

ABIOTIC SYNTHESIS OF GUANINE WITH HIGH-TEMPERATURE PLASMA

SHIN MIYAKAWA^{1*}, KEN-ICHI MURASAWA², KENSEI KOBAYASHI² and AKIRA B. SAWAOKA^{1**}

¹ *Department of Chemistry and Biotechnology, Faculty of Engineering, Yokohama National University, Yokohama 240-8501, Japan*

² *Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
(* Author for correspondence, e-mail: SMIYAKAWA@aol.com)

(Received 13 March, 2000; accepted in revised form 22 June, 2000)

Abstract. The origin of guanine has been unknown, though there are some reports concerning its abiotic synthesis. We show here that guanine, as well as uracil and cytosine, are synthesized from a 90%N₂–10%CO–H₂O gas mixture via a complex organic product produced with the high-temperature and rapid quenching technique. This result implies that a large amount of complex organic matter including precursors of bioorganic compounds might have been produced on the primitive earth after cometary impacts.

Keywords: abiotic synthesis, cometary impact, cytosine, guanine, high-temperature plasma, magneto-plasma dynamic arc-jet, origin of life, uracil

1. Introduction

Guanine can be synthesized from the polymerization of concentrated ammonium cyanide solutions. Levy *et al.* (1999) detected yields of 0.0007% of guanine and 0.028% of adenine in a 10 M ammonium cyanide (NH₄CN) solution heated at 80 °C for 24 hr, and yield of 0.0035% of guanine and 0.038% of adenine in a 0.1 M NH₄CN frozen at –20 °C for 25 yr. They suggested that guanine would have been formed in frozen regions of the primitive earth. The NH₄CN polymerization was apparently important in the origin of guanine. However, it is not certain whether NH₄CN polymerization could have selectively occurred on the primitive earth, because there must have been many types of compounds and reaction pathways on the primitive earth. For instance, hydrogen cyanide readily reacts with formaldehyde to form glycolonitrile (Schlesinger and Miller, 1973, 1983b). Then, if the primitive atmosphere were oxidized or weakly reduced, hydrogen cyanide might not have been able to polymerize, because formaldehyde is formed in excess of hydrogen cyanide from a spark discharge in CO₂–N₂–H₂O or CO–N₂–H₂O (Schlesinger and Miller, 1983b).

** Present address: Daido Institute of Technology, Minami, Nagoya 457-8530, Japan.



Origins of Life and Evolution of the Biosphere **30**: 557–566, 2000.
© 2000 Kluwer Academic Publishers. Printed in the Netherlands.

Yuasa *et al.* (1984) reported that guanine and adenine were synthesized from the electrical discharge in NH_3 (200 Torr), CH_4 (150 Torr), C_2H_6 (50 Torr), and water (50 mL) and subsequent acid hydrolysis. These purines were identified by UV spectrometry and paper chromatography. The yields of guanine and adenine were 0.00017 and 0.001%, respectively, based on total carbon input. However, it was not demonstrated conclusively that these compounds were not contaminants in this experiment.

Guanine, adenine, uracil, and thymine are produced in a Fischer-Tropsch synthesis (Hayatsu *et al.*, 1968, 1972). For instance, when an equimolar gas mixture of CO, H_2 and NH_3 is heated at 700 °C for 0.25–0.4 hr, followed by fast cooling and sustained reheating at 200–100 °C for 16–44 hr with an alumina catalyst, guanine and uracil are detectable from the non-volatile fraction after acid hydrolysis. It was shown that these were not contaminants by using CO, D_2 and ND_3 .

However, the prebiotic relevance of these experiments is sometimes questioned, because CH_4 , C_2H_6 , NH_3 , and H_2 may not have been abundant in the primitive atmosphere when life emerged. It is generally believed that the primitive atmosphere was probably dominated by N_2 and CO_2 with traces of CO, H_2 and reduced sulfur gases, though many uncertainties remain (Levine *et al.*, 1982; Canuto *et al.*, 1983; Kasting, 1993).

