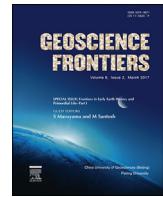




HOSTED BY

Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiersjournal homepage: www.elsevier.com/locate/gsf

Research paper

Nuclear geyser model of the origin of life: Driving force to promote the synthesis of building blocks of lifeToshikazu Ebisuzaki ^{a,*}, Shigenori Maruyama ^b^a RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan^b Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Tokyo, 152-8550, Japan**ARTICLE INFO****Article history:**

Received 24 February 2016

Received in revised form

13 September 2016

Accepted 17 September 2016

Available online 14 October 2016

Keywords:

Origin of life

Chemical evolution

Natural nuclear reactor

Aqueous electron

Radiation chemistry

ABSTRACT

We propose the nuclear geyser model to elucidate an optimal site to bear the first life. Our model overcomes the difficulties that previously proposed models have encountered. Nuclear geyser is a geyser driven by a natural nuclear reactor, which was likely common in the Hadean Earth, because of a much higher abundance of ^{235}U as nuclear fuel. The nuclear geyser supplies the following: (1) high-density ionizing radiation to promote chemical chain reactions that even tar can be used for intermediate material to restart chemical reactions, (2) a system to maintain the circulation of material and energy, which includes cyclic environmental conditions (warm/cool, dry/wet, etc.) to enable to produce complex organic compounds, (3) a lower temperature than 100 °C as not to break down macromolecular organic compounds, (4) a locally reductive environment depending on rock types exposed along the geyser wall, and (5) a container to confine and accumulate volatile chemicals. These five factors are the necessary conditions that the birth place of life must satisfy. Only the nuclear geyser can meet all five, in contrast to the previously proposed birth sites, such as tidal flat, submarine hydrothermal vent, and outer space. The nuclear reactor and associated geyser, which maintain the circulations of material and energy with its surrounding environment, are regarded as the nuclear geyser system that enables numerous kinds of chemical reactions to synthesize complex organic compounds, and where the most primitive metabolism could be generated.

© 2016, China University of Geosciences (Beijing) and Peking University. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

What is life has long been a central topic in biology, at least since the discussion of the origin of life by [Oparin \(1924\)](#). The most accepted definition is three-fold: (1) metabolism, (2) membrane, and (3) self-replication (e.g., [Oparin, 1924; Dyson, 1985](#)). Following these criteria, a virus is not a life, because it cannot replicate by itself. Viruses are in an intermediate position between life and the inorganic world, although intensive debates continue. So far, three possible formation sites of life have been proposed: a tidal flat, submarine hydrothermal vents, and outer space ([Fig. 1](#)).

Considered as one of the most famous experimentations to discuss the origin of life, [Miller \(1953\)](#) and [Miller and Urey \(1959\)](#) detected amino acids (glycine α -alanine, and β -alanine) from a

water condensation in the experiment with electric discharges in a gas mixture of H_2 , NH_3 , CH_4 , H_2O , considered to be possible chemical compositions in the primitive Earth's atmosphere. The electron discharges are used to produce radicals instead of lightning or ultraviolet photons from the Sun to promote reactions for HCN and HCHO and those for further complex organic compounds, such as amino acids, nucleotide, and hydrocarbons. Here, note that key to their success would be the application of electric discharge as a non-thermal energy source with energy density as high as several $\times 10^{-2} \text{ W cm}^{-2}$ ([Table 1](#)).

However, the tidal-flat model has a difficulty in obtaining a sufficient high-density energy source. [Chyba and Sagan \(1992\)](#) estimated global energy dissipation of lightning as $10^{18} \text{ J yr}^{-1}$ and that of ultraviolet light ($\lambda < 200 \text{ nm}$) in the stratosphere from the Sun as $6 \times 10^{20} \text{ J yr}^{-1}$. These correspond to $6 \times 10^{-9} \text{ W cm}^{-2}$ and $4 \times 10^{-6} \text{ W cm}^{-2}$, respectively ([Table 1](#)). Both of them are by far lower than what Miller and Urey used in their experiments. They also estimated the HCN global production rate ($3 \times 10^9 \text{ kg yr}^{-1}$) which corresponds to $20 \text{ nmol cm}^{-2} \text{ yr}^{-1}$. On the other hand,

* Corresponding author.

E-mail address: ebisu@postman.riken.jp (T. Ebisuzaki).

Peer-review under responsibility of China University of Geosciences (Beijing).

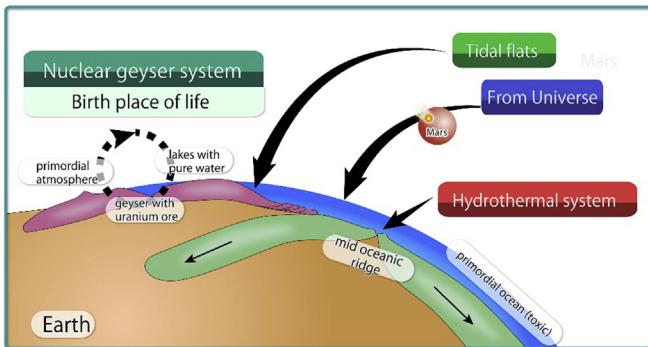


Figure 1. Proposed models for the birth place of life: tidal flats, submarine hydrothermal vents, outer space, and nuclear geyser system (the present work).

Table 1

Energy flux of energy source for the birth of life.

	Energy flux (W cm^{-2})	References
Miller & Urey experiment	$\sim 10^{-2}$	Miller and Urey (1959)
Lightning	6×10^{-9}	Chyba and Sagan (1992)
UV flux from the Sun	4×10^{-6}	Chyba and Sagan (1992)
Natural nuclear reactor		Meshik et al. (2004)
Core	1–10	
Peripheral	$10^{-2}\text{--}10^{-1}$	

Stribing and Miller (1987) estimated the concentration of HCN in the primitive ocean assuming the steady state of hydrolysis and production. At pH 8 and 50 °C, the concentration of HCN, however, was evaluated to be as low as 3×10^{-10} mol/L for the production rate of 100 nmol $\text{cm}^{-2} \text{ yr}^{-1}$. This very low concentration of HCN cannot sustain contraction reactions to form complex biopolymers. For example, Sanchez et al. (1967) pointed out that adenine cannot be formed through polymerization of HCN, when the HCN concentration is less than about $10^{-1}\text{--}10^{-2}$ mol/L; in this case, HCN hydrolysis takes place rather than polymerization.

Following the discovery of hyperthermophile bacteria in the mid-oceanic ridge associated with a deep hydrothermal system (e.g. L'Haridon et al., 1995; Grassia et al., 1996), the submarine hydrothermal vents have been proposed to be a promising site for the origin of life, because hyperthermophile bacteria occurs near the root of the phylogenetic tree by ribosomal RNA. In addition, considering the Hadean surface environment dominated by komatiite lava-flows on the surface, by which olivine-water reaction dominate to produce warm alkaline vents, like Lost City near the present Mid-Atlantic Ridge, driven by serpentinization of mantle materials, produce highly H_2 -enriched water in a temperature range of about 40–90 °C (Kelley et al., 2001; Proskurowski et al., 2006). Such an aqueous environment has been regarded as a favorable site for the formation of organic matters. Thus, Russell et al. (1994), Russel and Hall (1997), and Martin and Russell (2003) proposed the idea that life originated in an alkaline hydrothermal vent at a redox, pH, and temperature-gradient between sulphide-rich hydrothermal fluid and Iron (II)-containing waters along the Hadean ocean floor, because they had known the importance of continuous electron flow as a key, since the Miller-Urey's experiments. The serpentinization of olivine (magnesium–iron silicate) with water is an abundant source of geological reducing power. These reactions occur at a 2–8 km depth beneath the ocean floor in a temperature range of 80–200 °C. Proskurowski et al. (2008) observed C₁ to C₄ hydrocarbons dissolved in hydrogen-rich fluids venting at the ultramafic-hosted Lost City hydrothermal field and showed their abiotic origin through Fisher–Tropsch type reactions, in which

vapor phase mixtures of CO or CO₂ with H₂ occur in the presence of metal catalysts (Kugler and Steffgen, 1979; Anderson, 1984).

The ocean floors, however, lack a supply of necessary nutrients for life, which include nitrogen, phosphate, and potassium as major components of the life body (Maruyama et al., 2013). Concentrations of nitrogen-bearing inorganic molecules (e.g., ammonium and HCN) are found to be highly limited in hydrothermal vents. Although ammonium has been detected in submarine hydrothermal vents (Lilley et al., 1993; Lam et al., 2004), its concentration found to be less than mmol/L (i.e., insufficient to promote further reactions of complex biomolecules). Furthermore, there is few evidence of abiotic formation of amino-acid; although many authors have reported the detection of amino-acid from the fluid of the hydrothermal vents (Horiuchi et al., 2004; Takano et al., 2004; Klevenz et al., 2010; Lang et al., 2013; Fuchida et al., 2014), they are most likely derived from microorganisms living on the inner surface of the chimney.

As for HCN, so far, no reports of its detection have been made from submarine geothermal vents, though Mukhin et al. (1976) reported a trace of CN[−] from on-land volcanic gas of the Alaid volcanoes in the Kamchatka islands. Furthermore, ocean floors covered by basalt are absolutely poor in phosphate and potassium (Maruyama et al., 2013). In summary, a mid-oceanic ridge hydrothermal system lacks nutrients (e.g., biologically accessible nitrogen, phosphate, and potassium). Even if these nutrients are available, the almost infinite dilution by sea water makes accumulation of biosynthetic molecules extremely difficult, in particular, for the primitive biological organizations, which do not have sophisticated membrane structures and material-uptake systems.

The final alternative theory of the origin of life, considered as a last resort in many respects, the interstellar and interplanetary space outside the Earth system has been proposed to form organic materials, since many biosynthetic precursors such as HCN, NH₃, and HCHO are detected in interstellar space through millimeter wavelength radio observations (Snow and Bierbaum, 2008). Ice and dust grains in the cold interstellar environments are continually bombarded by high-energy particles and radiation, producing complex organic molecules (Strazzulla et al., 1991), with >170 molecules discovered so far in the interstellar medium or circumstellar shells. Many more organic compounds, which include amino acids and nucleobases (Kvenvolden et al., 1970), have been detected in meteorites (Engel et al., 1997; Schmitt-Kopplin et al., 2010) and comets (Bockelée-Morvan et al., 2000).

Chyba et al. (1990), however, estimated the accretion rate of organic matter onto the Earth through asteroid and comet impact and found that it is at most 10^9 kg yr^{-1} , and more likely as small as $10^{6}\text{--}10^7 \text{ kg yr}^{-1}$, if the empirical constraints on the impact record are taken into account. As discussed above, this accretion rate is far less than what is required to achieve the necessary contraction reactions of biosynthetic precursors, such as HCHO or HCN, in order to continuously produce biopolymers. The situation is much worse, if a 100 bar-thick atmosphere during Hadean Earth is assumed (Abe and Matsui, 1986; Zahnle et al., 2007). In summary, although interstellar and interplanetary space is a good place to form and accumulate organic matter, impact-induced thermal destruction of the organic matter during its delivery to the surface of the Earth ultimately makes it highly questionable as the origin of life (Hashimoto et al., 2007).

Here, we present the nuclear geyser model as the promising site to lead to the emergence of first life, in which an underground natural nuclear reactor supplied a continuous flow of material and energy to bear primitive life. As can be seen in Table 1, energy flux in the form of ionizing radiation is as high as $10^{-2}\text{--}10^{-1} \text{ W cm}^{-2}$, which would be a promising site to harbor primitive life, as discussed below.

This paper is configured as follows: Section 2 for the description of the surface environment of the Hadean Earth, Section 3 for a natural nuclear, Section 4 for the importance of radiation chemistry as the driving force to promote chemical reaction, Section 5 for the proposal of the nuclear geyser model as a cradle of life, and Section 6 for abiotic formation of biological molecules in a nuclear geyser, followed by discussion and conclusions.

2. Surface environment of the Hadean Earth

Information of the Hadean surface environment is a key to unravel the birth place of life on the Hadean Earth. Maruyama and Ebisuzaki (2017) theorize that the Earth formed as a naked planet without volatiles (i.e., no ocean and no atmosphere during 4.56–4.37 Ga), with subsequent addition of both atmospheric and oceanic components delivered from the outer asteroid belt during 4.37–4.20 Ga, followed by minor peaks until 3.90 Ga. Referring to this as the ABEL-Bombardment model, Maruyama and Ebisuzaki (2017) propose that this event is the most important through Earth's life history because of the delivery of oxidized materials onto reductive Earth initiated through the prebiotic chemical evolution which ultimately led to the birth of life (Maruyama and Ebisuzaki, 2017). After the formation of atmosphere and ocean on the Hadean Earth, plate tectonics started globally to provide a varied and dynamic surface environment.

