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CHEMICAL EVOLUTION: AN APPROACH FROM RADIATION CHEMISTRY*

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Abstract. *To explain the origin of life on Earth, a period in which the synthesis of bio-organic compounds was carried out from simple inorganic molecules under the influence of natural energy sources is assumed. However, many prebiotic reactions require the input of energy. Ionizing radiation is a very efficient source of energy and may have participated in prebiotic synthesis due to its unique qualities—e.g., its ubiquity, its energy deposition method, and the effectiveness of its reactions, via free radicals. The use of this source is substantiated by calculations of the energy available from the decay of radioactive elements with long half-lives. Cosmic radiation is an external energy source that also could have contributed to chemical evolution processes, especially in extraterrestrial environments. In the context of chemical evolution, radiation chemistry can be a very precise and useful tool to simulate the changes that take place in organic molecules that are exposed to high-energy radiation. This work highlights the importance of ionizing radiation in prebiotic synthesis, in both water and frozen solutions, which reproduces both terrestrial and extraterrestrial environments.*

Key words: *Prebiotic chemistry, ionizing radiation, chemical evolution*

1. INTRODUCTION

How did life begin? It has been a mystery for humankind in the past and remains so in the present [1]. One of the few things that it is possible to affirm is that the complexity of this scientific problem requires major contributions from different disciplines, and it is still an open question. Scientists have long made efforts to understand the origin of life; several hypotheses about early life have been proposed and coexist today. Among them, Alexander I. Oparin and John B. S. Haldane postulated the chemical evolution theory for the origin of life. According to them, physical and chemical processes, named chemical evolution [2], took place on the early Earth. Those coupled processes led to the formation of biologically relevant molecules, starting from simple inorganic compounds and under the influence of natural energy sources. The accumulation of organic matter on the primitive Earth and the generation of self-replicating molecules are two factors of prime importance in chemical evolution. Following these processes, biological evolution began.

The exact sequence of chemical events that led to the emergence of living beings is not known. However, scientists working on this matter have made a lot of effort. Chemical approaches are used to study this process in the laboratory (a discipline named prebiotic chemistry), by simulating the synthesis of compounds through a recreation of the inferred conditions that may have prevailed on the early Earth. Thus, studies of chemical evolution concern the chemistry of the primitive Earth before the emergence of life. The aim of this work is to emphasize the role of radioactivity and radiation-induced reactions on the early Earth and other extraterrestrial bodies. These processes resulted in chemical changes that might have been significant for chemical evolution to accomplish.

1.1. Chemical evolution

Chemical evolution of organic matter is part of the concept of the evolution of the universe. It is known that the universe is complex but once it was simpler in composition: the universe evolved, as did all the elements inside it.

Several approaches have been proposed to explain how life arose. The most notable are the genetic and metabolic hypotheses [3].

The genetic approach suggests that first a simple genetic code was formed [4]. The ability to copy the molecules that encode genetic information is an essential step in the origin of life. The genetic approach proposed that this ability probably first evolved in the form of an RNA self-replicator — an RNA molecule that could copy itself [3] and life arose from preexisting chemical compounds that led to the formation of complex molecules.

According to the metabolic approach, complex chemical systems (similar to primitive metabolism) arose from redox reactions [6, 7]. The main focus of this hypothesis was the catalysis of primary prebiotic reactions by geochemical energy. Probably, one of the most representative reactions is carbon fixation by the synthesis of acetate thioester from CO and H_2S catalyzed

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by surfaces [6]. Unfortunately, the spontaneous emergence of a highly complex and coordinated chemical system and the subsequent transition to a genomic replicative system are still unknown [3]. Although several lines of evidence are consistent with this hypothesis, it is far from certain and the investigation continues. Some scientists, like Alfonso L. Herrera (1868-1942), dealt with question of the origin of life from a different perspective. Herrera, a Mexican scientist, produced organized structures that mimicked cells in the 1930s [5].

1.2. Primitive scenarios

Chemical evolution arose in the context of some specific environmental conditions and factors that finally framed life on Earth. These factors include, among others, the time scale, the nature of the atmosphere, the amount of available energy for organic synthesis, the temperature of the planet, the conditions in the lithosphere and hydrosphere, and the pH of the oceans. Several disciplines have offered suggestions on this subject, providing a general picture of the conditions on the early Earth.