It is very difficult to synthesize bioorganic compounds from CO_2 – N_2 – H_2O . Schlesinger and Miller (1983a) investigated amino acid yields from the spark discharge in various types of gas mixtures. The amino acid yield from CO_2 – N_2 – H_2O was 0.0006%, which is much lower than the 1% from CH_4 – N_2 – H_2O or 0.05% from CO – N_2 – H_2O . In case of syntheses of nucleic acid bases from CO_2 – N_2 – H_2O , there are no literature reports as far as we know.

The difficulty of bioorganic compound synthesis from CO_2 – N_2 – H_2O may come from the strong triple bonds of $\text{C}\equiv\text{O}$ and $\text{N}\equiv\text{N}$. Moreover, if these bonds are broken, the carbon atoms are more likely to combine with the oxygen atoms to form CO, when the O/C ratio exceeds unity. Then, formation of C–C or C–N bonds, which are important to form bioorganic compounds, may be suppressed (Chameides and Walker, 1981).

Pyrimidine bases can be synthesized if the carbon source is CO instead of CO_2 . Uracil was synthesized from CO – N_2 – H_2O by irradiation of high energy protons (Kabayashi and Tsuji, 1997), together with precursors of a wide variety of amino acids (Kobayashi *et al.*, 1998, 1999). The yield of uracil was 0.0002%, based on initial carbon. Our previous study indicated that uracil and cytosine were synthesized by quenching a CO – N_2 – H_2O high-temperature plasma and subsequent acid hydrolysis (Miyakawa *et al.*, 1999b). The excitation temperature of the high-temperature plasma was estimated to be 10 000 K (Miyakawa *et al.*, 1999c). In this plasma, N, O and H atoms and CN radical were detected as dominant species by optical emission spectroscopy. This plasma is likely to have been quenched by colliding a wall before CO was formed. Then, a complex organic matter containing

precursors of uracil and cytosine was obtained. The yields of uracil and cytosine were 0.08 and 0.01%, respectively, based on carbon in complex organic matter.

High-temperature plasma is defined as a plasma in which the kinetic and excitation temperatures of ions and atoms are very high, similar to the electron temperature. This type of plasma is formed by lightning and meteor impacts. In contrast, low-temperature plasma, in which the electrons are highly superthermal, but ions and atoms remain near room temperature, is formed by corona discharges and electron and proton irradiation (Chyba and Sagan, 1991; Thompson *et al.*, 1991). These plasmas show different characters in organic synthesis. Formaldehyde, for instance, is not generated in lightning bolts (Chameides and Walker, 1981; Stribling and Miller, 1987), but corona discharges (Schlesinger and Miller, 1983b).

There are many reports concerning formation of organic compounds from lightning and meteor impacts. Gilvarry and Hochstim (1963) suggested that meteor impacts on water might have brought about formation of complex organic compounds, which were rained out to the hydrosphere with the cloud made by the impacts. Chyba and Sagan (1992) calculated the energy yields of organic compounds from various sources, suggesting that the heavy bombardment before 3.5 Gyr ago may have produced quantities of organics comparable to those produced by other energy sources such as coronal discharge and ultraviolet light. Oberbeck *et al.* (1988) discussed concentration of organic monomers and formation of oligomers by coalescence of compounds produced by cometary impacts. Small organic molecules seem to have been produced from a high-temperature plasma. Fegley *et al.* (1986) calculated the formation of HCN and H₂CO in shocked air, suggesting that bolide impacts would have caused HCN and H₂CO volume mixing ratios of approximately 10⁻³ to 10⁻⁵ and 10⁻⁷ to 10⁻⁹ in the impact region, respectively. Experimentally, organic compounds, such as HCN and C₂H₂, can be produced from a shock in nitrogen with hydrocarbons (Rao *et al.*, 1967) and from a high-power pulsed laser in CH₄-NH₃ (McKay *et al.*, 1988) and CH₄-N₂-H₂ (Scattergood *et al.*, 1989), simulating lightning and meteor impacts on Titan, and H₂O-CO₂-CH₄-N₂-H₂S (McKay and Borucki, 1997), simulating cometary impacts into earth's atmosphere. Amino acid may have been also produced from lightning and meteor impacts. Bar-Nun *et al.* (1970) demonstrated the shock synthesis of amino acids using a shock tube. From a CH₄-C₂H₆-NH₃-H₂O gas mixture, amino acids, such as glycine and alanine, were effectively synthesized. Volatile molecules released from meteorites during impacts were investigated using real meteorites. Mukhim *et al.* (1989) heated meteorite materials with a laser-pulse to detect organic compounds, such as HCN and CH₃CHO. In real events, the impact of Comet Shoemaker-Levy 9 with Jupiter would have brought about formation of organic matter like the organic residue in the Murchison carbonaceous chondrite, poly-HCN and tholins.