Rock components exposed on the Hadean Earth were distinct from those of modern Earth. Surface geology reflects the process of consolidation of magma. As the Earth interior cooled down after its initial formation, the residual melts became rich in the incompatible elements that are difficult to be contained in mantle minerals because of large ionic radii (large-ion lithophile elements (LILE): potassium, rubidium, cesium, strontium, and barium) or large ionic valences (high field strength elements (HFSE): zirconium, niobium, phosphorus, rare earth elements (REE), and actinides including thorium and uranium (Albarède, 2009). At last, the minerals enriched in these incompatible elements were crystallized to form a primordial crust at the surface of the Earth. The primordial crust of the Hadean Earth was likely composed of anorthosite, KREEP (potassium (K), rare earth materials (REE), and phosphorous (P))

basalt, as well as reductive iron minerals, such as pyrite (FeS_2) and schreibersite (Fe_3P). KREEP may have been a major component of the lower crust beneath the anorthositic upper crust. In addition, volcanic rocks, dikes, and sills with KREEP composition were likely common both at the surface and in the subsurface of the Hadean Earth before ABEL Bombardment. These rocks and their composing elements may have provided the necessary building blocks for life, especially through rock–water interaction since 4.37 Ga (Fig. 2).

Though Hadean atmospheric conditions remain controversial, there is little doubt that its composition was much thicker than that of the modern Earth. Even so, the visible radiation from the Sun may have always reached the surface of the Earth to drive hydrological circulation, since atmospheric pressure was maintained around 10 bar, according to recent numerical simulation (Hayashi et al., 2016, private communication). Thus, solar energy, weathering, erosion, and transportation of the continental crustal materials, including incompatible elements (P, K, U, and Th) that were critical for building blocks of life, occurred through riverine systems on the Hadean Earth, similar in many respects to what occurs on the modern Earth. Such cycling of nutrients among the landmass, ocean, and atmosphere, conditions of which are conducive for life, is known as Habitable–Trinity conditions (Dohm and Maruyama, 2014). On the other hand, the UV radiation from the Sun and galactic cosmic rays did not reach the surface of the Earth because of the relatively thick (~1–10 bar) atmosphere.

3. Natural nuclear reactors

3.1. Research history and principles of a natural nuclear reactor

The idea of a natural nuclear reactor was first suggested by Zel'dovich and Khariton (1940a,b). Wetherill and Inghram (1953) later showed that naturally occurring ^{235}U concentrated much higher than ^{238}U due to a shorter half-life. Thus, they concluded that natural uranium may have been at a nearly critical state at 2.0 Ga, when the fraction of ^{235}U was 3% more abundant than modern Earth. Subsequently, Kuroda (1956) presented the nuclear reactor theory in geochronology to explain certain interrelations between the age and the nuclear physical stability of the uranium

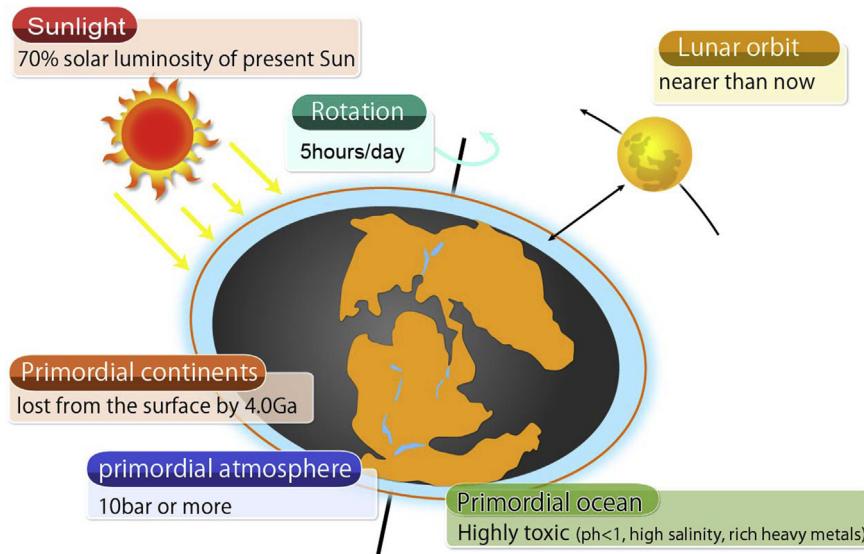


Figure 2. The environment of the Hadean Earth.

minerals and predicted the presence of a natural nuclear reactor. Following the discovery of the natural nuclear reactor in the Gabonese Republic on the west coast of central Africa in 1972 (Bodu et al., 1972; Neuilly et al., 1972; Gauthier-Lafaye and Weber, 2003; Ndongo et al., 2016).

A natural nuclear reactor functions through nuclear fission, which is a reaction of a nucleus upon being split into two or lighter nuclei. Fission may occur without external excitation; for example, ^{238}U (most common isotope of uranium) undergoes such spontaneous fission. During a spontaneous fission, ^{238}U produces 2.2 neutrons on average. Neutrons are classified, on the basis of their energy, into fast (>0.1 MeV), slow (about 1 eV), and thermal (about 0.025 eV). The thermal neutron can induce fission in ^{235}U , which produces two or three neutrons per fission event, while fast neutrons cannot induce fission. In order to achieve a self-sustainable chain reaction, the fast neutrons from such fissions have to lose energy to become thermal neutrons through collisions with protons (hydrogen nucleus). Water, which is rich in hydrogen atoms, is an efficient “moderator” to convert fast neutrons to thermal ones. Since ^{238}U , unlike ^{235}U , does not undergo fission when receiving a neutron, a $^{235}\text{U}/^{238}\text{U}$ ratio is required to be higher than 1% for a self-sustained chain reaction. Since ^{235}U (with half-life of 7.1×10^8 yr) decays faster than ^{238}U (with 4.5×10^9 yr), the $^{235}\text{U}/^{238}\text{U}$ ratio was higher in the past than today, estimated to be 3.5% 2 Ga ago, when the natural nuclear reactors in Oklo were operating (Adam, 2007; Fig. 3).

3.2. Proterozoic natural nuclear reactor in Oklo, Gabon (~2 Ga)

The concept of natural nuclear fission reactions was confirmed by the discovery of ancient (2.0 Ga) reactors in 1972 in uranium deposits of the Francevillian series in Gabon (Bodu et al., 1972; Neuilly et al., 1972). Since then, extensive physical, geochemical, petrological, and geological studies have been conducted (e.g. Draganic and Draganic, 1980; Gauthier-Lafaye and Weber, 2003; Ndongo et al., 2016). So far, 16 individual reactor zones (RZs) have been found in the Oklo in Gabon, several of which are characterized in Table 2. In addition, two more reaction zones have been identified within Okelobondo and Bangombe deposits close to Oklo (Hidaka and Kikuchi, 2010). The RZs consist of high-grade uranium ore (the reactor core) enveloped by a mantle of clay minerals (clays of the reactor core), which are mainly composed of chlorite or illite. The core is a thin layer with a thickness of 0.05–0.3 m, made of high-grade uranium ore (uranium concentration 20–87%;

Table 2
Selected characteristics of natural fission reactors (Janeczek, 1999).

Reactor zones ^a	Size (length × width (m × m))	Thickness of the core (cm)	Maximum UO_2 (%)	Maximum $^{235}\text{U}/^{238}\text{U}$ depletion (%)
RZ1	40 × 18	20–30	40	0.409
RZ2	12 × 18	20–50 locally 100	50–60	0.292
RZ7-8-9	Total length 30	A few	25–30	0.543 RZ9 0.579 RZ7
RZ10	27 × 30 × 15	a few to 100	65	0.479
RZ13	10 × 6	20–30	87	0.380
Bangombe	1.5 km ²	5–15	54	0.590

^a The region that show the anomaly in isotopes of uranium. They are considered as the reaction center of the ancient nuclear reactors.

Gauthier-Lafaye and Weber, 2003). The geology and genesis of a natural reactor are detailed in the following.

The inter-cratonic Franceville Basin contains the 1–4 km-thick Francevillian Series deposited ca. 2.1 Ga on a metagranitic late Archean basement (Gauthier-Lafaye and Weber, 2003), interpreted to be related to the opening stages of an intracontinental rift. The basal Francevillian Formation A (FA) and Francevillian Formation B (FB) are of particular interest from both petroleum and biogeochemical points of view regarding nuclear reactors (Figs. 4 and 5). The 10–100 m-thick basal FA Formation consists of deltaic and fluvial sandstones and conglomerates, which host uranium ore deposits and natural fission reactors. Their color mainly reflects the organic matter in pore spaces, which consists of solidified petroleum (pyrobitumen) that fills the primary and secondary pore spaces of the sandstones and fractures (Gauthier-Lafaye and Weber, 1981; Gauthier-Lafaye, 1986; Cortial et al., 1990; Nagy et al., 1991, 1993). The FA formation is overlain by 600–1000 m-thick marine black shales of the FB Formation. The uranium ore deposits formed along the normal faults which in turn were associated with basin formation.

High-grade U-ore is consistently associated with hydraulic fractures and hydraulic breccias (Gauthier-Lafaye and Weber, 1989; Mossman et al., 2001). Based on this observation, the U ores are believed to have been formed at basement mounds which form directly above the normal fault and radiate out from the basement (Fig. 5). The underground water sub-horizontally migrates just below the impermeable geologic contact between the FA formation (alternating conglomerate and sandstone) and FB (black shale) formation, and turns upwards along the normal fault to erupt on the mound (Fig. 5, Ndongo et al., 2016). Therefore, the U-ore formation occurred through two steps: (1) depositional enrichments of U-bearing minerals from the late Archean basement rocks during basin formation by rifting, and (2) sub-horizontal migration of high-T reduced fluid containing dissolved U ions under oxidizing conditions eventually are routed upward along a fault to accumulate at topographic highs where highly reduced environments were maintained (Ndongo et al., 2016).

Summarizing the formation history of the Oklo natural reactors, detrital U-bearing minerals were concentrated at the tidal off-shores of shallow marine environments. Due to the rapid increase of free oxygen called Great Oxidation Event (GOE) in the Paleoproterozoic, U became more soluble in water. Then, oxygenated surface water dissolved U from U-bearing minerals to penetrate in sandstone beds. U-dissolved underground water migrated from the oxygenated region to the reduced region to precipitate fine-grained U-minerals. Such sites were along the shear zone of the boundary between FA (sandstone dominated) and FB (mudstone-dominated) formations.

The reactor materials show clear isotopic signatures of ^{235}U and ^{239}Pu fission and neutron-capture reactions (Meshik et al., 2004,

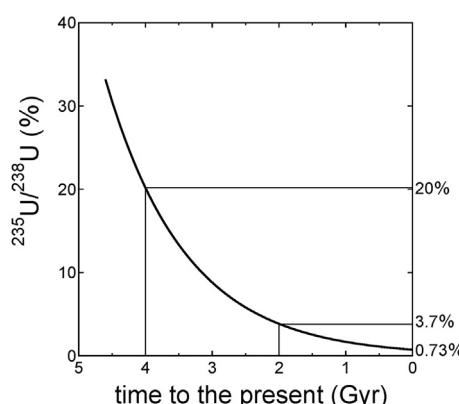


Figure 3. The $^{235}\text{U}/^{238}\text{U}$ ratio was higher than the present (0.73%), being as high as 20% in Hadean Earth (>4 Ga). The isotope ratio $^{235}\text{U}/^{238}\text{U}(t)$ in the past (t Gyr from the present) is calculated by $\exp\left(\frac{0.678}{0.71} - \frac{0.678}{4.5}\right)t$, based on the half-lives of ^{235}U (7.1×10^8 yr) and ^{238}U (4.5×10^9 yr).