The Earth was formed about 4750 Ma, based on the age of Calcium, Aluminum-rich inclusions (CAIs) and chondrules from Allende and Efremovka meteorites [8]. The earliest forms of life date to about 3500 Ma [9]. During the chemical evolution period, between these two events, many changes on Earth were produced.

Geological evidence indicates that the primitive atmosphere did not contain more than traces of molecular free oxygen. However, a point of debate is its constitution and redox character. The primordial Earth's atmosphere was formed by impact degassing of planetesimals, and it collapsed once the accretion process finished. Researchers agree that the secondary atmosphere was neutral in composition—namely, dominated by N_2 and CO_2 instead of NH_3 and CH_4 [10]. Photo dissociation processes in the atmosphere destroyed CH_4 and NH_3, and they would not last for long [11].

The first rock type primarily consisted of olivine and glass characterized by spinifex texture (skeletal-acicular olivine or, more rarely pyroxene) and chemistry with 18-30 MgO wt. % derived from the large proportions of mantle melting at temperatures exceeding 1,400 °C [12]. The lithosphere was formed by micro-continents probably constituting less than 5% of the present continental area. The chemical composition of the primitive ocean is not known. Although there is geological evidence of liquid water on Earth after 3800 Ma, similar evidence does not exist for the period between accretion and 3800 Ma, the deposition time of the oldest preserved sedimentary rocks. Geological evidence such as pillow lavas (3500 Ma ago) and ripple marks (3300 Ma ago) in the Swaziland Super group undoubtedly indicate the presence of liquid water about 3300 Ma ago [13]. The earliest life forms can be traced by the study of fossil records. The first evidence of life, stromatolites (macroscopic structures formed by sediment-trapping algae), is found at 3500 to 3300 Ma ago [9, 13]. The evidence suggests that life originated on Earth before 3500 Ma ago. Nonetheless, controversial evidence implies that life may have existed by 3800 Ma ago [14].

1.3. Energy sources

A great variety of energy sources may have been available on primitive Earth for prebiotic synthesis (e.g., UV, heat, lightning) [15]. Some of these sources may have been useful in particular reactions because the action may have caused different effects. In the laboratory, similes of these forms of energy are used to simulate primitive conditions. The energy sources used to induce chemical reactions need to be available, abundant, and efficient. Ultraviolet light from the Sun produces a total energy of 260 000 cal cm^2 $year^{-1}$, and it is by far the most abundant source of all. Sunlight is very effective for the synthesis of organic compounds, mainly because atmospheric components could be activated in the region between 120 and 220 nm.

Besides UV light, other energy sources are effective in generating organic compounds and are also of considerable importance. Sources like heat from volcanoes and hot springs, electric discharges produced in the atmosphere and in very energetic eruption of volcanoes, ionizing radiation (cosmic rays, radionuclides), sonic energy generated from ocean waves, and shock waves from thunderstorms or meteorites entering the Earth's atmosphere are also proposed. The problem of evaluating these energy sources is difficult and in general entails non-equilibrium conditions, product quenching, and protection. The estimated abundance depends on the model used for calculation. Ionizing radiation has been considered a minor partner as an energy source. Nonetheless, the main qualities of an energy source include not only its abundance but also its way of energy deposition and penetration (which differ between solid, aqueous matter and gases), and this could have been a key element to induce prebiotic reactions.

1.4. Why ionizing radiation?

Since the formation of our planet, it has been permanently exposed to ionizing radiation of both terrestrial and extraterrestrial origin. Terrestrial sources refer to natural radioactivity, which has its origin in primordial radionuclides and their daughter products. Primordial radionuclides were synthetized in the stars by nuclear processes and incorporated into solar system bodies, including the Earth, when they were formed. Radionuclides are distributed on Earth in soil, rocks, the atmosphere, and the hydrosphere [16]. On the other hand, there are also extraterrestrial sources of ionizing radiation, mainly in form of cosmic rays.