In the present study, synthesis of purine bases, as well as pyrimidine bases, was conducted by quenching a CO-N₂-H₂O high-temperature plasma, which might be seen during cometary impacts.

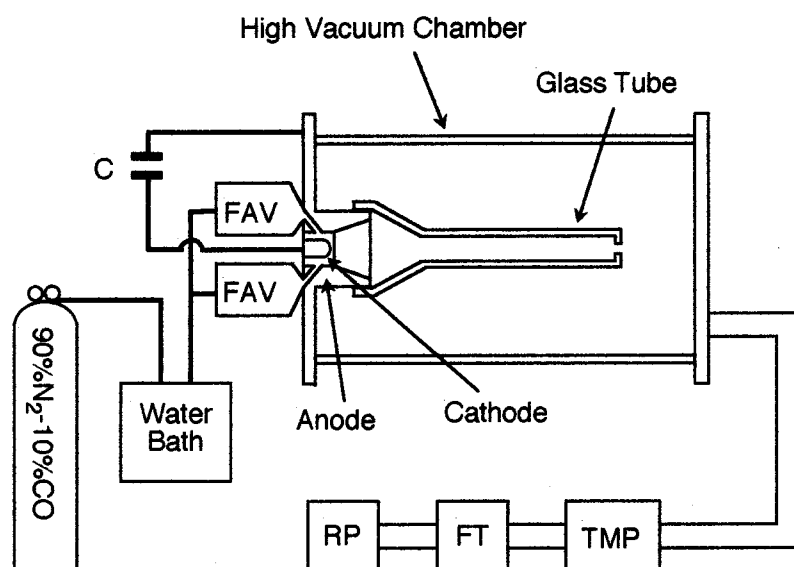


Figure 1. Schematic diagram of the magneto-plasma dynamic arc-jet. C: 9 mF condenser, FAV: fast acting valve, TMP: turbo molecular pump, FT: foreline trap, RP: rotary pump. Iron electrodes were cylindrical.

2. Experimental

High-temperature plasma was produced with a magneto-plasma dynamic arc-jet, as shown in Figure 1 (Miyakawa *et al.*, 1997; Tahara *et al.*, 1987; Kuriki and Ishikawa, 1982). Approximately 1 cm³ of gas mixture at standard state was injected into a vacuum chamber with fast acting valves. While this gas mixture went through a gap between an anode and a cathode, electric energy of about 180 J was instantaneously introduced to form high-temperature plasma. This plasma was accelerated forward and collided against the inner surface of a glass tube to deposit the complex organic matter. After the 5,000 pulsed discharges, the complex organic matter was withdrawn and acid hydrolyzed with 6 M HCl at 110 °C for 24 hr. The hydrolysate was separated and purified by HPLC and subjected to GC/MS after derivatization with bis(trimethylsilyl)acetamide. The N/C atomic ratio in the complex organic matter was determined by elementary analysis.