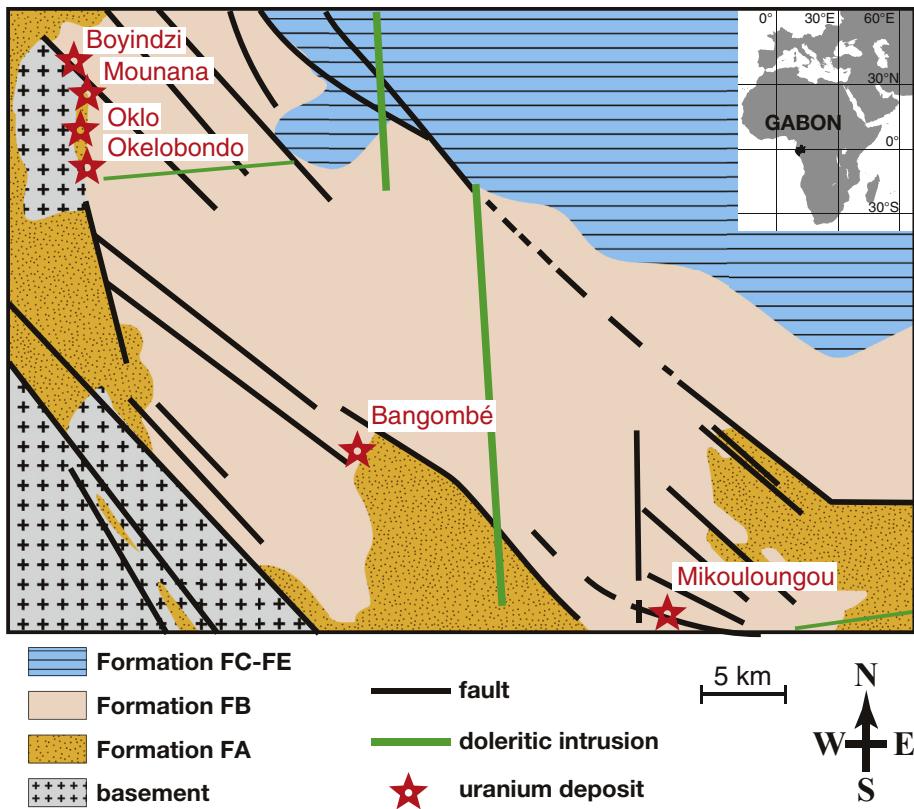


Figure 4. Geological map of Oklo area, Gabon, on the west coast of Central Africa. The map shows the locality of six major U-deposits. Note the ore-body occurs along the shear zones originally generated by high-angle normal faults made when basins were formed (after Bentridi et al., 2013).

reference therein). Isotopic compositions of these elements allowed for reconstruction of effective neutron fluence (up to 10^{21} n/cm²), the amount of consumed ^{235}U (>5 tons), and the energy released (~ 15 GW-yr = 4.7×10^{17} J). Also using fission products of 2400 yr ^{239}Pu , the effective duration of this nuclear fission chain reaction is estimated to be 150,000 yr. The average power is therefore only 100 kW. The specific and isotopic structure of xenon in the mineral defines a cycling operation for a reactor with 30 min active pulses separated by 2.5 h dormant periods (Meshik et al., 2004). This periodic activity is likely to be controlled by water, which works as a moderator to reduce energies of fast neutrons.

The hydrothermal fluids produced by the fission reactions were similar to diagenetic fluids (Mathieu et al., 2001) but their temperatures, as measured in fluid inclusions, were higher, ranging from 280 to 420 °C. They also contained traces of CH₄, CO₂, O₂, H₂, and H₂O₂ (Dubessy et al., 1988; Mathieu et al., 2001), with the latter three species resulting from the radiolysis of water in the core of the reactor.

4. The importance of radiation chemistry: driving force to promote chemical reaction

4.1. Free electrons are key to promote chemical reaction

In a natural nuclear reactor controlled by water, a group of distinctive chemical reactions (so-called radiation chemistry) effectively work because of the strong ionizing radiation emitted by the chain reaction of ^{235}U . Ionizing radiation carries high-energy quanta, which includes charged particles (electrons, protons, helium nuclei, or heavy nuclei), photons (ultraviolet photons, X-rays, and gamma-rays), or neutral particles (neutrons). As defined, high-energy quanta by ionizing radiation have the ability to ionize

molecules and atoms. A high-energy charged-particle perturbs electrons in the atoms to produce free electrons and ions (ionization) through electro-magnetic interaction (Fig. 6; e.g. Lang, 1980). When this process occurs with water containing solved CO₂ and N₂, highly reactive radicals are produced such as aqueous electrons (e⁻_{aq}), hydrogen ions (H⁺), hydrogen molecules (H₂), hydrogen peroxide (H₂O₂), carbon monoxide (CO), and hydrogen (H^{*}), hydroxyl (OH^{*}), carbon dioxide (C^{*}O₂), nitrogen (N^{*}₂), and methyl radicals (CH₃; Getoff, 1994). All of them are reactive enough to activate inert molecules.

Among the above reactive radicals, aqueous electrons are particularly important in radiation chemistry. Aqueous electrons (or hydrated electrons) are free electrons in an aqueous solution surrounding water molecules. They have a life time nearing 10 μs (Hart and Boag, 1962) with a strong reductive power reacting rapidly with many species (Getoff, 1994). Aqueous electrons are originally known as the products of ionizing radiation. However, they can also be produced by UV photons (wavelength of <300 nm) from an UV lamp (Pownier et al., 2009; Pownier and Sutherland, 2010; Ritson and Sutherland, 2012, 2013), and suprathermal electrons or UV photons from electric discharge (Miller, 1953; Miller and Urey, 1959).

In terms of the production of electrons, the electric discharge that Urey and Miller used (Miller, 1953; Miller and Urey, 1959) can be recognized to be the same as the effect of ionizing radiation. Though the mechanism to carry electrons is different from ionizing radiation, it likewise involves the flow of electrons to promote chemical reactions. In addition, a photon with a wavelength shorter than ~300 nm (gamma-ray, X-ray, and UV photon) is the same in its role with ionizing radiation, which kicks out an electron from an atom to produce electrons and a positive ion (Fig. 7).

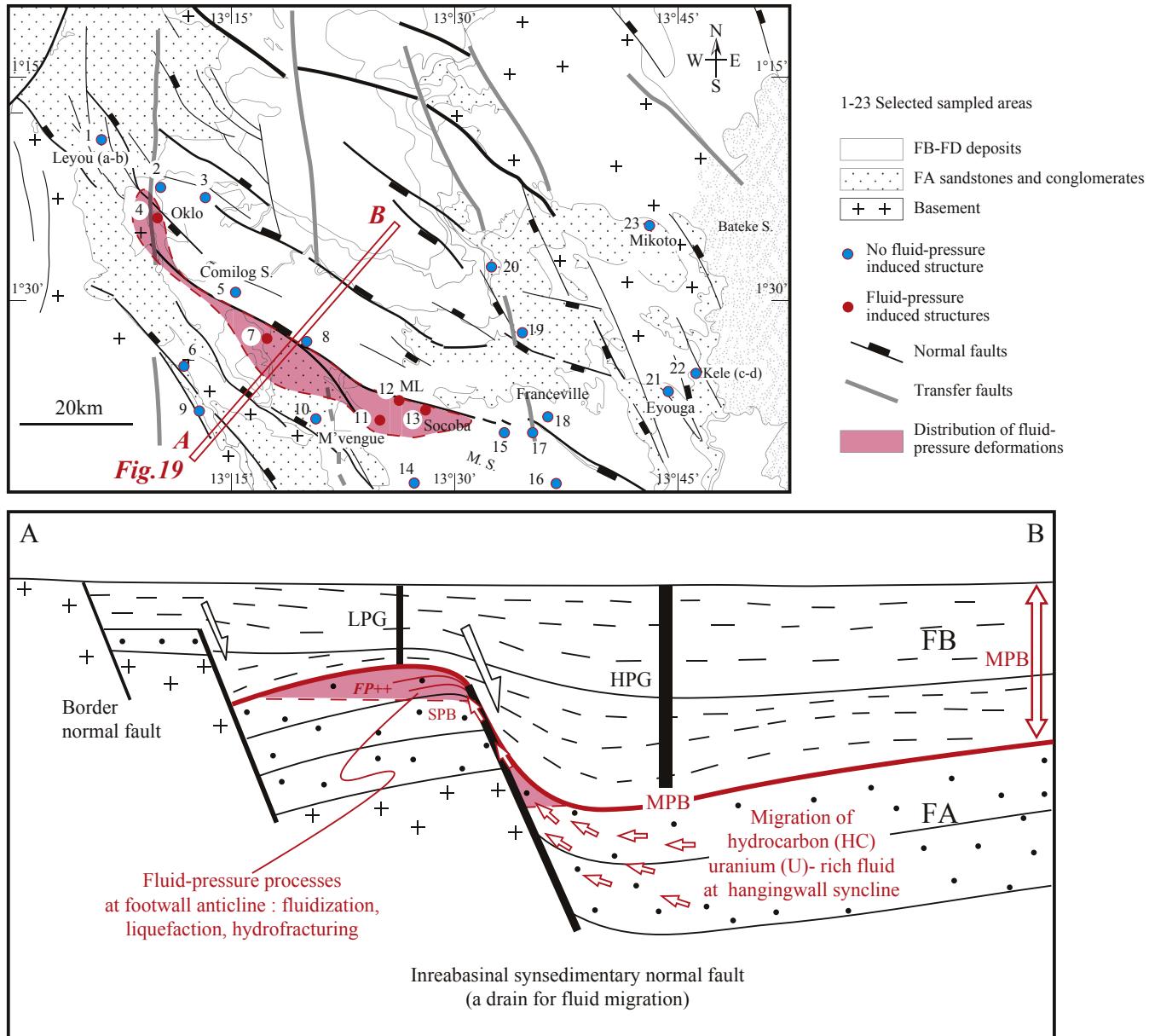


Figure 5. (Top) Geological map of Oklo area, Gabon, West Africa. Top figure shows the locality of six major U-deposits. Note the ore-body occurs along the shear zones originally generated by high-angle normal faults when the basins were formed. Middle figure shows the enlarged map of the Oklo region showing transect A–B of the cross section shown in the bottom figure. (Bottom) Geologic cross section depicting U-enriched underground water circulating to the left in the coarse-grained FA Formation below the Main Permeability Barrier (MPB) until reaching a normal fault (shear zone). Along the fault, the water migrates upward into a reduced environment (black mudstone, FB Formation) where U-minerals are precipitated (LPG, Low Pressure Gradient; HPG, High Pressure Gradient; FP, Fluid Pressure; after Ndongo et al., 2016).

Therefore, the essential process for the chemical reaction is to provide free electrons or ions, whatever their origins may be. Such free electrons or ions become the energy to drive chemical reaction. However, the key is the density of energy flux. For example, the famous Miller and Urey experiment utilized about 10^{-2} W/cm² to produce amino acids, which is an extremely high density of energy flux compared to 6×10^{-9} generated by lightning (Table 1). In other words, the density of energy flux has to be high enough to produce organic compounds. Regarding this point, a natural nuclear reactor is the best energy source with high energy density (Table 1). In contrast, UV flux from the Sun and the energy from hydrothermal vent is extremely small as shown in Table 1.

The advantage of a natural nuclear reactor is the occurrence of radiolysis. Radiolysis is the dissociation of a molecule by ionizing or nuclear radiation. When radiolysis occurs with water containing solved CO₂ and N₂, highly reactive radicals are produced, as described above.

In summary, a chemical reaction is promoted by high-energy free electrons, ions, and highly reactive radicals such as aqueous electrons. They are provided by more than one method, such as ionizing radiation, UV photons, and electric discharges. Therefore, in terms of the source of electrons, they are equal in the production of free electrons. However, the density of energy varies. The density has to be high enough to promote a chemical reaction. Thus, too weak UV photon or energy from a hydrothermal

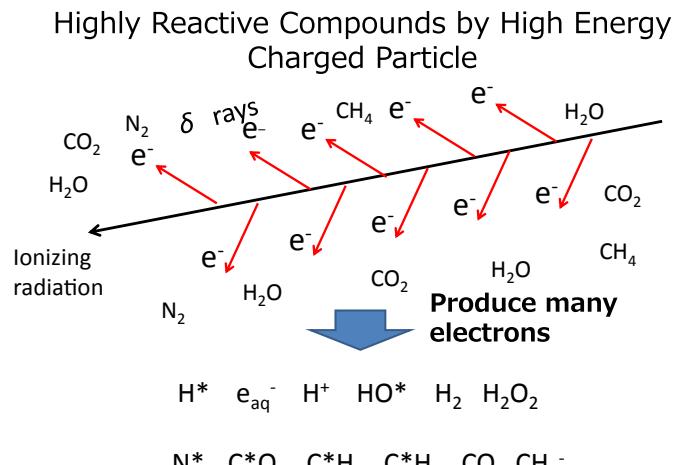


Figure 6. Ionization by a high-energy charged particle produces many electrons and results in a lot of highly reactive radicals and molecules.

