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Author(s)	Takano, Yoshinori; Marumo, Katsumi; Yabashi, Suguru; Kaneko, Takeo; Kobayashi, Kensei
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Pyrolysis of complex organics following high-energy proton irradiation of a simple inorganic gas mixture

Yoshinori Takano^{a)} and Katsumi Marumo

Institute for Marine Resources and Environment (MRE), National Institute for Advanced Industrial Science and Technology (AIST), AIST Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

Suguru Yabashi, Takeo Kaneko, and Kensei Kobayashi

Department of Chemistry and Biotechnology, Yokohama National University, Hodogaya-ku, Yokohama 240-8501, Japan

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Complex organics formed by 3 MeV proton irradiation of a simple inorganic gas mixture with a composition representative of the primitive earth atmosphere (carbon monoxide, nitrogen, and water) were characterized by application of Curie-point pyrolysis. Pyrolysis products consisted of a wide variety of organic compounds including amide compounds, heterocyclic, and polycyclic aromatic hydrocarbons. The present data showed that primary and primitive organic matter serving as “precursors” to fundamental building blocks associated with life might have been formed in a gaseous mixture of a similar composition to that of the primitive earth atmosphere. Large numbers of endogenous organic compounds and protocatalysis components produced by cosmic rays may have contributed significantly to the early stages of chemical evolution on the primitive earth.

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It has been suggested that the primitive earth atmosphere formed due to the high velocity impact of an exogenous body with the growing planet that resulted in the impact degassing of volatiles and the formation of an impact-induced atmosphere at high temperature.^{1,2} According to these hypotheses, the resulting impact-induced atmosphere contained carbon monoxide or carbon dioxide and dinitrogen as the major carbon and nitrogen sources, respectively.³ Thus, the primitive earth atmosphere may have possessed only a mildly reducing gaseous component.⁴ Organic compounds were necessary as the fundamental building blocks for the emergence of life on earth. The generation of fundamental organic compounds that may have served as the necessary building blocks for the emergence of life on earth was demonstrated in the historic prebiotic synthesis experiment of Miller in 1953.⁵ Miller's work added credence to models concerning “Chemical Evolution” that have generally been accepted.

The energy required to drive the chemical reactions on the early earth may have come from a variety of sources. Cosmic rays are predominantly comprised of high-energy protons, followed by high-energy helium ions and electron-charged particles. In addition to primary cosmic rays, secondary particles, nuclear and electromagnetic cascades generated in the atmosphere, also may have contributed to the abiotic synthesis of amino acid precursors. Kobayashi *et al.*⁶ reported that only amino acid precursors (molecules which provide amino acids following hydrolysis), and not the free amino acids themselves, were generated among the primary products following proton irradiation of a primitive earth atmosphere consisting of carbon monoxide, nitrogen, and water. Additionally, with the development and use of a 1–2 keV x-ray beam generated from a synchrotron, amino acids were synthesized following irradiation of a simulated primitive earth atmosphere.⁷ The primary matrixes of prod-

ucts that resulted from this irradiation are biologically interesting and need to be clarified from the point of view of earth and planetary sciences. Here, we report on the composition of pyrolyzed complex organics generated following irradiation of a simulated primitive earth atmosphere with high-energy protons generated from a Van de Graaff accelerator. The pyrolysis experiment employed revealed the primary composition of endogenous complex organics and the significance of cosmic rays as an energy source.

Experiments employing high-energy proton irradiation simulating the main component of cosmic rays⁸ in the presence of atmospheric conditions resembling those found in the primitive earth were performed at the Tokyo Institute of Technology as shown in Fig. 1. A Pyrex glass tube was filled with inorganic gas components consisting of 350 Torr carbon monoxide (CO) and 350 Torr nitrogen (N₂) over liquid water (H₂O) to provide 20 Torr of water vapor at room temperature in an effort to simulate conditions that may have been present on the primitive earth. The gas mixture was irradiated with 3 MeV protons generated by a Van de Graaff accelerator at the Tokyo Institute of Technology.⁸ The total energy delivered to the gas mixture, as determined by the product of the number of particles delivered and the ionization energy loss of a single particle in the gas mixture, was 4000 J. Irradiation was performed at ambient room tempera-