3. Results and Discussion

In a previous study, cytosine and uracil were synthesized from an equimolar gas mixture of N₂ and CO including water vapor at room temperature (50%N₂-50%CO-H₂O) (Miyakawa *et al.*, 1999b), but no purines were detectable. The possible reason for the absence of purines may be the low N/C atomic ratio in the complex organic matter, which was 0.71. If the N/C ratio were increased, purines might be

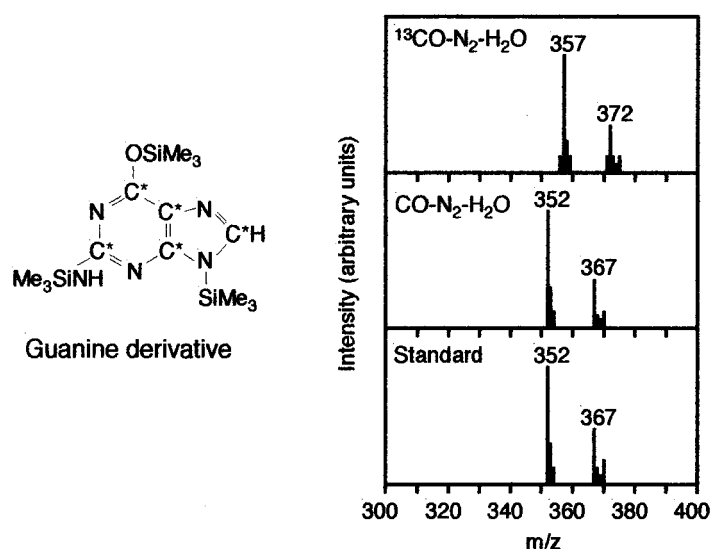


Figure 2. Mass spectra of guanine derivatives. The upper spectrum is from the 10% ^{13}C O–90% N_2 – H_2O gas mixture, the middle is from 10% ^{12}C O–90% N_2 – H_2O , and the lower is from standard guanine. Original carbons of the guanine in its derivative are labeled with asterisks (*). The peaks in 10% ^{13}C O–90% N_2 – H_2O shifted for the number of carbons from the authentic standard. The mass of molecular ion of the guanine derivative is 367. Me is the methyl group ($-\text{CH}_3$).

obtained, because the N/C in guanine ($\text{C}_5\text{N}_5\text{OH}_5$) and adenine ($\text{C}_5\text{N}_5\text{H}_5$) are 1, which is larger than 0.75 for cytosine ($\text{C}_4\text{N}_3\text{OH}_5$) and 0.5 for uracil ($\text{C}_4\text{N}_2\text{O}_2\text{H}_4$). Therefore, we conducted an experiment with a 90% N_2 –10% CO gas mixture including water vapor at room temperature (90% N_2 –10% CO – H_2O), which was expected to raise the N/C ratio in the complex organic matter.

After the discharge experiment, the complex organic matter, in which the N/C ratio was 1.8, was obtained. This N/C ratio is higher than that of 0.71 in 50% N_2 –50% CO – H_2O according to expectation.

Guanine, uracil and cytosine corresponding to 4, 40 and 50 nmol, respectively, were detectable, after the complex organic matter was acid-hydrolyzed. The mass spectra of the guanine obtained are shown in Figure 2. The upper spectrum is from 90% N_2 –10% ^{13}C O– H_2O that has ^{13}C carbon isotope, the middle is from 90% N_2 –10% ^{12}C O– H_2O , and the lower is from standard guanine. The peaks in 90% N_2 –10% ^{13}C O– H_2O shifted for the number of carbons from the authentic standard, indicating that the guanine detected was not from contamination. The cytosine and uracil were also shown to be indigenous by the ^{13}C carbon isotope labeling method. The carbon yields of guanine, uracil and cytosine were 0.001, 0.009 and 0.01%, respectively, where the carbon yield is defined as percentage of carbon in products based on carbon in complex organic matter (Table I). A peak of

TABLE I
Carbon yields^a of nucleic acid bases from various gas mixtures

| Initial gas mixtures | N/C ^b | Ura Cyt Gua Ade | | | |
|---|------------------|-----------------|------|-----------------|---------|
| | | (nmol) | | | |
| 90%N ₂ -10%CO-H ₂ O ^c | 1.80 | 0.009 | 0.01 | 0.001 | <0.0001 |
| 50%N ₂ -50%CO-H ₂ O | 0.71 | 0.08 | 0.01 | ND ^d | ND |
| 33%N ₂ -33%CO-33%H ₂ | 0.71 | ND | ND | ND | ND |
| 50%N ₂ -50%CO ₂ -H ₂ O | - | ND | ND | ND | ND |

^a The carbon yields are based on carbon in complex organic matter.