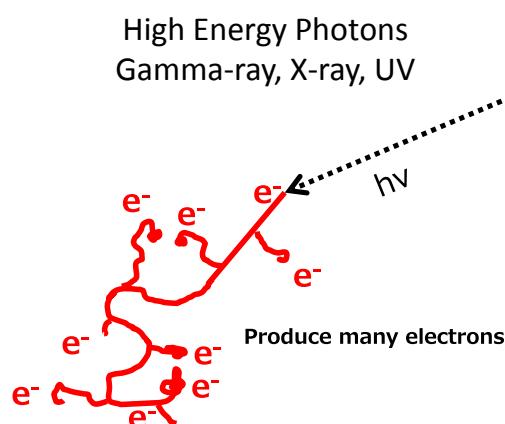


Figure 7. A high-energy photon produces a high-energy electron, which further loses energy through an ionizing process with atoms in media.

vent is insufficient particularly for synthesizing biomolecules. An electric discharge is often regarded to be as strong as ionizing radiation, but a continual supply of energy through an electric discharge is impossible. Therefore, a natural nuclear reactor is considered here to be an optimal energy source to synthesize the building blocks of life through a continual supply of high-density energy.

4.2. Previous works of radiation chemistry associated with biology

The idea that radiation chemistry may play an important role in the chemical evolution of life dates back to the 1940's, after World War II. It was advanced by the discovery of a natural nuclear reactor in Oklo, the Gabonese Republic in central-west Africa. In one case, Adam (2007) conducted a laboratory experiment restoring Miller-Urey type tidal flat environment in a flask to mimic the Hadean tidal beach. Sands, which include minor amounts of monazite, apatite, among other constituents at the bottom with water, and reduced air containing NH₄, CH₄, CO and H₂O, were heated up using radioactive materials in lieu of lightning. Run products of this experiment were confirmed to be

complex organic compounds such as acetonitrile and methanol (Adam, 2007). His experiment was pioneering with regard to the utilization of radioactive material instead of lightning. Although he successfully obtained a small amount of acetonitrile and ethyl acetate in his experiment, it was limited to few cases. Extensive and comprehensive studies of chemical reactions driven by strong ionizing radiation flux have not been conducted yet, despite the individual data of radiolysis yields and radio chemistry which has been accumulating since the initial operation of man-made nuclear reactors (e.g. Draganic, 2005, references therein). On the other hand, chemical reactions driven by aqueous electrons which are produced by UV have been extensively studied (Pownall et al., 2009; Pownall and Sutherland, 2010; Ritson and Sutherland, 2013, 2014).

5. Proposal of nuclear geyser model as a cradle of life

As we explained in earlier sections, previously proposed models for the birth place of first life have various difficulties to bear life. In particular, the energy source to promote chemical reactions to produce organic compounds from inorganic matter is critical. Despite that numerous kinds of synthetic experiments have been conducted, all have remained fragmental. This is because the chemical reaction stops before the syntheses of more complex organic compounds due to production of stable substances like tar (e.g. Benner et al., 2010). The essential point of the tar problem is an insufficient energy supply to promote reaction between tar and other materials. Even if the tar problem was cleared, several more difficulties to emerge life remain, such as the accumulation of gases, mixing of reductive and oxidized materials, among many others. Here, we propose the nuclear geyser model, which reasonably provides a promising site to clear all difficulties, including a chemical reaction that can lead to the emergence of life.

5.1. A natural nuclear reactor associated with geyser

Fig. 8 shows the nuclear geyser model we propose in this paper. A geyser driven by a nuclear reactor composed of uranium ore sprays boiled water into the surface environment periodically. Once the boiled water is sprayed out, surface water flows into the geyser. The return flow of water into the geyser system plays a role as a mediator, so nuclear fission reaction becomes critical for the chain reaction to start to work as a nuclear reactor within a period of several hours. The illumination of ionizing radiation, mainly gamma-rays and neutrons with the energies of ~MeV produces aqueous electrons, radicals, and highly reactive chemicals. They activate inert molecules, such as CO₂, H₂O, and/or CH₄ to form biomolecules through intermediate compounds, such as HCN, HCHO, glycoaldehyde, and glyceraldehyde (details in the next section). High-energy electrons can enable chemical reactions even for the tar-like material. This is the most important factor to suggest the nuclear geyser as the best candidate for the origin of life.

The other important factor of the nuclear geyser is to maintain material circulation in the "nuclear geyser system". A nuclear geyser system comprises a set of environmental factors centered on a nuclear geyser and surrounded by both subsurface and surface environments where material/energy is circulated. Periodic geyser spray can mix various materials between surface materials (basically oxidized) and underground materials (possibly reductive depending on the combination of rock types exposed along the geyser wall). For example, elongation of biopolymers requires repeated dry/wet cycles which is possible both in the underground space of the geyser and in the surface

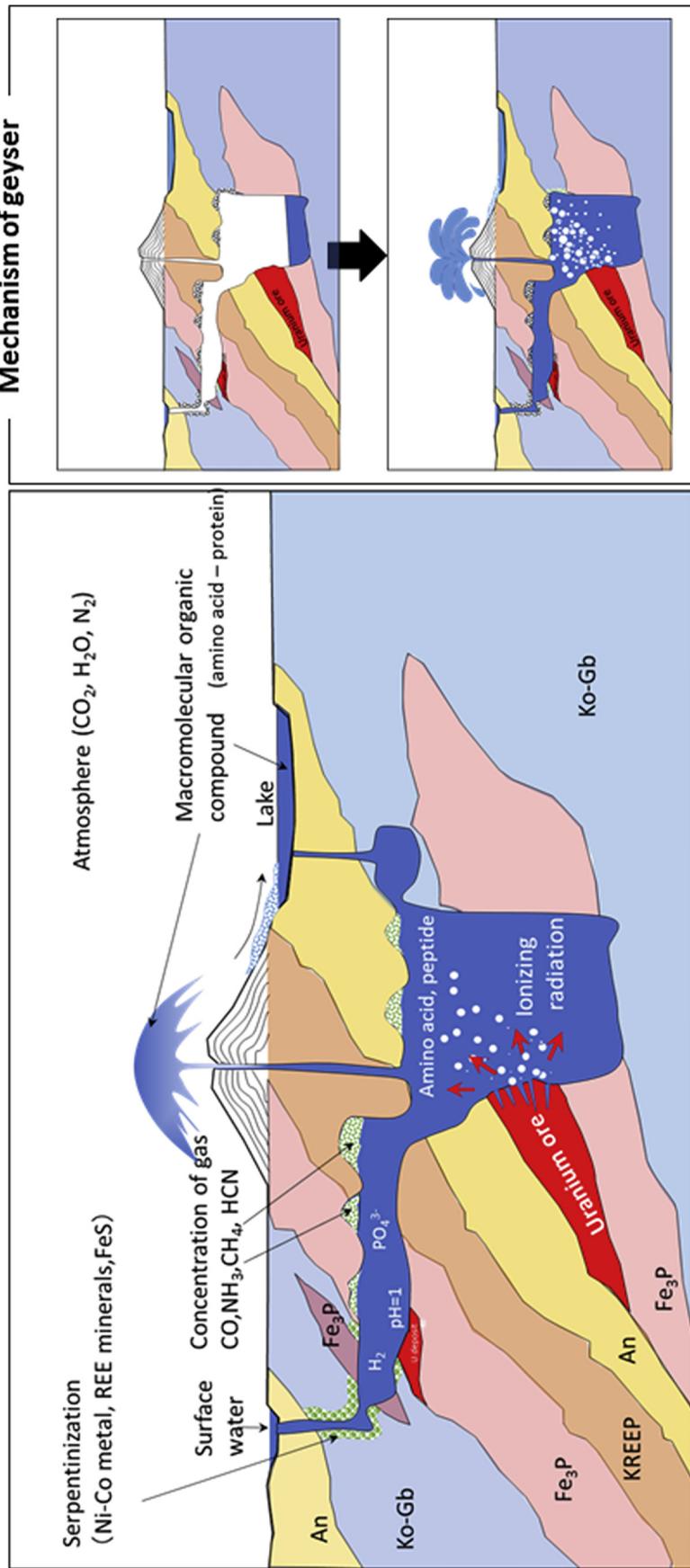


Figure 8. Nuclear geyser model.

environment of the Earth (Lahav et al., 1978; Bujdak et al., 1995, 1996; Lahav et al., 2001; Pant et al., 2009; Shanker et al., 2012). Produced biopolymers can be circulated in nuclear geyser system to interact with other various organic compounds or reductive materials which are generated within the geyser. This circulation process makes it possible to promote next-step synthesis. Furthermore, nutrients (e.g. P, K, S) and transition metals (e.g. Fe, Ni, Co, Zn, Mo, Cu) are supplied continuously from the surface rocks or wall rocks inside of a geyser for the synthesis of more complex biological molecules. Due to the periodic geyser spray, cyclic nature such as warm/cool is also possible. Moreover, the temperature of the geyser's interior is kept under 100 °C, therefore, synthesized macromolecular organic compounds are not broken down.

In addition, the basement rock of Hadean Earth likely contained anorthosite, KREEP basalt, schreibersite, and other various types of rocks exposed at the geyser's interior (Fig. 8). The water running into the geyser causes water-rock interaction with wall rocks to produce reductive gases which is essential to produce biomolecules from highly oxidized molecules such as H₂O and CO₂. Volatile chemicals, such as HCN and HCHO, are confined in an underground space (subterranean cavern) and accumulated in high concentrations along the ceiling of the geyser of the order of 0.1 mol/L, which is required for the polymerization reactions. This contrasts with an open air environment (i.e., subaerial and atmosphere) in which case it is extremely difficult to achieve concentrations that are high enough for polymerization reactions, since the winds disperse the volatile compounds as much as several hundred kilometers away from the point of production.

The nuclear geyser model is the first one to combine radiation chemistry and surface environment to suggest a promising site enabling abiotic chemical reaction to lead to the emergence primitive life. As mentioned in Subsection 4.1, free electrons are key to promote chemical reaction from abiotic process to synthesize organic compounds, regardless of the primary source of those electrons. The nuclear geyser system can clear all difficulties, which includes energy source, density of energy flux, and the accumulation of reductive gases, where most of the biologically important compounds, amino acids for metabolism, nucleotides for self-production, and fatty acids for membrane can be produced by utilizing rich aqueous electrons by ionizing radiation.

Fig. 9 summarizes the chemical reactions driven by ionizing radiation. Operation of a nuclear reactor is controlled by the presence of water, which is driven by the geyser. In case of a low radiation level, which is the dormant phase of the reactor, free electrons or aqueous electrons are not supplied, so chemical compounds do not react with others. H₂O, CO₂, and N₂ is also stable or inert. However, when the reactor reaches a high-radiation level, a flood of aqueous electrons are supplied to promote chemical reactions between inert materials by generation of CH₄, glyco-aldehydo, and glyceraldehyde which can produce more complex chemical compounds. It is worth noting that even nitriles, which are the dead-end products (or tar; Benner et al., 2010) at a low-radiation level, are able to react again to become important starting materials once a nuclear geyser is in an active mode. Therefore, tar is not just a dead-end material but an important reservoir of the intermediate materials.

5.2. Principle of nuclear reactor driving a geyser

Based on the knowledge of the Oklo natural reactor, we constructed a model to express the behavior of a reactor (Fig. 10). It is governed by two ordinal differential equations:

$$\frac{dT}{dt} = \frac{E}{\pi D^2 z C_v} - \frac{k(T - T_0)}{z^2 C_v} - \frac{h_s q_s - h_w q_w}{z C_v} \quad (1)$$

and

$$\frac{dw}{dt} = \frac{q_w - q_s}{z \phi \rho_w} \quad (2)$$

where T and w are the temperature of the core and the water fraction in the coarse grained sand layer, respectively. Here E , C_v , k , T_0 , q_s , q_w , h_s , and h_w are respectively the power of the nuclear reactor, the specific heat of the reactor material, k ($\sim 1 \text{ J K}^{-1} \text{ m}^{-2}$), the heat conduction coefficient, the external temperature, steam outflow flux, water inflow flux, and specific enthalpies of steam and liquid water. The power is given by:

$$E = E_0(w - w_c)$$

where E_0 is a constant determined by the thickness and grades of the reaction core, and w_c is the critical water fraction. The steam outflow flux is assumed to be expressed by a linear function of excess pressure as:

$$q_s = (c_0 \max(p_e - p_0, 0) + c_1)w \quad (3)$$

and water inflow flux:

$$q_w = \begin{cases} 0 & \text{for } t < \tau \\ c_3(\phi - w) & \text{for } t > \tau \end{cases} \quad (4)$$

where ϕ is the porosity of the coarse grained sand layer, p_e is the evaporation pressure, p_0 is the external pressure, and τ the recovery time of water inflow (Fig. 10). We simulated the operation of the nuclear reactor by integrating Eqs. (1) and (2) in the condition summarized in Table 3. The periodic operation was clearly simulated (Fig. 11). In the periodic operation of the reactor, water containing the CO₂, N₂, and CH₄ flows into the reactor zone, is heated and irradiated to be steam containing HCN, HCHO, and NH₃, and then flows out from the reactor zone (Fig. 10). The reactor operates as a geyser:

- (1) when water fraction (w) exceeds the critical water fraction (w_c), a chain reaction initiates because of an increase in thermal neutrons by water, and the temperature increases because of the excess energy production over conduction cooling;
- (2) when temperature (T) reaches the boiling temperature, the boiling of water and the outflow of steam initiates simultaneously, while water inflow terminates;
- (3) because of the steaming outflow, w decreases and eventually reduces down to w_c . The reduction in thermal neutrons shuts down the chain reaction, and the temperature starts to decrease through conduction. On the other hand, when T decreases down to the boiling temperature, the outflow of steam terminates, but the water inflow does not recover until the recovery time τ passes;
- (4) after water inflow recovers, the water fraction increases to initiate the next cycle.