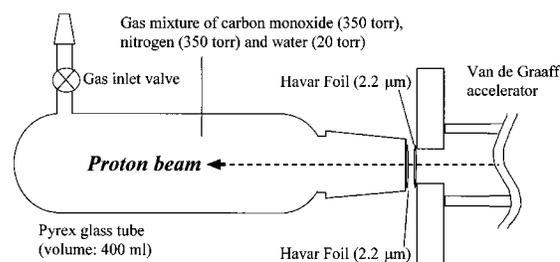


FIG. 1. Schematic view of 3 MeV proton irradiation experiment (Ref. 8) with simple inorganic gas mixtures simulated primitive earth atmosphere.

^{a)}Electronic mail: takano.yoshinori@aist.go.jp

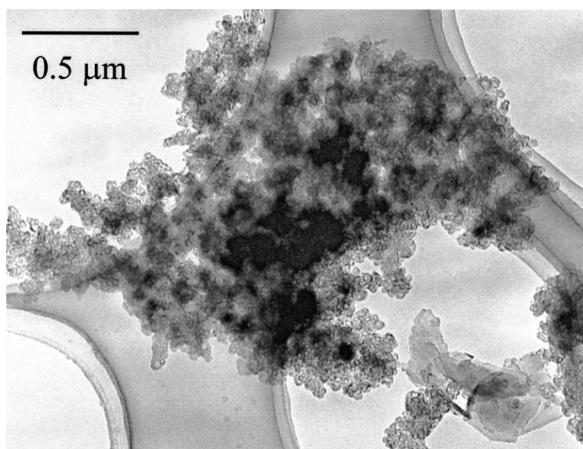


FIG. 2. TEM image of aggregated high-molecular-weight organic matter before pyrolysis experiment. Number of proteinous and nonproteinous amino acids were found after acid hydrolysis, (see Refs. 4, 6, and 13).

ture for 2 h. All glassware was heated in a high-temperature oven (DR-22, Yamato Co. Tokyo, Japan) at 500°C to eliminate any possible contaminants prior to use. Deionized water was further purified with a Millipore Milli-Q LaboSystem™ and a Millipore Simpli Lab-UV (Japan Millipore Ltd., Tokyo, Japan) to remove inorganic ions and organic contaminants.

Following irradiation, products were recovered in 5 ml of pure water and subsequently freeze dried. Approximately 0.3 mg of a yellow-brown residue was wrapped in pyrofoil (Japan Analytical Industry, Tokyo, Japan). Pyrofoil samples were inserted in the furnace of a Curie Point Pyrolyser JHP-5 (Japan Analytical Industry, Tokyo, Japan) and pyrolyzed at the Curie point of 764°C for 10 s. The pyrolyzed compounds were carried with helium (>99.9999%) directly to a connected gas chromatograph (GC) and a mass spectrometer (MS) (Shimadzu GC-MS-QP2010, Shimadzu Co. Kyoto, Japan). GC separation was carried out in a DB-5 capillary column (30 m × 0.25 mm inner diameter, J&W Scientific Co. Tokyo, Japan) using the following oven temperature program: An increase from 30 to 40°C at a rate of 1°C/min, from 40 to 60°C at 2°C/min, from 60 to 100°C at 3°C/min, from 100 to 200°C at 4°C/min, and finally, from 200 to 350°C at 5°C/min.⁹ Mass fragmentograms produced by MS scans every 0.30 s over a m/z of 40–500 with the electron impact mode set at 70 eV were recorded on a computer, and used in searches of the National Institute for Standards and Technology mass spectra library (the National Institute of Standards and Technology, USA, 1998) to identify the organic compounds released by application of the Curie-point pyrolysis system. Aliquots of the irradiated samples were prepared for imaging by transmission electron microscopy [(TEM) Philips CM-12, USA]. The MALDI-time-of-flight-mass spectra of irradiation products showed preliminary evidence of high molecular weight compounds, suggesting the occurrence of abiogenic proton irradiation-induced polymerization.⁸ Continuous small signals up to $m/z=1500$ are indicative of the formation of complex mixtures of high molecular weight compounds.¹⁰

The TEM images of irradiated samples show particulate cottony images of high molecular weight complex organic compounds obtained prior to pyrolysis (Fig. 2). A wide variety of organic compounds—including a number of amide

