FORMATION OF THE BUILDING BLOCKS OF PRIMITIVE LIFE

André Brack
Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, F-45071 Orléans cedex , France brack@cnrs-orleans.fr

James P. Ferris
Department of Chemistry, Rensselaer Polytechnic Institute, Troy NY 12180-3590, USA ferri@rpi.edu

Keywords: Prebiotic chemistry, organic molecules, water, amino acids, nucleotides, lipids, primitive atmosphere, hydrothermal systems, comets, meteorites, cosmic dust, homochirality

Contents

Abstract

Life - defined as a chemical system capable of transferring its molecular information via self-reproduction and of evolving - probably originated from the reaction of reduced carbon-based organic matter on the primitive Earth. Primitive carbon was available as gaseous compounds, either oxidized (carbon dioxide, carbon monoxide) or reduced (methane). More complex organic molecules might have been formed by the action of UV light, shockwaves and electric discharges on the primitive atmosphere. For example, Stanley Miller exposed a mixture of methane, ammonia, hydrogen and water to electric discharges to mimic the action of lightening on the primitive atmosphere. He obtained four of the twenty amino acids utilized in life today, via the intermediary formation of hydrogen cyanide and aldehydes. In the laboratory, hydrogen cyanide and formaldehyde have been shown to lead to many of the building blocks of the biopolymers, such as amino acids and nucleic acid bases. However, the composition of the primitive Earth's atmosphere was probably dominated by carbon dioxide and thus is only weakly reducing. Very low levels of amino acids are formed from these gas mixtures. Deep-sea hydrothermal systems may also represent an environment for the

synthesis of prebiotic organic molecules. Reduced organic molecules have been obtained in experiments carried out under conditions simulating the hydrothermal vents. The collection and analysis of meteorites and micrometeorites, formed by the collisions of asteroids and delivered to the Earth, has allowed close examination of extraterrestrial organic material. Eight protein amino acids have been identified in the Murchison meteorite among more than 70 amino acids found therein. Some non-biological amino acids present contain 9% L-enantiomeric excesses (54.5% L), a finding which may provide a clue to the emergence of a homochiral (one-handed) life on Earth. Purines and pyrimidines, components of RNA, and amphiphilic molecules have also been detected. From recent collection and analysis of micrometerorites in Antarctica ice sheets, the amount of extraterrestrial carbon delivered to the Earth during the late bombardment phase has been estimated to 3×10^{19} g. This material appears to have been one of the primary sources of reduced carbon compounds on the primitive Earth. This amount represents about 30 times the amount of carbon recycled on the surface of the Earth today. Organic molecules present in the protosolar molecular cloud not processed by the planetary accretion phases may have also been delivered to the primitive Earth via dust eroded from comets passing through the inner solar system.

1. Introduction

Terrestrial life probably appeared about 4 billion years ago. It contained chemical systems capable of transfering their chemical information content via self-reproduction and it evolved as a result of the mistakes made in reproduction. It is generally believed that life on Earth arose in the presence of liquid water by the processing of organic molecules that contained carbon and hydrogen atoms associated with oxygen, nitrogen and sulfur atoms and are often called the CHONS. It is likely that these reactions were catalyzed by minerals and metal ions. Schematically, the organic components of primitive life can be compared to parts of “ molecular robots ”. By chance, some parts self-assembled to generate robots capable of assembling other parts to form identical robots. From time to time, a minor error in the building generated more efficient robots which became the dominant species. The number of parts required for the first robots, i.e. their complexity, as well as their chemical nature are still unknown. The remains of the early life have probably been erased by geological processing, i.e. the plate tectonics, and its consumption by the more efficient life that evolved from it.

2. The role of water

Assembling parts of the primitive biological molecules must have occurred at a reasonable rate and the process probably occurred in water. Solids are unable to migrate and to react. A gaseous phase would allow fast diffusion of the parts but the limited inventory of stable volatile organic molecules would constitute a severe restriction. A liquid phase offers the best milieu for the diffusion and the reaction of organic molecules. Water was the most abundant solvent on the early Earth.

Liquid water exists at temperatures above 0°C at pressures above 0.006 atmosphere. Therefore, the size of a planet and its distance from its star are two basic characteristics that will determine if liquid water is present. If a planet is too small, like Mercury or the Moon, its gravitational attraction is low and it will not be able to retain water or other atmospheric gases. If the planet is too close to its star, its temperature will be high due to the star's radiation. Any water present would evaporate and deliver large amounts of water vapor to the atmosphere which thus contributes to the greenhouse warming of the planet. The water vapor would undergo photodissociation by ultraviolet light and would break into hydrogen atoms and hydroxyl radicals. The hydrogen atoms would escape into space and the hydroxyl radicals would form hydrogen peroxide and oxygen. If a planet is far from the star, it may have liquid water providing that it can maintain a temperature above 0°C with greenhouse gases, such as CO_2, in its atmosphere. Liquid water would dissolve CO_2 which would then be trapped by formation of insoluble carbonates. The loss of CO_2 would lower the surface pressure and the temperature and result in freezing the water. A volcanically active planet could recycle the carbon dioxide by breaking down subducted carbonates. The size of the Earth and its distance from the sun are such that the planet never experienced total evaporation or total freezing of its oceans.