It should be noted that the maximum temperature is determined by P_0 , and the period of the cycle is determined by τ of the water inflow and cooling time of the core ($\sim k/\pi D^2 z^2 C_v$).

5.3. Potential sites to have a nuclear geyser system

The Oklo natural nuclear reactor at 2.1 Ga is an example of a reactor formed in a natural environment at a rifted basin during

Radiation drives biomolecule production

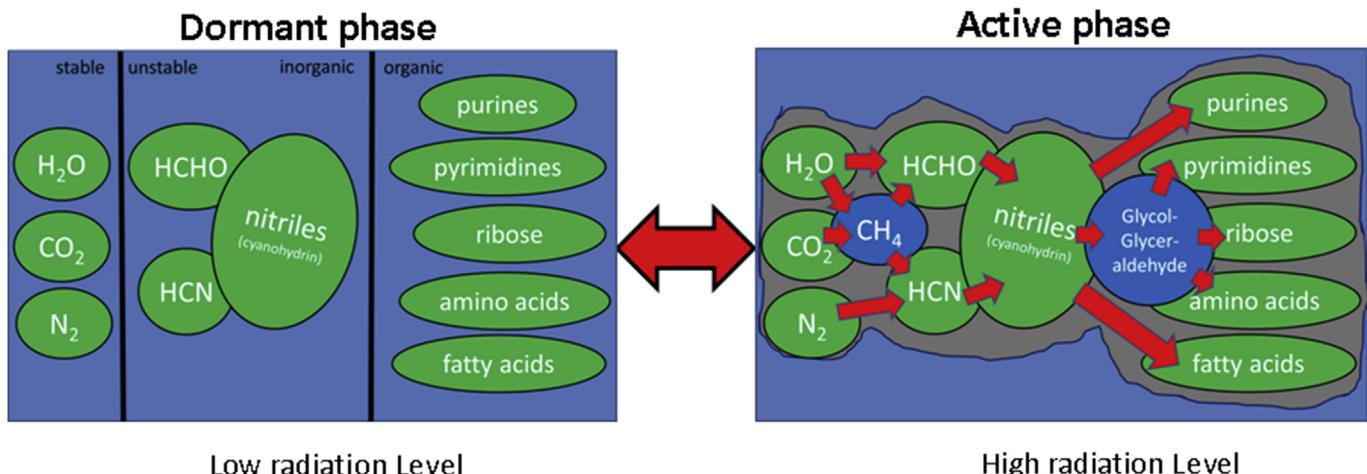


Figure 9. Ionizing radiation from nuclear reaction drives chemical reactions from H₂O, CO₂, and N₂ to biological compounds (amino acids, nucleotides, and fatty acids) through intermediate molecules (HCN, HCHO, glycoaldehyde, and glyceraldehyde). The network of abiotic chemical compounds in a natural nuclear reactor. (Left) Compounds are isolated from one another in a dormant phase without ionizing radiation. (Right) The ionizing radiation drives chemical reactions to form most of the biological compounds abiotically.

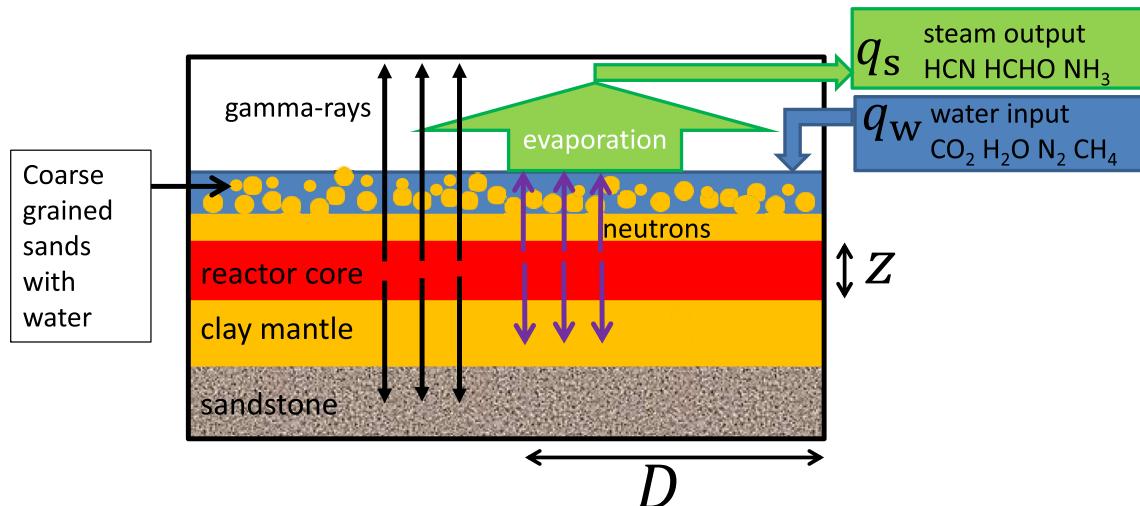


Figure 10. The schematic cross section of the numerical model of the reactor region. The reactor core is composed of a disk made of high-grade uranium ore with a radius of D and the thickness of z . It is sandwiched by a clay mantle, overlaid by a layer composed of coarse-grained sands. Liquid water flows in and accumulates in the sand layer. Neutrons and gamma-rays, emitted from ²³⁵U, deposit in both the water and steam. Water containing the CO₂, N₂, and CH₄ flows into the reactor zone, the water is heated and irradiated to be steam containing HCN, HCHO, and NH₃, and then flows out from the reactor zone. The radiation chemistry to produce these chemical compounds is discussed in Section 4.

Paleoproterozoic Earth. Natural nuclear reactors are rare in the Proterozoic, because of exponential U decay, rare U-bearing minerals, and right after the Great Oxidation Event events (e.g. Catling et al., 2001).

Compared to the modern Earth, however, natural nuclear reactors were much more common on Hadean Earth largely because of the following two points: (1) the concentration of nuclear fuel was about 30 times higher at 4.6 Ga (Fig. 3; Adam, 2007), considering that ²³⁵U has a half-life equaling 7×10^8 yrs, compared to the much longer half-life of ²³⁸U equaling 4.5×10^9 yrs, and (2) a higher possibility of the formation of uranium ore deposits on the Hadean Earth, as the total planet was once melted to form magma ocean and then solidified under the highly reduced condition of Hadean Earth without volatiles. During the

solidification of magma-ocean at 4.53 Ga, actinides such as uranium and thorium as well as P and K were highly concentrated in residual liquids as they cooled down, since they had larger ion radii and were difficult to be included in mantle minerals. The residual liquids produced KREEP basalt together with a buoyant anorthositic upper felsic crust. The KREEP liquids often erupted on the surface fed by feeder dikes and sills, but mostly underplated to form relatively thick (>100 km) lower mafic crust. U-bearing minerals were crystallized as igneous minerals such as uraninite, and others in magma pockets and/or finally veinlets together with quartz, apatite, zircon, monazite, schreibersite, and others (Fig. 12).

Therefore, crustal materials with highly concentrated uranium were ubiquitous on Hadean primordial continent. Together with

Table 3
Parameters of the Nuclear geyser.

Parameters	Values
Radius (D)	3 m
Thickness (z)	0.3 m
Porosity (ϕ)	0.1
Critical water fraction (w_c)	0.05
Power coefficient (E_0)	6×10^7 W
External pressure (p_0)	1 bar
Flow conduction coefficient	$c_0 = 1.0 \times 10^{-2}$ kg s $^{-1}$ m $^{-2}$ /bar $c_1 = 1.0 \times 10^{-2}$ kg s $^{-1}$ m $^{-2}$ $c_2 = 3.0 \times 10^{-3}$ kg s $^{-1}$ m $^{-2}$
Inflow recovery time (τ)	7×10^3 s
Maximum temperature	100 °C
Period	1.3×10^4 s
Average power	4.2×10^4 W
Average steam production rate	1.2×10^{-2} kg s $^{-1}$

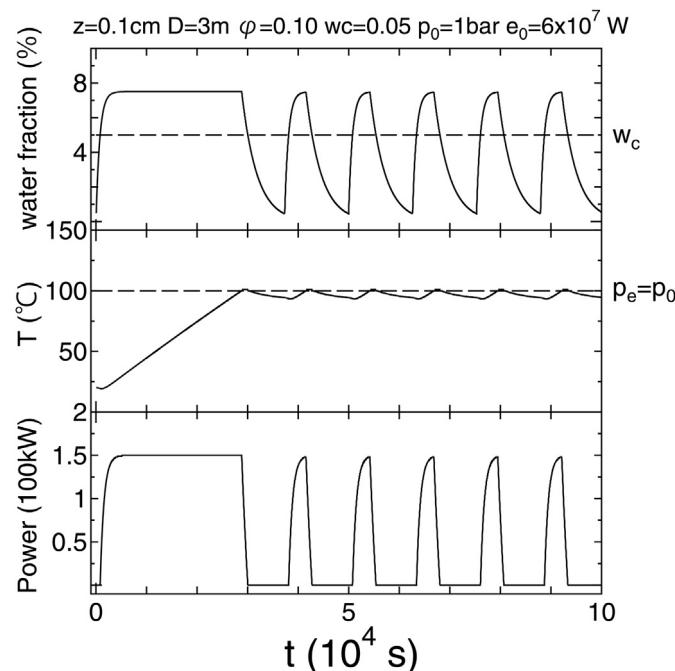


Figure 11. The numerical simulation of a modeled natural nuclear reactor.

the ratio of $^{235}\text{U}/^{238}\text{U}$, which is estimated to be 20% more than Oklo, potential occurrence of uranium deposits is thought to be high.

160 million years after the solidification of the magma ocean, ABEL Bombardment began to deliver water, CO_2 , N_2 , and other volatiles to the Earth (Maruyama and Ebisuzaki, 2017), through extensive destruction of the primordial continents to expose the mid- to sub-crustal level rocks including U-ore bodies. For example, huge asteroid impacts formed impact basins reaching thousands of kilometers in diameter, and mantle materials remelted and to form KREEP basalts filling the crater. Such KREEP basalts became the oceanic lithosphere, which is overlaid by the liquid water landed by the bombardment. As a result, ca. 4 km thick ocean was formed and initiated plate tectonics (Fig. 12: middle and bottom).

It is likely that the ocean appeared by the middle of the Hadean, presumably by 4.37 Ga or at latest by 4.2 Ga, water had been circulated in the surface environment. When plate tectonics started to operate, plate-boundary (divergent, convergent, and transform) processes began. The development of a divergent plate boundary often included the formation of numerous faults and the deposition

of abundant sedimentary materials. As large amounts of sedimentary rocks were amassed, organic matters were buried to accumulate oxygen in the atmosphere (Maruyama et al., 2014). If such a process adequately progressed, an Oklo-type nuclear reactor could occur along a normal fault at a divergent boundary. Also, a subduction zone is another potential site to have a nuclear reactor where active volcanism and sedimentation occurred. Or it could be formed directly by the igneous origin of U-ores. Thus, there were likely two types of nuclear reactors: primary (magmatic) and secondary (Oklo type). By the end of the Hadean, lacustrine environments (e.g., lakes and swamps) were abundant. The combination between an underground cave, water, and uranium deposits was likely a common occurrence, with nuclear geysers producing the building blocks of life.