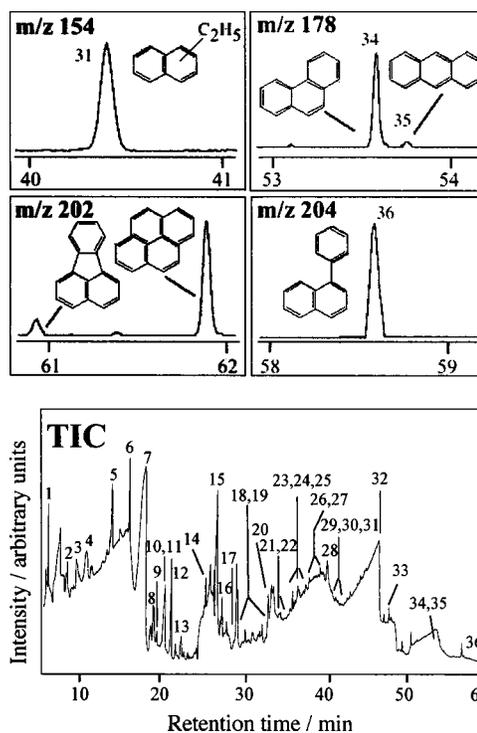


FIG. 3. Total ion chromatogram and SIM chromatograms of 3 MeV proton irradiation products released by Curie-point pyrolysis. The peak numbers are as follows: (1) 2-butanamine; (2) C₆H₇N (aniline ?); (3) methylpyrimidine; (4) styrene; (5) 2-furanone; (6) ethenylpyridine; (7) acetamide; (8) benzotriazole; (9) 1,4-dihydro-3-pyridinecarboxitrile; (10) 2-propenamide; (11) phenol; (12) pyridinecarboxitrile; (13) guanidine; (14) imidazole/pyrazole; (15) dimethylpyrazine; (16) aminopyradine; (17) pyridinamine; (18) methylpyradine; (19) pyrazinecarboxamide; (20) naphthalene; (21) C₆H₇NO (1-methyl-2-pyridinone ?); (22) 3,4-pyridinedicarbonitrile; (23) quinoline; (24) isoquinoline; (25) C₇H₆N₂; (26) 2-methyl naphthalene; (27) 1-methyl naphthalene; (28) 1-pyrrole-3-carboxitrile; (29) and (30) methyl quinoline; (31) ethenyl naphthalene; (32) urea; (33) butylurea; (34) phenanthrene; (35) anthracene; and (36) 1-phenyl naphthalene.

compounds, cyclic and heterocyclic compounds—were detected and identified in the total ion chromatogram of the Curie-point pyrolysis products following GC-MS analysis (Fig. 3, Table I). Identification of the released compounds were performed by selected ion mass chromatograms (SIMs). A relative abundance of released compounds were indicated by the signal intensity of SIM.⁹ Acetamide (CH₃CONH₂; peak 7) and urea [(NH₂)₂CO; peak 25] were the most predominant compounds among the amide analogs. Terasaki *et al.*^{11,12} demonstrated a unique feature of urea as a potential nitrogen source in a highly polar reaction medium as it related to the condensation pathway on the primitive earth.

Imidazole is a component of histidine, and imidazole itself possesses certain catalytic activity in relation to the hydrolysis of esters. It was reported that abiotically synthesized imidazole possessed esterase catalytic activity toward specific ester bonds.¹³ Although peaks corresponding to imidazole (C₃H₄N₂) and pyrazole (C₃H₄N₂) were detected in the pyrolysis reactions, these heterocyclic compounds could not be separated since they have the same molecular formula. However, detection of imidazole in the hydrolysate following proton irradiation of a gas mixture simulating the primitive earth atmosphere has been reported.¹⁴ Imidazole is also an important compound since imidazolides of nucleotides act

TABLE I. Relative abundance of organic compounds released from Curie-point pyrolysis experiment from the gas mixture of carbon monoxide, nitrogen and water.