The application of ionizing radiation to prebiotic synthesis is based on its omnipresence, its specific way of energy deposition, and its distribution. Chemical reactions induced by ionizing radiation proceed via free radicals; in aqueous solutions, the radiation creates radical-rich pathways in the water, in which chemical reactions occur. The use of this source is also substantiated by calculations of the energy available from the decay of radioactive elements like potassium-40, uranium-235, uranium-238 and thorium-232 [17], all of which have half-lives on the order of 109 years. Several other naturally radioactive isotopes of long half-life, like rubidium-87 and indium-115, may have contributed, but to a minor extent. Under present conditions, the radiation effects on Earth's surface are quite negligible. However, those radionuclides may have been quite important historically, acting at the time when chemical evolution occurred. In the case of the Earth's crust, it is possible to calculate the corresponding amount of energy available 3.8 x 10^9 years ago, in the form of ionizing radiation and heat, from the rates at which major long-lived radioactive species decay [18, 19].

For example, potassium is widely distributed throughout the Earth and dissolved in the hydrosphere, but it is also concentrated in major rock types. It has higher concentrations in acid igneous rocks and sedimentary alumino-silicates; ^{40}K has a concentration of 0.0117 %; despite its small isotopic concentration ^{40}K plays an essential part in heat production of the Earth. Its natural abundance on the primitive Earth 3.8 x 10^9 years ago was around eight times higher than it is today [18,19]. The homogeneous distribution of potassium salts in primitive oceans, lagoons, and tide pools may have been an effective internal source of energy and contributed in the transformation of the molecules present in solutions.

The distribution of radionuclides is widely determined by the geophysical conditions that existed in various stages of the Earth's development. The accumulation of heavy elements such as thorium and uranium in the upper layers took place in the early stages of the Earth. Table 1 shows the radioactive sources present on the early Earth.

Table 1. Sources of ionizing radiation in chemical evolution*

SOURCE	COMMENTS
CERTAIN	
Radionuclides with half-life 10^7-10^9	^{40}K, ^{232}Th, ^{235}U, ^{238}U, ^{244}Po
PROBABLE	
Natural nuclear reactors and the radionuclides produced by them	Oklo type reactors
POSSIBLE	
Radionuclides with half-life estimated between 10^8-10^9 years	Super heavy elements with an atomic number around 114.

*modified from [16]

The localized nature of radiation from radionuclides like uranium and thorium may have produced microenvironments of high activity. In these places, simple molecules could have reacted and formed other, more complex molecules. Additionally, mineral deposits associated with these isotopes may have enhanced catalytic processes, contributing to the increase of molecular complexity. Here lies the importance of minerals (especially clay minerals) and other surfaces in chemical evolution [20].

2. PREBIOTIC CHEMISTRY

Chemical reactions are used to understand the processes that preceded the origin of life. Simulations in the laboratory include the synthesis of compounds and the recreation of the possible conditions of the early Earth. These studies are not restricted to Earth, since chemical processes are universal and reactions take place in many extraterrestrial environments such as comets, meteorites, interplanetary and dust particles.

The recreation of primitive Earth conditions in the laboratory is called "prebiotic chemistry." Stanley Miller, working with Harold Urey at the University of Chicago, carried out one of the first experiments in this field in 1953 [21]. Some life-related substances were synthesized, including amino acids, simple fatty acids, and urea. After this experiment, many others were performed using different sources of energy including heat, ionizing radiation, or UV light. These various experiments produced many building blocks of life such as amino acids, purines, pyrimidines, and carbohydrates [22-26]. Still, there are several compounds whose syntheses present problems such as low yields of formation, unrealistic experimental conditions, and the formation of homochiral molecules.

There are several approaches to perform simulated experiments. A crucial aspect to consider in planning a prebiotic synthesis is to re-create in the laboratory the geologically relevant scenarios for the primitive Earth and other bodies in the solar system. It is important to choose an appropriate raw material and energy source; it is also fundamental to consider a plausible concentration, typically in the order of 10^{-3} mol/L. In most prebiotic experiments, the raw material contains very reactive chemical groups like C=O, C≡N, or C=C. Simulations also take into account the pH. In an alkaline pH, which is believed to have existed in the primitive oceans, condensation reactions are very likely to occur—for example, formaldehyde in alkaline medium yields carbohydrates [27]. Another example is the Strecker synthesis of amino acids from an aldehyde and ammonia [28].