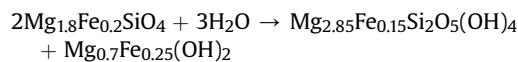
6. Abiological formation of biological molecules in a nuclear geyser

In this section, we explain how organic compounds are produced from inorganic compounds, like H_2O , CO_2 , and N_2 , which were available from the atmosphere of the Hadean Earth, or mineral components such as P and K derived from the Hadean landmass.

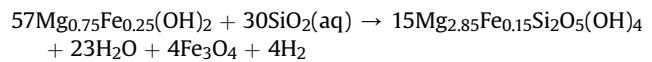
6.1. H_2 and CH_4

In the Hadean, surface-predominant rocks were anorthosite, KREEP basalt, and komatiite. Komatiite consists of 60% olivine, 15% plagioclase, and 10% Ca-poor and Ca-rich pyroxenes with subordinate amount (a few %) of Cr-spinel. Komatiitic magma is similar to mantle composition due to a high degree of melting, hence referred to as ultramafic magma (e.g. Svetov et al., 1999). Water-rock interaction by ultramafic komatiite causes serpentinization to generate hydrogen gas (Sleep and Meibom, 2004), which is typically produced when a mineral assemblage is dominated by serpentine along with magnetite, brucite, and/or talc (Bach et al., 2006; McCollom and Bach, 2009). The serpentinization results in the predominance of serpentine associated with accessory minerals including chromite, FeS_2 , NiS_2 , and native metal. Generation of H_2 during serpentinization results from the reaction of water with ferrous iron [Fe(II)] derived from the fayalite component in olivine and the FeSiO_3 component of pyroxene. In the reaction, ferrous Fe is oxidized by water to ferric iron [Fe(III)], which precipitates magnetite, while hydrogen from water is reduced to H_2 .

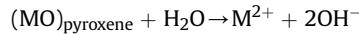
At moderate temperatures, serpentine and ferrobrucite are products from two stages of serpentinization of komatiite, both Mg-rich and Al_2O_3 -poor olivines (Bach et al., 2006; McCollom and Bach, 2009), as shown by the following reaction:



Olivine serpentine ferrobrucite



These solutions can become alkaline because of high solubility of brucite releasing OH^- , as shown by the following reaction:



Although free silica is rendered extremely soluble as H_2SiO_4^- and H_3SiO_4^- at pH > 10 (Kehew, 2001), aqueous silica from orthopyroxene would tend to react with ferrobrucite in the convective

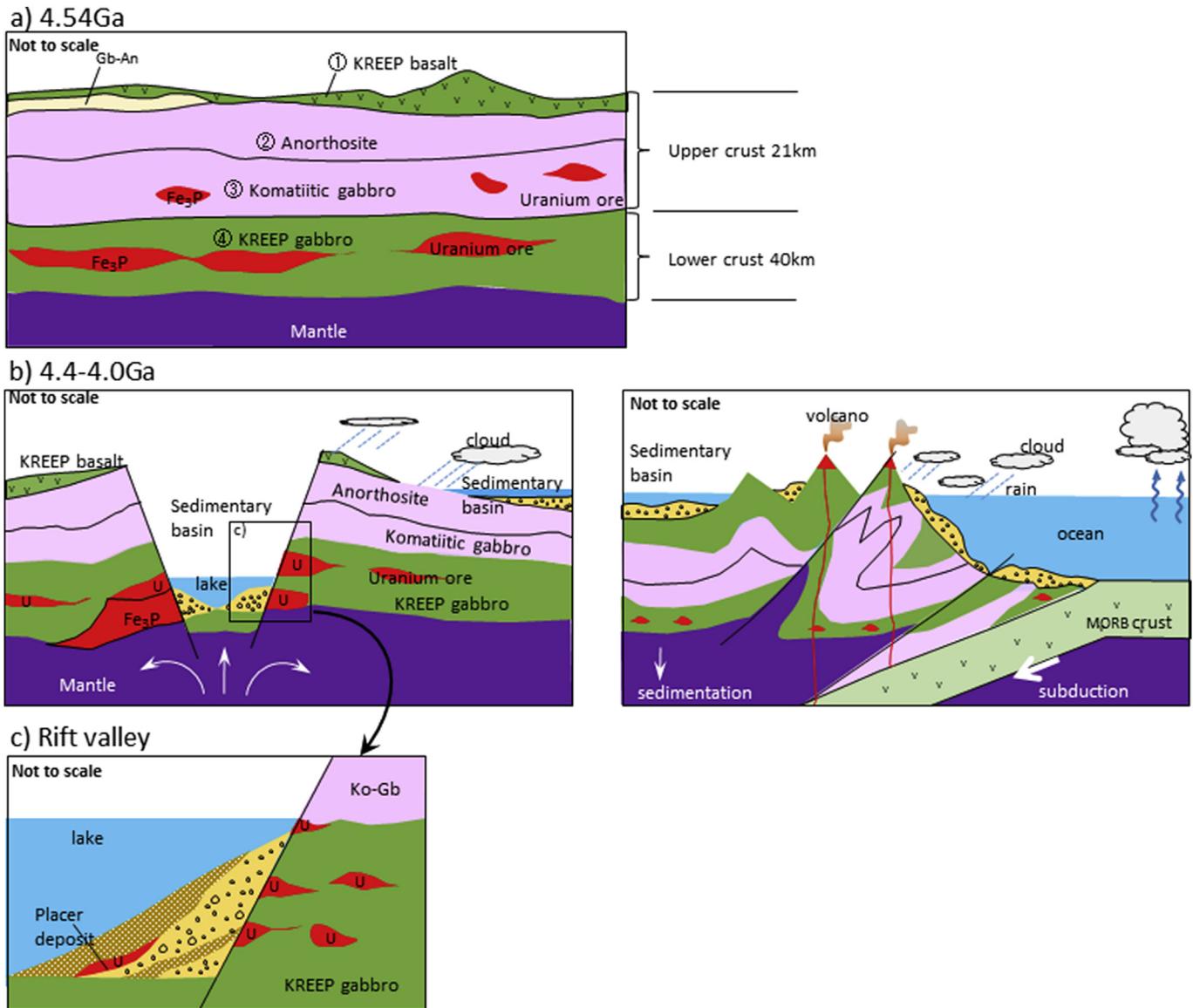
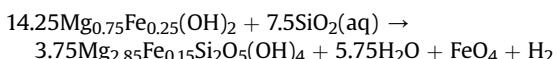
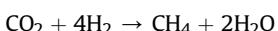


Figure 12. Possible sites for the nuclear geyser on the Hadean Earth. Left-top shows a schematic illustration of primordial continents through the solidification of magma ocean. The three-fold components of topmost cover of KREEP volcanics, anorthositic middle crust underplated by KREEP mafic lower crust on the mantle. Small red parts show U-ore formed through the final and latest solidification of magma ocean. When plate tectonics started to operate, plate boundary processes began, divergent (middle left), convergent (middle right) and transform boundaries. Left bottom: Along the normal fault, the Oklo-type nuclear geyser can be expected to occur commonly either two-steps process same as in Oklo or directly geyser system in Fig. X on the igneous origin of U-ores. Right: Along the subduction zone, a variety of U-ore can be formed, either type of primary (magmatic) or secondary (Oklo type).

updrafts to further produce serpentine, magnetite, and hydrogen (Bach et al., 2006; Frost and Berard, 2007), as shown by the following reaction:



On the other hand, methane is formed by a Fisher–Tropsch type reaction or Sabatier reaction from H_2 and CO_2 (Foustoukos and Seyfried, 2004), as shown by the following reaction:



This reaction often takes place in the present Earth around ultramafic minerals including olivine and ophiolite (Abrajano et al., 1988; Charlou et al., 2002; Etiope, 2011; Tassi et al., 2012; Etiope et al., 2013; Etiope and Lollar, 2013). Neubeck et al. (2011)

conducted a series of low-temperature ($30\text{--}40^\circ\text{C}$), long-term (up to 10 months) weathering experiments in which they tested the CH_4 - and H_2 -formation potential of forsterite olivine; they determined that it is likely that minerals such as magnetite (Fe_3O_4) and chromite (FeCr_2O_4) and other metal-rich minerals found on the surface of olivine catalyze the formation of CH_4 .

6.2. Phosphate (PO_4)

The source of solid Earth is assumed to be enstatite chondrite-like materials (Maruyama and Ebisuzaki, 2017), with schreibersite ($(\text{Fe}, \text{Ni})_3\text{P}$) as a minor constituent (Pasek and Lauretta, 2008). Through the consolidation of the magma ocean, phosphorus as a typical incompatible element was concentrated in the residue of magma. Therefore, schreibersite was likely commonly present on the primordial continent where a reductive surface environment

was maintained due to no ocean and atmosphere (Pasek and Lauretta, 2005; Bryant and Kee, 2006; Pasek et al., 2007; Bryant et al., 2009; Maruyama et al., 2013; Maruyama and Ebisuzaki, 2017). Such an environmental condition is also corroborated by the discovery of schreibersite in Apollo samples returned from the Moon (El Goresey, 1971).

After water and other volatile elements accumulated during the ABEL Bombardment (Maruyama and Ebisuzaki, 2017), schreibersite would have begun to react with water to release P compounds, including P^{3+} phosphite HPO_3^{2-} and P^{1+} hypophosphite $H_2PO_2^-$ (Pasek and Lauretta, 2005; Bryant and Kee, 2006; Pasek et al., 2007; Pask et al., 2008; Bryant et al., 2009; Pech et al., 2009). This exothermic reaction could drive reactions to produce nucleotides from HCN, cyanoacetylene, glycoaldehyde, and glyceraldehyde. In these reactions, phosphates are essential as an acid/base catalyst, a nucleophilic catalyst, a pH buffer, and a chemical buffer, as well as a reactive ligand (Pownall et al., 2009).

Hydrogen-containing phosphate minerals like whitlockite ($Ca_{18}Mg_2H_2(PO_4)_{14}$), newberryite ($MgHPO_4 \cdot 3H_2O$), brusite ($CaHPO_4 \cdot 2H_2O$), and struvite ($MgNH_4PO_4 \cdot 6H_2O$) are important secondary phosphate minerals on the Hadean Earth (Handschuh and Orgel, 1973). By heating, their protonated orthophosphates react to form condensed phosphates and water (Sales et al., 1993; Arrhenius et al., 1997). The phosphate condensation is attributed to the protonation of the phosphate, because the hydrogen reacts with one of the oxygen ligands of the phosphorous through heating, and subsequently becomes a water molecule. As a result, the structure of the orthophosphate (PO_4^{3-}) is rearranged to form one or more anhydride P–O–P bonds (Arrhenius et al., 1997), which is the backbone of condensed phosphates. Experiments of newberryite have revealed that dehydration of this crystalline mineral upon heating results in an amorphous and more soluble phase (Sales et al., 1993). During the initial stage of the dehydration process (100–300 °C), condensation of pyrophosphate occurred, while at about 200 °C, triphosphate (PPPi) appeared.

6.3. Hydrogen cyanide (HCN)

Hydrogen cyanide (HCN) is formed in a reductive atmosphere (with CH_4 or NH_3) through the supply of high-energy electrons generated by ionizing radiation, electric discharge, among other processes. Table 4 shows the energy yield for HCN measured under various conditions. Under the presence of CH_4 , the energy yield of HCN is as high as $1\text{--}30\text{ nmol J}^{-1}$.

The production rate (K_{HCN}) of HCN by a nuclear reactor is given by:

$$K_{HCN} = G_{HCN}P = 1.0 \times 10^{-3} \left(\frac{G_{HCN}}{\text{nmol J}^{-1}} \right) \left(\frac{P}{\text{MW}} \right) \text{ mol s}^{-1} \quad (5)$$

Table 4
Energy yield of HCN by electric discharge experiments.

Gas mixture	Yield (nmol J ⁻¹)	Reference
$CH_4 + N_2$	27	Toupance et al. (1975)
$CH_4 + NH_3$	27	Capezzuto et al. (1973)
$CH_4 + N_2$	4.7–96	Briner and Baerfus (1919), Briner et al. (1938), Briner and Hoefer (1940)
$CO + N_2 + H_2$		
$CH_4(100) + N_2(100) + H_2O(400)^a$	2–10	Stribling and Miller (1987)
$CO(100) + N_2(100) + H_2O(400)^a$	1–4	
$CO_2(100) + N_2(100) + H_2O(400)^a$	0.1–0.4	

^a The numbers in parentheses are the partial pressure of gas in torr.

where G_{HCN} is the production yield of HCN and P is the power of the reactor. The concentration (X_{HCN}) of HCN in a nuclear reactor cooled by water is given by:

$$X_{HCN} = \frac{PG_{HCN}}{P/H} = G_{HCN}H \\ = 0.23 \left(\frac{G_{HCN}}{\text{nmol J}^{-1}} \right) \left(\frac{H}{2.3 \text{ MJ kg}^{-1}} \right) \text{ mol/L} \quad (6)$$

where H is the evaporation enthalpy of water. The availability of H_2 and CH_4 in a Hadean nuclear geyser is discussed in Subsection 6.1 and that of NH_3 in Subsection 6.3.

