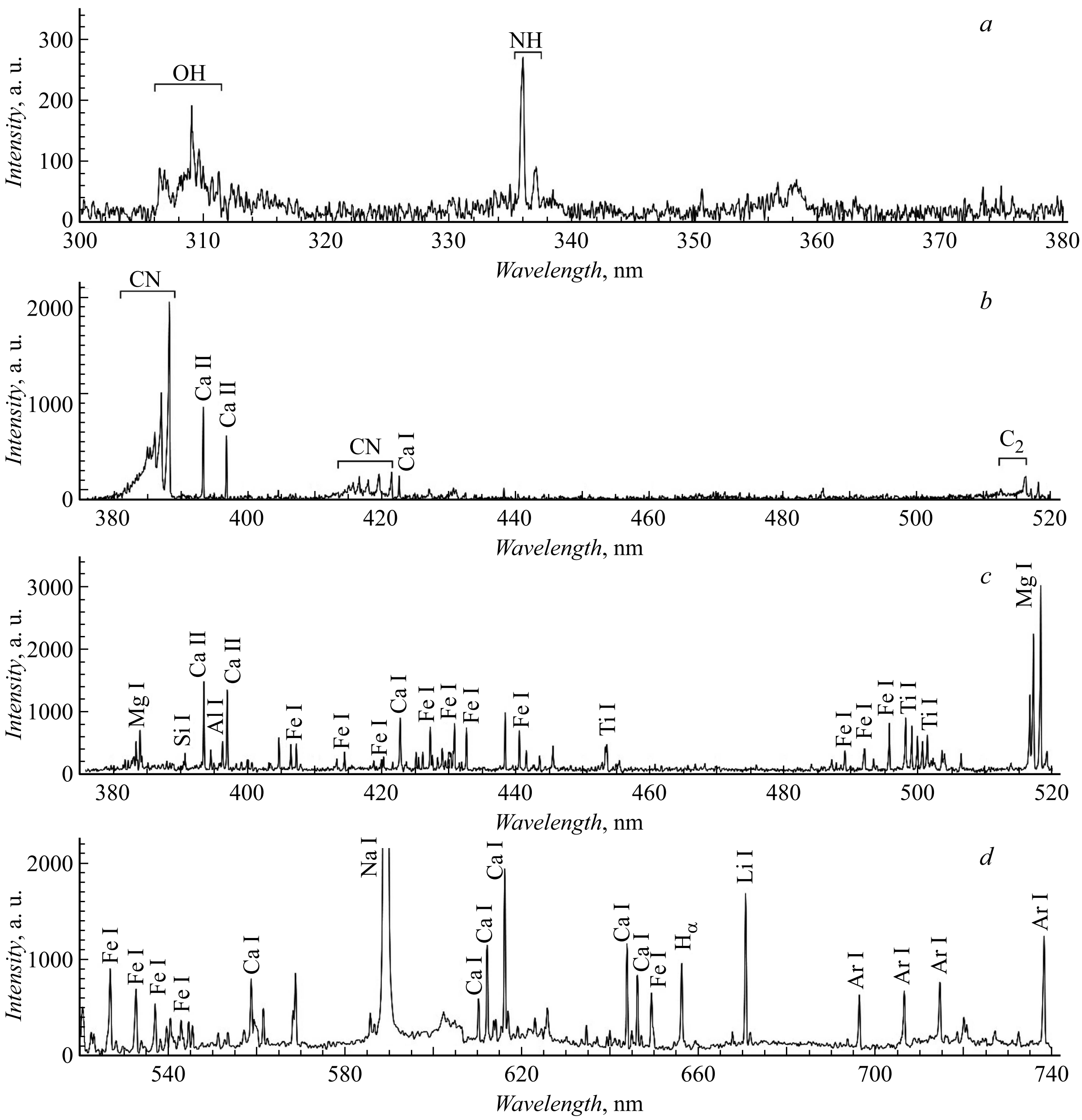

Figure 3. Fragments of discharge emission spectra. *a, b* — First pulse; *c, d* — third pulse.

first-pulse emission spectra contained molecular bands of OH ($A^2\Sigma \to X^2\Pi$, 306.4 nm), NH ($A^3\Pi \to X^3\Sigma$, 336 and 337 nm), CN ($B^2\Sigma \to X^2\Sigma$, 386–388.5 and 415–422 nm), and C_2 ($d^3\Pi \to a^3\Pi$, 516.5 nm) (Figs. 3, *a, b*). With the arrival of subsequent pulses, numerous lines of iron Fe I, magnesium Mg I, titanium Ti I, silicon Si I, and calcium Ca I emerged in the spectra (Figs. 3, *c, d*). Oxides of these elements were present in the sample as petrogenic components. The intensities of OH, NH, CN, and C_2 bands in the second and third pulses were significantly lower.

The H_α line width ($\Delta\lambda = 0.39$ nm) is close to the instrument function of the spectrometer (0.35 nm), which precluded us from determining the plasma density. The broadening of line H_α, which was recorded earlier using an M833 monochromator spectrograph with a higher spectral resolution, revealed that the characteristic values of plasma density for the microwave discharge in powder samples were $n_e = (4–8) \cdot 10^{14}\,\mathrm{cm}^{-3}$. The vibrational ($T_v = 5000$ K) and rotational ($T_r = 2500$ K) CN ($B^2\Sigma$) temperatures were determined by comparing the experimental profiles of bands within the 386–388.5 nm interval corresponding to the electronic-vibrational transitions of CN ($B^2\Sigma \to X^2\Sigma$, $\Delta\nu = 0$) to those calculated in LIFBASE [11].

The addition of nitrogen-containing precursor substances to an evaporated target has already been tried in the study of prebiological synthesis [12]; however, our experiment is the first in which this was coupled with a microwave discharge in powder samples. The produced plasma may serve as a laboratory model of dusty plasma of meteoroid tails passing through the early atmosphere of the Earth. The formation of plasma-dust clouds, the destruction of petrogenic oxides, and the presence of lines and bands of radicals (precursors of organic compounds or products of their decay) in the emission spectra suggest that a microwave discharge may well be used in the proposed experiment for modeling of individual stages of prebiological synthesis of organic compounds.

Conflict of interest

The authors declare that they have no conflict of interest.

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