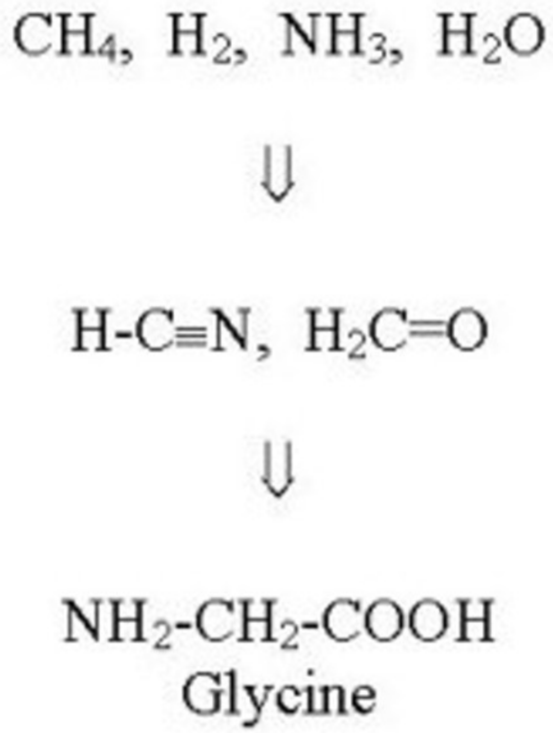
The origin of primitive Earth’s water is difficult to determine. The source of the primitive terrestrial water can be found in a combination of H_2O trapped in the rocks that made the bulk of the planet’s mass (“internal reservoir”) and a late accreting veneer of extraterrestrial material (“external reservoir”). The formation of the internal reservoir is a natural consequence of the accretion of the planet. A volatile-rich veneer may have replaced the atmosphere produced by the planet’s early accretion, which was subsequently blown off by the giant impact between the Earth and a Mars-sized planetesimal that generated the Moon and caused the early atmosphere to undergo massive hydrodynamic loss. The abundance and isotopic ratios of the noble gases neon, argon, krypton, and xenon suggest that meteorites alone or in combination with planetary rocks could not have produced the Earth’s entire volatile inventory and that a significant contribution from icy planetesimals was required (Owen, 1998).

3. Possible environments for the production of prebiotic organic molecules

The simplest sources of carbon susceptible to lead to prebiotic organic molecules are gaseous, i.e. carbon dioxide (CO_2) and monoxide (CO) for the oxidised forms and methane (CH_4) for the reduced one. CO has an intermediary oxidation state: although it is oxidised relative to carbon, it is close to the oxidation state of biomolecules. The oxidation state of an active atmosphere relative to prebiotic chemistry is determined from an inventory of the different environments where gaseous carbon compounds are present and can be transformed into more complex organic molecules. This environment must produce reduced organic molecules, i.e. carbon-based molecules in which carbon atoms are dominantly associated with hydrogen atoms to the expenses of oxygen ones.

3.1. Production of CHONS in the atmosphere

Oparin suggested that the small reduced organic molecules needed for primitive life were formed in a primitive atmosphere dominated by methane. The idea was tested in the laboratory by Stanley Miller (Miller, 1953) who exposed a mixture of methane, ammonia, hydrogen and water to electric discharges. In his initial experiment, he obtained four of the twenty naturally occurring amino acids, via the intermediary formation of hydrogen cyanide and aldehydes. In the laboratory, mixtures of hydrogen cyanide, aldehydes and ammonia have been shown to lead to many of the building blocks of the biopolymers, such as amino acids and nucleic acid bases. In general, simple gaseous molecules like H_2, N_2, H_2O, CH_4 require a supply of energy (UV, heat, electric discharges, cosmic rays, shock waves) to react with each other. They generate compounds like hydrogen cyanide and formaldehyde which store chemical energy in their double and triple chemical bonds. These multiple-bonded molecules react in water to form building blocks of life like amino acids.



Scheme 1. (figure 1) *From simple gaseous molecules to glycine, the simplest amino acid and a building block of protein.*

Miller's laboratory synthesis of amino acids occurs efficiently when a reducing gas mixture containing significant amounts of hydrogen is used. However, the actual composition of primitive Earth's atmosphere is not known. The dominant view in recent years is that the primitive atmosphere consisted mainly of CO_2, N_2, and H_2O, along with small amounts of CO and H_2 (Kasting and Brown, 1998). Only small yields of amino acids are formed in such a mixture.