It is worth noting that the oligomerization of HCN cannot occur unless the concentration of HCN is sufficiently high at least 0.01 M (e.g., Oro, 1960; Sutherland and Whitfield, 1997a,b), as seen in Section 6.

6.4. Formaldehyde (HCHO)

Formaldehyde (HCHO) is formed by the supply of high-energy electrons under a reductive atmosphere (with CH_4 or NH_3) as shown in Table 5, which we summarize the energy yield for HCHO measured under various conditions. Under the presence of CH_4 , the energy yield of HCHO is as high as $1\text{--}15\text{ nmol J}^{-1}$. The concentration of HCHO can be estimated by substituting HCN with HCHO in Eqs. (1) and (2).

6.5. Glycoaldehyde, glyceraldehyde, ammonia, and amino acids

Hydrogen cyanide (HCN) and formaldehyde (HCHO) react with each other to form glycolonitrile (hydroxyacetonitrile; Fig. 13), which was thought to be the termination product of the reaction (e.g., Galimov, 2006). However, in the presence of aqueous electrons produced by ionizing radiation, it is converted to glycolaldehyde and NH_3 , as an important starting point of the reactions that form various organic chemicals (Ritson and Sutherland, 2012, 2013). The glycolaldehyde further reacts with hydrogen cyanide which yields glyceraldehyde and NH_3 through 2,3-dihydroxipropanenitrile (Ritson and Sutherland, 2012, 2013). A series of reactions produce precursors to form glycine, alanine, serine, and threonine through Strecker's reaction with hydrogen cyanide (Fig. 14).

It should be noted that glyceraldehyde is one of the key compounds in prebiotic synthesis of biological molecules not only for amino acids (this subsection), but also nucleotides (Subsection 6.6) and ribose (Subsection 6.7). One of its phosphorylated forms, glycolaldehyde-3-phosphate also occurs in the middle point of the glycolysis in the modern biological organism as discussed in Subsection 7.2.

6.6. Nucleobases, nucleoside, and nucleotide

A series of contraction reactions of HCN, one of the major products of spark discharge in the various gas containing methane

Table 5
Energy yield of HCHO by electric discharge experiments.

Gas mixture	Yield (nmol J ⁻¹)	Reference
$CH_4 + H_2O$	13	Thornton and Sergio (1967)
$CH_4 + H_2O$	0.87	Mourey et al. (1981); Boussard and Toupance (1981)
$CH_4(100) + N_2(100) + H_2O(400)^a$	3–14	Stribling and Miller (1987)
$CO(100) + N_2(100) + H_2O(400)^a$	0.4–3	
$CO_2(100) + N_2(100) + H_2O(400)^a$	0.1–0.3	

^a The numbers in parentheses are the partial pressure of gas in torr.

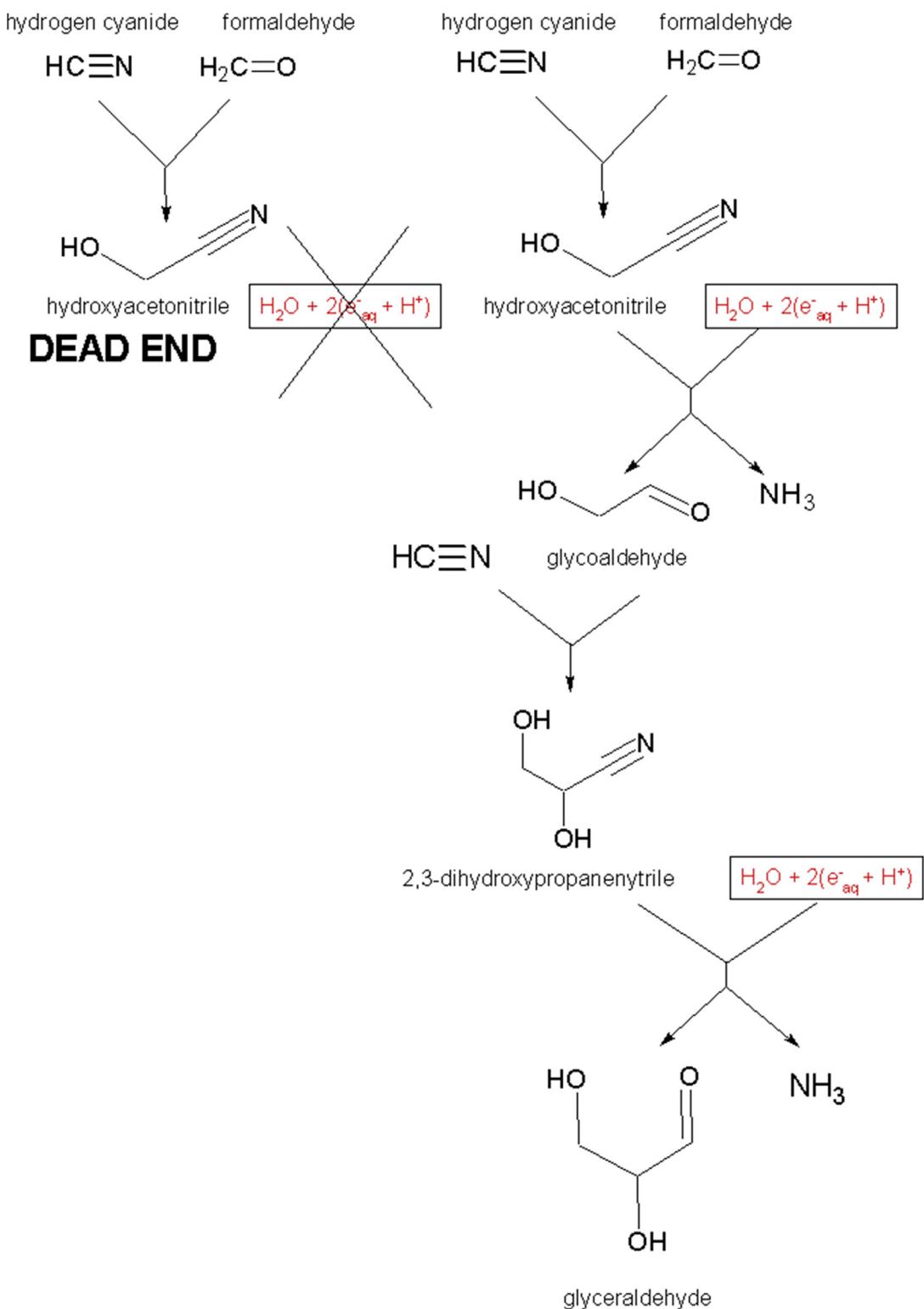


Figure 13. The formation of glycoaldehyde, glyceraldehyde, and ammonia from HCN and HCHO is driven by aqueous electrons, supplied by ionizing radiation (right). Hydroxynitrile was the dead end of the reaction for the case of no hydrated electrons (left).

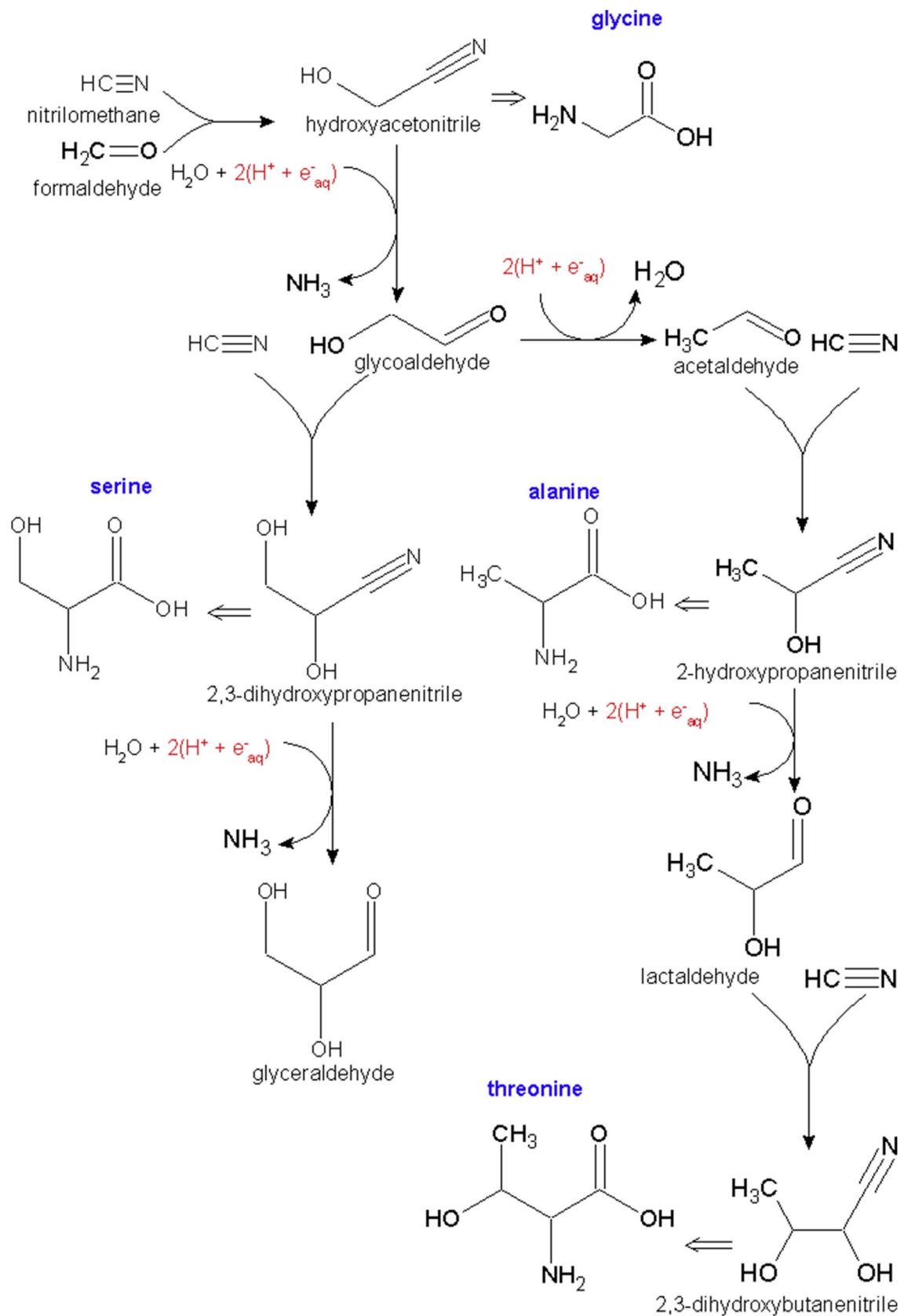


Figure 14. Strecker precursors of amino acids are produced by a series of reactions driven by aqueous electrons (Ritson and Sutherland, 2012; Ritson and Sutherland, 2013).

and nitrogen (Oro, 1960; Lowe et al., 1963; Ferris and Orgel, 1966a,b; Sanchez et al., 1967; Orgel and Lohrmann, 1974; Ferris, 1984), gives a HCN tetramer, diaminomaleonitrile (Fig. 15). Both the intermolecular photochemical reaction which yields to 5-aminoimidazole-4-carbonitrile (AICN) and subsequent hydrolysis of AICN to 5-aminomidazole-4-carboxamide (AICA) were demonstrated over 40 years ago (Fig. 15).

However, the further contraction of aminoimidazoles and AICA to give the purine nucleobase and subsequent ribosylation and phosphorylation to provide the adenine has both low yield and non-selective over their isomers. Furthermore, other canonical nucleotides, guanine, cytosine, and uracil do not give any of their respective nucleotides under similar conditions (Anastasi et al., 2007).