^b N/C atomic ratio in complex organic matter.

^c H₂O is water vapor at room temperature.

^d Not detected.

0.0001% corresponding to adenine was present in the HPLC chromatogram but its identification was tentative.

Guanine is generally believed to have been formed by HCN polymerization. Following this scenario, favorable conditions for HCN formation are required for guanine formation. Therefore, we demonstrated the same experiment as described above with an equimolar gas mixture of N₂, CO and H₂. This gas mixture should give a more favorable condition for HCN formation than N₂-CO-H₂O (Miyakawa *et al.*, 1999a). However, no nucleobases were detected from N₂-CO-H₂ (Table I). This suggests that the mechanism of the guanine formation by quenching the high-temperature plasma is different from the HCN polymerization.

Comparison of the yields from 90%N₂-10%CO-H₂O and 50%N₂-50%CO-H₂O gives some information about the mechanism of guanine formation. Guanine came to be synthesized by increasing the partial pressure of nitrogen in the initial gas mixture, which caused increase of the ratio of nitrogen atoms to carbon atoms in the complex organic matter. In contrast, the yield of uracil decreased with an excess of the N/C ratio in the complex organic matter over that in authentic uracil. From these facts, formation of nucleic acid bases apparently relates with the N/C ratio in the complex organic matter, which is controlled by the partial pressure of nitrogen in the initial gas mixture. Precursors of nucleic acid bases might have been directly synthesized from atoms and radicals by quenching them without involving intermediates such as HCN (Miyakawa *et al.*, 1998).

The dominant components of the primitive atmosphere are believed to have been CO₂, N₂ and H₂O when life emerged. Therefore, we investigated the formation of nucleic acid bases from an equimolar gas mixture of CO₂ and N₂ including water vapor at room temperature. The experimental procedures were same as described above. No nucleic acid bases were detectable from this gas mixture (Table I). However, this may not indicate that nucleic acid bases could not be formed on the early earth, because CO₂, N₂ and H₂O were the average components and more

reduced environments should have been able to exist at local places and/or for short periods. Cometary impacts, for instance, could have made a mildly-reduced environment because a comet has a large amount of CO in its body (Senay and Jewitt, 1994; Jewitt *et al.*, 1996; Biver *et al.*, 1996; Kasting, 1990).

This study indicates that at least three nucleic acid bases can be formed by quenching the N₂-CO-H₂O high-temperature plasma. Cometary impacts might have been able to provide similar conditions, because when comets collided with the earth, a high-temperature plasma including a large amount of CO would have been produced, called a post-impact plume. In this plume, the components of the comets, the earth's crust and the ambient atmosphere would have been variously mixed, reacted and rapidly cooled. In this study, electric energy of 180 J was input to each discharge and it was repeated 5,000 times to obtain the detectable amount of nucleic acid bases. Then, the total input energy was 9×10^5 J. Compared with this, real cometary impacts would have released much more energy. For instance, when a comet of 1 km in diameter and 1 g cm^{-3} in density collides at 20 km s^{-1} , which is claimed to have been a typical cometary impact (Chyba, 1987, 1990), a kinetic energy of 10^{20} J is released. This is 10^{13} times as much as the total energy used in this study, if 54% of the kinetic energy is imparted to the post-impact plume (Emiliani, 1981). Although it is not certain what exactly occurred when such an energy of 10^{20} J was instantaneously released, if the cometary impacts had given conditions similar to this experiment in some phases, the precursors of nucleic acid basis could have been formed on the primitive earth.