Intense bombardment of the Earth about 4 billion years ago could have caused the chemical reprocessing of the Earth primitive atmosphere. Modeling of the shock heating and rapid quenching caused by the impact of large bodies into an atmosphere composed of N_2, CO_2 and H_2O, suggests that hydrogen cyanide and formaldehyde could have been produced. Solar UV, electric effects and impact shocks were the major energy sources driving atmospheric prebiotic syntheses (Chang, 1993). All of these appear capable of adding to the oceanic stock of organics depending on the reduction state of the primitive atmosphere.

-
-
-

Bibliography

Bonner, W.A. (1991). The origin and amplification of biomolecular chirality, *Origins Life Evol. Biosphere* **21**, 59-111.
A review on the origin of biological one-handedness

Chang S. (1993). Prebiotic synthesis in planetary environments, in *The chemistry of life's origin*, Greenberg J.M., Mendoza-Gomez C.X., Pirronello V. (Eds), pp. 259-300, Kluwer Academic Publ., Dordrecht.
A review on the extraterrestrial organic molecules delivered to the primitive Earth

Cronin, J.R. and Pizzarello S. (1997). Enantiomeric excesses in meteoritic amino acids, *Science*, **275**, 951-955.
Describes the amino acids found in carbonaceous meteorites and rhe excess of left-handed ones

Deamer, D.W. (1998). Membrane compartments in prebiotic evolution, in *The molecular origins of life: assembling pieces of the puzzle*, ed. A. Brack, pp. 189-205, Cambridge University Press, Cambridge.
Describes the primitive membranes

Ehrenfreund P. and Charnley S.B. (2000). Organic molecules in the interstellar medium, comets and meteorites, *Ann. Review Astron. Astrophys*. **38**, 427-483.
Describes the production of extraterrestrial organic molecules (interstellar medium, comets,..)

Holm, N.G. ed. (1992). Marine hydrothermal systems and the origins of life. Special issue. *Origins Life Evol. Biosphere*, **22**, 1-191.
A survey of the role of submarine hydrothermal systems in the origins of life

Huber, C. and Wächtershäuser G. (1997). Activated acetic acid by carbon fixation on (Fe, Ni)S under primordial conditions, *Science*, **276**, 245-247.
Brings arguments in favor of an autotrophic primitive life metabolizing CO_2 *on mineral surfaces*

Kasting, J.F. and Brown L.L. (1998). The early atmosphere as a source of biogenic compounds, in *The molecular origins of life: assembling pieces of the puzzle*, ed. A. Brack, pp. 35-56, Cambridge University Press, Cambridge.
Describes the environment of the early Earth

Maurette, M. (1998). Carbonaceous micrometeorites and the origin of life, *Origins Life Evol. Biosphere*, **28**, 385-412.
Description of the organic inventory delivered by micrometeorites to the Earth

Miller, S.L. (1953). The production of amino acids under possible primitive Earth conditions, *Science*, **117**, 528-529.
Historical experiment demonstrating that amino acids can be formed from gas mixtures

Müller, D., Pitsch, S., Kittaka, A., Wagner, E., Winter, C. and Eschenmoser, A. (1990). Aldomerisierung

von glycolaldehyd-phosphat zu racemischen hexose-2, 4, 6-triphosphaten und (in gegenwart von formaldehyd) racemischen pentose-2, 4-diphosphaten: *rac*-allose-2, 4, 6-triphosphat und *rac*-ribose-2,4-diphosphat sind die reactionshauptproduckte. *Helv. Chim Acta* **73**, 1410-1468.
Describes the synthesis of a pyranosyl-RNA, an RNA analog based on pyranose

Owen, T.C. (1998). The origin of the atmosphere, in *The molecular origins of life: assembling pieces of the puzzle*, ed. A. Brack, pp. 13-34, Cambridge University Press, Cambridge.
Describes the origins of terrestrial atmosphere

Biographical Sketches

André Brack is Directeur de Recherche at the Centre National de la Recherche Scientifique, Centre de Biophysique Moléculaire, Orléans, France. He was trained in peptide chemistry at the University of Strasbourg. His field of expertise concerns the chemistry of the origin of life, as well as the search for life in the solar system. He served as President of the International Society for the Study of the Origin of Life (1996-1999) and became Fellow of that society in 1999. He is also active in science popularization as President of the centre for the popularization of science which he founded in Orléans in 1990.

Jim Ferris is Professor of Chemistry at the Department of Chemistry at the Rensselaer Polytechnic Institute at Troy. He is presently Director of the New York Center for Studies on the Origins of Life: A NASA NSCORT. He was trained as an organic chemist at Indiana University. His fields of expertise includes the synthesis and polymerization of nucleotides on clay minerals and the laboratory simulation of photochemical processes in the atmospheres of Jupiter, Saturn and Titan, the largest moon of Saturn. He served as President of the International Society for the Study of the Origin of Life (1993-1996) and received the Oparin Medal of that scientific society in 1996.