Using ionizing radiation as a source of energy gives rise to chemically reactive species, which in turn lead to chemical changes in the irradiated medium. Water is the medium in many experiments; conveniently, the radiolytic behavior of water has been studied extensively [29]. The interaction of water with ionizing radiation produces ionization and excitation of water molecules, which leads to the formation of highly reactive intermediates. These intermediates interact with the solutes present in water. In these interactions, free radicals and radical ions play an important role. Many reactions induced by radiation have been studied in aqueous solutions, which have applications in prebiotic chemistry. For this, radiation-induced reactions have been proposed as a mechanism for synthesizing organic compounds under the conditions that likely existed when chemical evolution took place. Therefore, simple precursors give rise to a large variety of compounds in radiation-induced reactions. In our laboratory, a systematic investigation of radiation-induced reactions of possible interest for prebiotic chemistry has been carried out over the last 30 years. We are studying the behavior of simple cyano compounds, carboxylic acid associated with metabolic pathways, nitrogen bases, and amino acids.

In lakes and oceans, it is hard to imagine high concentrations of the reactants required for an effective prebiotic synthesis. For this reason, it has been proposed that clays and other mineral surfaces might have played a key role in prebiotic Earth. Clay minerals may have been crucial for chemical evolution due to several properties such as their ancient origin, adsorption capacity, and wide distribution on Earth. In this way, mineral surfaces could have provided templates and surfaces for sorption and may also have acted as catalysts for chemical reactions. A review of several experiments using a mineral surface to enhance the prebiotic synthesis induced by radiation and protection role of clays is shown in [18, 20] and the references therein. The study of the behavior of bio-organic compounds in the presence of clay minerals is necessary to extend the knowledge of their role in the prebiotic epoch.

The experimental modeling of the possible formation of organic compounds on the primitive Earth, with ionizing radiation as an energy source, is conducted by using gamma radiation or accelerator machines. To simulate extraterrestrial processes, gamma rays of ^{60}Co are a useful tool, because the most abundant protons in cosmic rays have energies of about 2 GeV and a LET similar to ^{60}Co gamma rays [16]. Consequently, radiation chemistry can be a very precise and useful tool to simulate the evolution of organic molecules on the primitive Earth and other bodies in space.

In this context, many experiments have been designed to analyze the radiolytic behavior of different molecules. Some experiments have been performed with biologically relevant molecules or their precursors [30]. For example, the irradiated acetic acid produced several carboxylic acids, some of them intermediates of the Krebs cycle. The effect of ionizing radiation on purines and pyrimidines has also been studied. The main finding in irradiation with X-rays is the deamination and some ring fission of the constituent purine and pyrimidine bases [31]. Hems [32] reported that pyrimidines are destroyed to a greater extent than purines when irradiated in aqueous solutions.

Other experiments have been conducted with irradiating precursors. The CN-containing compounds represent a challenging starting material, and we have performed radiation chemistry studies with these kinds of compounds. For example, solutions of HCN and simple nitriles produced aldehydes, ketones, and carboxylic acids [33]. Dondi *et al.* [34] studied the aqueous solutions of simple organic compounds (methanol and acetonitrile) under gamma-rays and detected the formation of complex organic mixtures. These previous and non-exhaustive examples give a good idea about the important role that radiation chemistry may have played as an energy source.

2.1. Minerals and radiation chemistry

The idea that minerals may have been a clue element for prebiotic synthesis has led researchers to include them in heterogeneous systems exposed to ionizing radiation. Their behavior is strongly dependent on both the nature of the molecule and on the mineral. Lopez-Esquivel *et al.* studied the adsorption of some amino acids into Na-montmorillonite and exposed the system to gamma-rays [35]. Their findings showed that adsorbed molecules are protected from radiation. In the case of adenine [36], the mineral also acts to protect the molecule from degradation caused by the radiation. Other molecules as nucleosides have also been explored. Cytidine and adenosine, when adsorbed on clay, showed lower decomposition rates than samples irradiated in aqueous solutions [37]. It is clear that both chemical evolution and ionizing radiation are common in the universe. Comets, asteroids and all the matter in space suffer the action of radiation and undergo chemical reactions. It has also been proposed that early Earth was enriched with molecules coming from meteorites and comets, so radiation chemistry has also been considered a useful tool for exploring reactions in those bodies.