Fossils of cyanobacterium-like microorganisms indicate that life originated on the earth more than 3.5 Gyr ago (Schopf, 1993). Since these microfossils are structurally complex, the emergence of life must have been much earlier than 3.5 Gyr ago. Studies on the carbon-isotope composition in sedimentary rocks provide some evidence for the emergence of life by at least 3.8 Gyr ago (Schidlowski, 1988; Mojzsis *et al.*, 1996). At that time, the primitive earth may have been continuously bombarded by many projectiles (Maher and Stevenson, 1988; Melosh and Vickery, 1989; Chyba, 1990). Therefore, emergence of life should have related with the bombardments. Some heavy bombardments would have led to sterilization (Maher and Stevenson, 1988; Sleep *et al.*, 1989), but some would have contributed to producing bioorganic compounds. The present study suggests that a large amount of complex organic matter including precursors of bioorganic compounds might have been produced on the primitive earth after the cometary impacts.

4. Conclusions

Three types of nucleic acid bases were synthesized from a 90%N₂-10%CO-H₂O gas mixture via a complex organic matter produced with the high-temperature plasma and rapid quenching technique. Guanine was formed by increasing the partial pressure of nitrogen in the initial gas mixture, which caused increase of the N/C

ratio in the complex organic matter. The mechanism of guanine formation seems to be different from the HCN polymerization. Since no nucleic acid bases were synthesized from N_2 - CO_2 - H_2O , CO is likely to have been needed for the origin of nucleic acid bases. A large amount of complex organic matter including precursors of bioorganic compounds might have been produced on the primitive earth after cometary impacts, because they must have produced a post-impact plume including a large amount of CO.

Acknowledgements

The authors are grateful to Prof. Stanley L. Miller and Mr. H. James Cleaves, University of California, San Diego, for their advice and encouragement. The present work was supported in part by Grant-In-Aid for JSPS fellows (No. 5023) from the Ministry of Education, Science, Sports and Culture, Japan. The author (S. M.) is supported by JSPS Research Fellowships for Young Scientists.

References

- Bar-Nun, A., Bar-Nun, N., Bauer, S. H. and Sagan, C.: 1970, Shock Synthesis of Aminmo Acids in Simulated Primitive Environments, *Science* **168**, 470–473.
- Biver, N., Rauer, H., Despois, D., Moreno, R., Paubert, G., Boekelee-Morvan, D., Colom, P., Crovisier, J., Gerard, E. and Jorda, L.: 1996, Substantial Outgassing of CO from Comet Hal-Bopp at Large Heliocentric Distance, *Nature* **380**, 137–139.
- Canuto, V. M., Levine, J. S., Augustsson, T. R., Imhoff, C. L. and Giampapa, M. S.: 1983, The Young Sun and the Atmosphere and Photochemistry of the Early Earth, *Nature* **305**, 281–286.
- Chameides, W. L. and Walker, J. C. G.: 1981, Rates of Fixation by Lightning of Carbon and Nitrogen in Possible Primitive Atmospheres, *Origins Life* **11**, 291–320.
- Chyba, C. F.: 1987, The Cometary Contribution to the Oceans of Primitive Earth, *Nature* **330**, 632–635.
- Chyba, C. F.: 1990, Impact Delivery and Erosion of Planetary Oceans in the Early Inner Solar System, *Nature* **343**, 129–133.
- Chyba, C. and Sagan, C.: 1991, Electrical Energy Sources for Organic Synthesis on the Early Earth, *Origins Life Evol. Biosphere* **21**, 3–17.
- Chyba, C. and Sagan, C.: 1992, Endogenous Production, Exogenous Delivery and Impact-Shock Synthesis of Organic Molecules: An Inventory for the Origins of Life, *Nature* **355**, 125–132.
- Emiliani, C., Kraus, E. B. and Shoemaker, E. M.: 1981, Sudden Death at the End of the Mesozoic, *Earth Planet. Sci. Lett.* **55**, 317–334.
- Fegley Jr., B., Prinn, R. G., Hartman, H. and Watkins, G. H.: 1986, Chemical Effects of Large Impacts on the Earth's Primitive Atmosphere, *Nature* **319**, 305–308.
- Gilvarry, J. J. and Hochstim, A. R.: 1963, Possible Role of Meteorites in the Origin of Life, *Nature* **197**, 624–625.
- Hayatsu, R., Studier, M. H., Matsuoka, S. and Anders, E.: 1972, Origin of Organic Matter in Early Solar System – Catalytic Synthesis of Nitriles, Nitrogen Bases and Porphyrin-Like Pigments, *Geochim. Cosmochim. Acta* **36**, 555–571.
- Hayatsu, R., Studier, M. H., Oda, A., Fuse, K. and Anders, E.: 1968, Origin of Organic Matter in Early Solar System – Nitrogen Compounds, *Geochim. Cosmochim. Acta* **32**, 175–190.