Compounds	Chemical formula	Relative abundance
Urea	(NH ₂) ₂ CO	++++
Acetamide	CH ₃ CONH ₂	++++
Imidazole and pyrazole	C ₃ H ₄ N ₂	+++
2-Propenamide	CH ₂ =CHCONH ₂	+++
2-Butanamine	C ₂ H ₅ CH(NH ₂)C ₃	+++
2-Furanone	C ₄ H ₄ O ₂	+++
Aminopyrazine	C ₄ H ₅ N ₃	+
Pyrazinecarboxamide	C ₄ H ₃ N ₂ CONH ₂	+
1-Pyrrole-3-carbonitrile	C ₅ H ₄ N ₂	++
Methylpyradine	C ₅ H ₆ N ₂	+
Methylpyrimidine	C ₅ H ₆ N ₂	++
Pyridinediamine	C ₅ H ₇ N ₃	+
Guanidine	(NH ₂) ₂ C=NH	++
Butylurea	C ₅ H ₁₂ N ₂ O	+
Phenol	C ₆ H ₆ O ₆	+
(Aniline ?)	C ₆ H ₇ N	++
(1-Methyl-2-pyridinone ?)	C ₆ H ₇ NO	+
Pyridinecarbonitrile	C ₆ H ₄ N ₂	+++
1,4-dihydro-3-pyridinecarbonitrile	C ₆ H ₆ N ₂	+
Dimethylpyradine	C ₆ H ₈ N ₂	++++
Benzonitrile	C ₇ H ₅ N	++
Ethenylpyridine	C ₇ H ₇ N	+++
3,4-Pyridinedicarbonitrile	C ₇ H ₃ N ₃	+
Styrene	C ₈ H ₈	++
Isoquinoline/quinoline	C ₉ H ₇ N	+
Methylquinolinene	C ₁₀ H ₉ N	+
Naphthalene	C ₁₀ H ₈	+
1-Methyl naphthalene	C ₁₁ H ₁₁	+
2-Methyl naphthalene	C ₁₁ H ₁₁	+
Biphenyl	C ₁₂ H ₁₀	-
Ethyl naphthalene	C ₁₂ H ₁₂	-
Phenanthrene	C ₁₄ H ₁₀	+
Anthracene	C ₁₄ H ₁₀	-
Fluoranthene	C ₁₆ H ₁₀	-
Pyrene	C ₁₆ H ₁₀	+
1-Phenyl naphthalene	C ₁₆ H ₁₂	-

Note: Symbols: +, ++, +, +, + and - indicate very major, major, moderate, minor, and trace amounts of compounds obtained from the residue of 3 MeV proton irradiation.

as useful starting materials in the synthesis of oligonucleotides.¹⁵⁻¹⁷

A number of polycyclic aromatic hydrocarbons (PAHs) including di-, tri-, and tetracyclic compounds were detected in the pyrolysis product as shown in Fig. 3. Among these, naphthalene (C₁₀H₈) and phenanthrene (C₁₄H₁₀) represented the most predominant PAH analogs. Application of SIM showed that the amount of phenanthrene (C₁₄H₁₀) was greater than that of anthracene (C₁₄H₁₀). PAHs represent one of the most abundant forms of carbon in the interstellar medium, and many variations of these molecules have been detected in interplanetary dust particles,¹⁸ comet Halley,¹⁹ in addition to circumstellar graphite grains extracted from primitive meteorites.²⁰ The formation of basic PAHs under conditions simulating primitive earth conditions has been demonstrated in this study. Cyclic compounds may have been converted to biologically interesting amino acid analogs, such as phenylalanine and tyrosine. When subjected to ultraviolet irradiation, PAHs were converted to secondary

biogenic products including alcohols, quinones, and ether analogs.^{21,22}

In summary, the present study suggested that endogenous organic matter is carried in matrices containing a number of organic compounds as endogenous products.²³ Application of Curie-point pyrolysis revealed the primary components possessing biologically important compounds. Hence, high kinetic energy input by cosmic rays contributed to the formation of organic compounds in the atmosphere. Furthermore, the present findings suggested that bio-organic compound, in addition to organic catalysts, could have been abiotically synthesized on the primitive earth under a mildly reducing atmosphere, consisting of a mixture of carbon monoxide, nitrogen, and water, provided that cosmic rays and solar flare particles acted as energy sources for prebiotic synthesis in the early stage of chemical evolution.

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