2.2. Experiments in ices

The chemical radiation approach is critical when trying to understand chemical processes that take place in space—in particular, in comets, meteorites and dust particles that are exposed to high radiation doses. Therefore, much attention has been paid to the study of ices that constitute comets.

Zheng *et al.* [38] provided an excellent review of this field of research. Among the variables taken into account in experiments are the temperature, the thickness of the film, and the type of radiation employed. Water is the most abundant icy component in astrophysical environments and planetary systems and most of the experiments have been carried out with water ice as the main component. In our solar system, water is present in Kuiper belt objects, satellites, the nuclei of comets, and some planetary rings.

Many authors have studied the irradiation of pure icy water systems with ions of different energies. Brown *et al.* [39-41] studied the irradiation (with He^+ and H^+) of water films at different temperatures (15-110 K). Other authors employed the same particles but different energy for irradiation [42-49]. Other radiation sources include ^{19}F ions [50], UV radiation [51, 52, 42], and electrons [53-56, 44, 38, 57]. Regardless of the irradiation source, the final products formed by radiolysis of water [29] were the same, including molecular products as hydrogen, oxygen, and hydrogen peroxide [58, 59].

Other experiments consist of the irradiation of simple molecules such as CO, which yields mainly CO_2 [60], or CO_2 (irradiated with H^+), which generates carbonic acid (H_2CO_3) through the incorporation of implanted ions [61]. Experiments with mixed molecular species are important because interstellar and cometary ices comprise not only pure ices, but also non-polar (dominated by N_2, O_2, and CO_2) and polar (dominated by H_2O and containing CO and CH_3OH) ices [62]. For example, Hudson and Moore (1999) detected the formation of CO_2 and methanol by ion irradiation of H_2O and CO mixtures. Hydrocarbons are also synthesized when different gas combinations (H_2, CO, NH_3, and H_2S) react with materials containing silicate grains [63]. Hudson and Moore [64] identified the formation of methanol and ethane by the irradiation of icy mixtures of methane and water at 16 K [65].

PAH molecules are so common in ISM and carbonaceous chondrites that they can be considered the most widespread class of organic molecules in the universe [66, 67]. In dense molecular clouds, these compounds can condense onto refractory dust grains. Their presence has been revealed by astronomical detection of their stretching bands of C-H. The photolysis of naphthalene, a PAH molecule, diluted in water ice produces a significant quantity of oxidized naphthalene compounds, including both ketones and alcohols. In the context of chemical evolution [68], irradiated propane and methane or carbon monoxide with high energy protons in the presence of water and ammonia, after an acid hydrolysis, detected the formation of amino acids. The behavior of over-irradiated frozen HCN solutions has been studied by Colin-Garcia *et al.* [69, 70]. Their analysis confirmed that gamma-ray irradiation generates several organic products, among them carboxylic acids, amino acids, and urea, all of which have biological relevance.

3. CONCLUSIONS

Chemical evolution is a common process in the universe, based on the fact that matter and energy are present in every single place of the universe, and primitive Earth was not an exception. It has been suggested that a period of synthesis and further accumulation or organic matter preceded the origin of life on Earth, and many energy sources have been considered for promoting those chemical reactions. From a historical perspective, ionizing radiation may have been a critical energy source due to its energy deposition and penetration power. Experiments demonstrate that this energy source induces chemical changes that could have promoted an increase in the complexity and diversity of organics. This effect is not restricted to primitive Earth, due to the universality of radiation. Therefore, a radiation chemistry approach can be used to explore chemical evolution on primitive Earth, to elucidate decomposition patterns of biomolecules (when looking for life on other bodies), or to study the formation of molecules on other bodies such as comets and asteroids.

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