- Jewitt, D., Senay, M. and Matthews, H.: 1996, Observations of Carbon Monoxide in Comet Hale-Bopp, *Science* **271**, 1110–1113.
- Kasting, J. F.: 1990, Bolide Impacts and the Oxidation State of Carbon in the Earth's Early Atmosphere, *Origins Life Evol. Biosphere* **20**, 199–231.
- Kasting, J. F.: 1993, Earth's Early Atmosphere, *Science* **259**, 920–926.
- Kobayashi, K. and Tsuji, T.: 1997, Abiotic Synthesis of Uracil from Carbon Monoxide, Nitrogen and Water by Proton Irradiation, *Chem. Lett.*, 903–904.
- Kobayashi, K., Kaneko, T., Saito, T. and Oshima, T.: 1998, Amino Acid Formation in Gas Mixtures by High Energy Particle Irradiation, *Origins Life Evol. Biosphere* **28**, 155–165.
- Kobayashi, K., Kaneko, T. and Saito, T.: 1999, Characterization of Complex Organic Compounds Formed in Simulated Planetary Atmospheres by the Action of High Energy Particles, *Adv. Space Res.* **24**, 461–464.
- Kuriki, K. and Ishikawa, Y.: 1982, Laboratory Simulation of Interstellar Chemical Evolution, *Ap. J.* **259**, 411–422.
- Levine, J. S., Augustsson, T. R. and Natarajan, M.: 1982, The Prebiological Paleatmosphere: Stability and Composition, *Origins Life* **12**, 245–259.
- Levy, M., Miller, S. L. and Oro, J.: 1999, Production of Guanine from NH_4CN Polymerizations, *J. Mol. Evol.* **49**, 165–168.
- Maher, K. A. and Stevenson, D. J.: 1988, Impact Frustration of the Origin of Life, *Nature* **331**, 612–614.
- McKay, C. P. and Borucki, W. J.: 1997, Organic Synthesis in Experimental Impact Shocks, *Science* **276**, 390–392.
- McKay, C. P., Scattergood, T. W., Pollack, J. B., Borucki, W. J. and Ghyseghem, H. T. V.: 1988, High-Temperature Shock Formation of N_2 and Organics on Primordial Titan, *Nature* **332**, 520–522.
- Miyakawa, S., Kobayashi, K. and Sawaoka, A. B.: 1999a, Amino Acid Synthesis from CO-N_2 and $\text{CO-N}_2\text{-H}_2$ Gas Mixture Via Complex Organic Compounds, *Adv. Space Res.* **24**, 465–468.
- Miyakawa, S., Murasawa, K., Kobayashi, K. and Sawaoka, A. B.: 1999b, Cytosine and Uracil Synthesis by Quenching with High-Temperature Plasma, *J. Am. Chem. Soc.* **121**, 8144–8145.
- Miyakawa, S., Sawaoka, A. B., Ushio, K. and Kobayashi, K.: 1999c, Mechanisms of Amino Acid Formation Using Optical Emission Spectroscopy, *J. Appl. Phys.* **85**, 6853–6857.
- Miyakawa, S., Tamura, H., Kobayashi, K. and Sawaoka, A. B.: 1997, New Application of a Magneto-Plasma Dynamic Arc-Jet to Amino Acid Synthesis, *Jpn. J. Appl. Phys.* **36**, 4481–4485.
- Miyakawa, S., Tamura, H., Kobayashi, K. and Sawaoka, A. B.: 1998, Amino Acid Synthesis from an Amorphous Substance Composed of Carbon, Nitrogen, and Oxygen, *Appl. Phys. Lett.* **72**, 990–992.
- Melosh, H. J. and Vickery, A. M.: 1989, Impact Erosion of the Primordial Atmosphere of Mars, *Nature* **338**, 487–489.
- Mojzsis, S. J., Arrhenius, G., McKeegan, K. D., Harrison, T. M., Nutman, A. P. and Friend, C. R. L.: 1996, Evidence for Life on Earth Before 3,800 Million Years Ago, *Nature* **384**, 55–59.
- Mukhin, L. M., Gerasimov, M. V. and Safonova, E. N.: 1989, Origin of Precursors of Organic Molecules During Evaporation of Meteorites and Mafic Terrestrial Rocks, *Nature* **340**, 46–48.
- Oberbeck, V. R., McKay, C. P., Scattergood, T. W., Carle, G. C. and Valentin, J. R.: 1989, The Role of Cometary Particle Coalescence in Chemical Evolution, *Origins Life Evol. Biosphere* **19**, 39–55.
- Rao, V. V., McKay, D. and Trass, O.: 1967, A Shock Tube Study of the High Temperature Reactions of Nitrogen with Hydrocarbons, *Can. J. Chem. Eng.* **45**, 61–66.
- Scattergood, T. W., McKay, C. P., Borucki, W. J., Giver, L. P., Ghyseghem, H. V., Parris, J. E. and Miller, S. L.: 1989, Production of Organic Compounds in Plasma: A Comparison Among Electric Sparks, Laser-Induced Plasmas, and UV Light, *Icarus* **81**, 413–428.
- Schidlowski, M.: 1988, A 3,800-Million Year Isotopic Record of Life from Carbon in Sedimentary Rocks, *Nature* **333**, 313–318.

- Schlesinger, G. and Miller, S. L.: 1973, Equilibrium and Kinetics of Glyconitrile Formation in Aqueous Solution, *J. Am. Chem. Soc.* **95**, 3729–3735.
- Schlesinger, G. and Miller, S. L.: 1983a, Prebiotic Synthesis in Atmospheres Containing CH₄, CO, and CO₂. Amino Acids, *J. Mol. Evol.* **19**, 376–382.
- Schlesinger, G. and Miller, S. L.: 1983b, Prebiotic Synthesis in Atmospheres Containing CH₄, CO, and CO₂. Hydrogen Cyanide, Formaldehyde and Ammonia, *J. Mol. Evol.* **19**, 383–390.
- Schopf, J. W.: 1993, Microfossils of the Early Archean Apex Chert: New Evidence of the Anquity of Life, *Science* **260**, 640–646.
- Senay, M. C. and Jewitt, D.: 1994, Coma Formation Driven by Carbon Monoxide Release from Comet Schwassmann-Wachmann 1, *Nature* **371**, 229–231.
- Sleep, N. H., Zahnle, K. J., Kasting, J. F. and Morowitz, H. J.: 1989, Annihilation of Ecosystems by Large Asteroid Impacts on the Early Earth, *Nature* **342**, 139–142.
- Stribling, R. and Miller, S. L.: 1987, Energy Yields for Hydrogen Cyanide and Formaldehyde Syntheses: The HCN and Amino Acid Concentrations in the Primitive Ocean, *Origins Life* **17**, 261–273.
- Tahara, H., Yasui, H., Kagaya, Y. and Yoshikawa, T.: Experimental and Theoretical Researches on Arc Structure in a Self-Field Thruster, *AIAA Paper 87-1093*.
- Thompson, W. R., Henry, T. J., Schwartz, J. M., Khare, B. N. and Sagan, C.: 1991, Plasma Discharge in N₂ + CH₄ at Low Pressures: Experimental Results and Applications to Titan, *Icarus* **90**, 57–73.
- Wilson, P. D. and Sagan, C.: 1997, Nature and Source of Organic Matter in the Shoemaker-Levy 9 Jovian Impact Blemishes, *Icarus* **129**, 207–216.
- Yuasa, S., Flory, D., Basile, B. and Oro, J.: 1984, Abiotic Synthesis of Purines and Other Heterocyclic Compounds by the Action of Electrical Discharges, *J. Mol. Evol.* **21**, 76–80.