Recently, Powner et al. (2009) found a step-by-step reaction route starting from cyanamide, cyanoacetylene, glycolaldehyde, glyceraldehyde, and inorganic phosphate to produce cytidine and uridine (Fig. 16). All of them are likely to be available in a natural nuclear reactor. First, Schimpl et al. (1965) found that cyanamide is formed by either UV irradiation of CN solution or electron beam irradiation of a mixture of CH₄, NH₃, and H₂O. Second, cyanoacetylene is produced by electric discharge in a CH₄ and N₂ mixture (Sanchez et al., 1967). Third, the availability of glycolaldehyde and glyceraldehyde has been shown in the previous section and that of inorganic phosphate will be discussed in Subsection 6.2. It is worth noting that the presence of inorganic phosphate is essential from the beginning as it controls three reactions in the earlier stages by

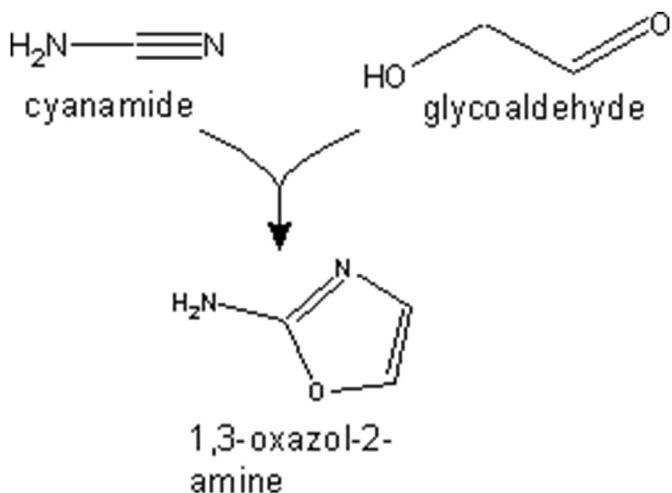


Figure 16. The contraction reaction of glycolaldehyde and cyanamide produces 2-aminoxizalo which is key to form β-ribonucleotide phosphate (Powner et al., 2009).

acting as a general acid/base catalyst, a nucleophilic catalyst, a pH buffer, and chemical buffer, although inorganic phosphate is only incorporated into the nucleotide at the last stage of the sequence (Powner et al., 2009).

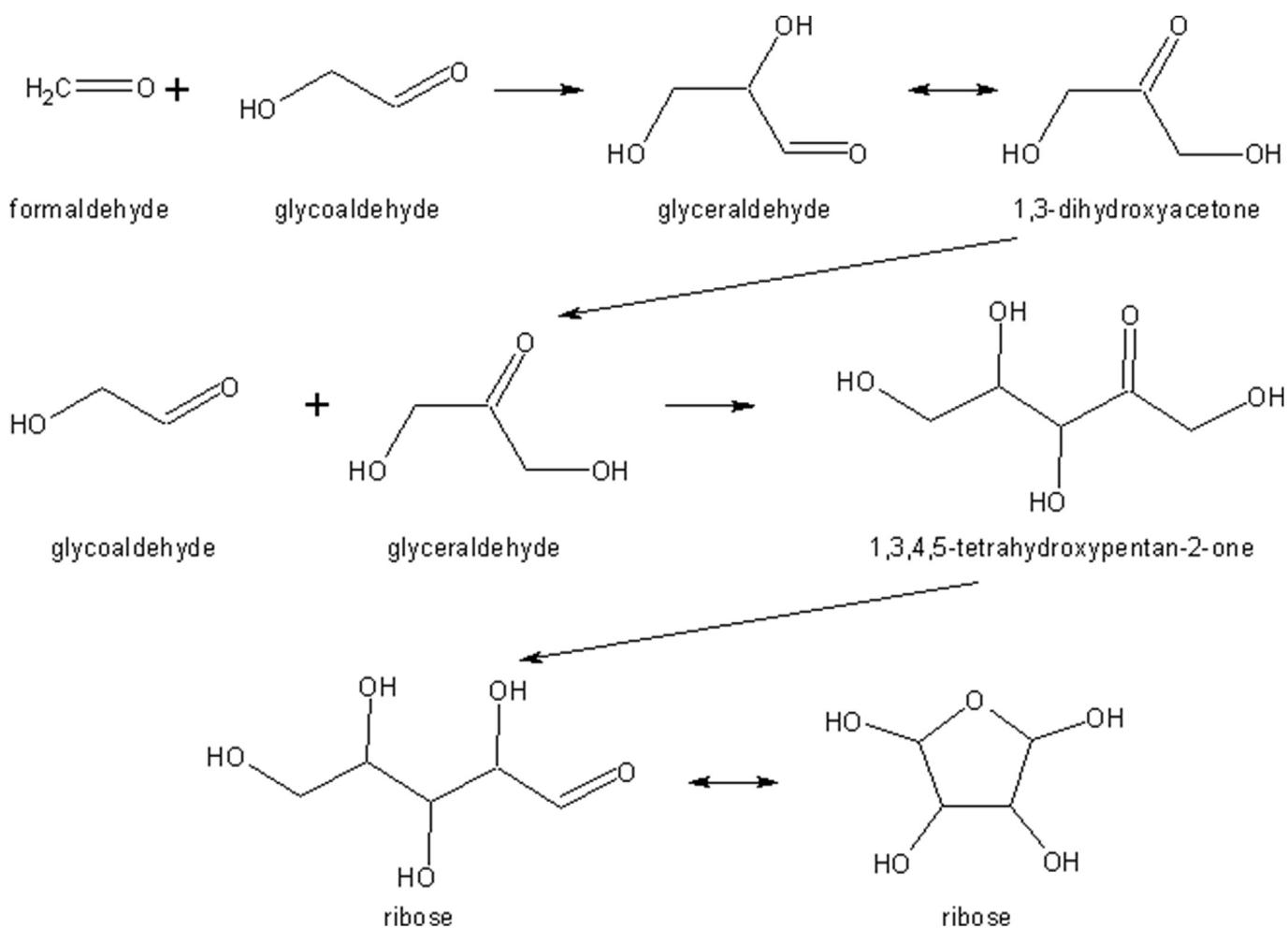


Figure 15. A series of contraction reactions of HCN produce 5-aminoimidazole-4-carbonitrile (AICN) and subsequent hydrolysis of AICN to 5-aminomidazole-4-carboxamide (AICA; Orgel L.E., 2004; Ferris, 2005).

The reaction of cyanamide and glycoaldehyde gives 2-amino-oxazole (Fig. 16), and then adds to glyceraldehyde to give pentose amino-oxazolinos. Under the phosphate buffering in pH 6.5, the reaction of pentose amino-oxazolinos with cyanoacetylene then gives the anhydroarabinonucleoside, which subsequently undergoes phosphorylation with rearrangement to furnish β -ribocytidine-2'-3'cyclic phosphate (Pownier et al., 2009). In subsequent photochemical steps, it is partly converted to the corresponding uracil derivative, with synthetic co-products largely being destroyed. Siouri et al. (2015) studied the intrinsic photochemical properties of nucleobases and base pairs using double-resonant spectroscopy in the gas phase of isolated bases and clusters. They found that excited-state lifetimes of canonical bases are between 1.8–12 ns, much longer than those of others (shorter than 10 ps).

On the other hand, Pownier and Sutherland (2010) found a three-component reaction among 5-aminoimidazole-4-carbonitrile (AICN), glyceraldehyde, and 2-amino-oxazole yielding rac-tetrahydroimidazo[1',3']-2"-aminooxazolo[1',2']-pyrimidines, which further leads to a potential stepwise regioselective pathway for purine β -ribofuranosyl-nucleotide (right-hand side of Fig. 17). They further found that the products are different depending on pH; examples include ribose aminoolizazoline leading to pyrimidine nucleotides in pH 7, and, rac-tetrahydroimidazo[1',3']-2"-aminooxazolo[1',2']-pyrimidines leading to purine nucleotides in pH 5 (Fig. 17; Pownier and Sutherland, 2010). This multi-component reaction has a high yield and suggests that both the pyrimidine and the purine ribonucleotides could be made concurrently in intermediate pH \sim 6.5.

In a natural nuclear reactor, biochemical compounds, such as HCN, HCHO, HCCCN, PO_4 glycoaldehyde, and glyceraldehyde are continuously supplied from CO_2 , H_2O , and CH_4 through radiochemistry driven by ionizing radiation. It therefore provides the perfect environment to drive the chemical pathway to produce nucleotides proposed by Pownier and Sutherland (2010). The availability of phosphates (PO_4) in the Hadean nuclear geyser is discussed in Subsections 5.1 and 5.3.

6.7. Ribose

Some amounts of glycoaldehyde are produced either directly or by the condensation of HCOH in the presence of a catalyst such as calcium carbonate or alumina (Gabel and Ponnampерuma, 1967; Reid and Orgel, 1967; Joyce, 1989). Glycoaldehyde begins a cascade of aldol condensations and enolization that rapidly convert most of the available formaldehyde into trioses, tetroses, and higher sugars through glyceraldehyde (Fig. 18).

6.8. Fatty acid and thiols

Fatty acids are formed on the surface of pyrite $[(\text{Fe},\text{Ni})\text{S}_2]$ through the following process (Fig. 18; Davis, 2001; Cody, 2005). First, a CO molecule and a methyl (C^*H_3) radical are produced by radiation chemistry (Section 4.1 and Fig. 6). They are then absorbed on the surface of pyrite (Fig. 18). The CO and CH_3 bases combine to form an acetyl base (C_2). Second, another CO molecule and two H_2O molecules are absorbed on the surface of pyrite. A series of reactions among them and the acetyl base lead to a one-step elongation of the carbon chain. The chain can be elongated in the same process (Fig. 19).

Due to the presence of hydrosulfide radical (HS^-), a carbon chain is terminated by a HS base to form a thiol. Heinen and Lanwers (1996) demonstrated the formation of thiols, mainly CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$ (Heinen and Lanwers, 1996). Subsequently, the interaction of CO with catalytic FeS_2 , CoS_2 , or NiS_2 was investigated under a variety of conditions (Huber and Wachtershauser, 1997; Cody et al., 2000), whereby carboxylic acids (up to C4) were detected along with mercaptans, the simplest acetyl-CoA analogue,

methylthioacetate ($\text{CH}_3-\text{CO}-\text{S}-\text{CH}_3$), or higher homologs (Huber et al., 2012).

7. Discussions

We summarize our proposed model of the birth place of life, then compare it with the previously proposed models, and discuss the next steps of the research.

7.1. Essential condition for the birth of life: chain reaction driven by constant supply of energy

The most popular and generally accepted definition of “life” is threefold: (1) metabolism, (2) membrane, and (3) self-replication. However, these would not be sufficient enough to discuss about the birth place of life, because the environmental conditions control the birth of life. For example, metabolism, one of the most essential phenomena of life, is the never-ending chain reaction, which is possible only when necessary material and driving energy is supplied continuously. In other words, life cannot emerge nor survive without material/energy circulation system. For example, on the modern Earth, plants utilize the visible photons from the Sun for the photosynthesis to produce materials to maintain metabolism to live. A huge ecological network of biological organisms among prokaryotes, eukaryotes, and metazoans depends on the basic production by plants on present Earth. Almost all animals eat other animals or plants to obtain energy (through metabolism) under the Earth system with terrestrial material circulation driven by the energy from the Sun.

The situation must have been the same on the Hadean Earth. To emerge life, necessary elements must be supplied through material circulation to produce the building blocks of life. At the same time, driving energy for material circulation has to be maintained. Only under such a material/energy circulation system, life can be born. It is worth noting that a nuclear reactor is responsible for local circulation around the geyser, while, it depends on the global water circulation driven by the solar energy.

7.2. The possible oldest metabolism produced in natural geyser

Glyceraldehyde is a key compound to link inorganic material with organic compounds, and also an important intermediate compound in glycolysis. Glycolysis is the metabolic pathway which converts a glucose to pyruvate, leading to acetyl-CoA (Fig. 20). The free energy produced in this process is used to generate high-energy compounds such as ATP and NADH (Brasen et al., 2014).

By attempting to define the essential genes in bacteria, Xu et al. (2011) found that glycolysis is one of the most essential metabolic pathways, while the tricarboxylic acid (TCA) cycle is non-essential. This result suggests that glycolysis could be the most primitive pathway for the production of energy, as well as the most biologically essential with involving amino acid, nucleotides, ribose, and fatty acids, rather than TCA cycle, including revers TCA cycle (Zang and Martin, 2006).

Glyceraldehyde and its phosphorylated form (Glyceraldehyde 3-phosphate; G3P) are key compounds appearing at the middle of glycolysis, which requires the highest free energy to synthesize. So far, researchers have revealed that glycolysis has three branches: (1) Classical Entner–Doudoroff (ED) pathway, (2) semi-phosphorylative branch of modified ED pathway (spED pathway), which produces G3P as the intermediate with the highest free-energy, and (3) the non-phosphorylative of the modified ED pathway (npED pathway) producing glyceraldehyde instead of G3P (Fig. 19). A natural nuclear reactor is able to supply high energy aqueous electrons continuously, therefore, it is expected that glyceraldehyde or G3P could be

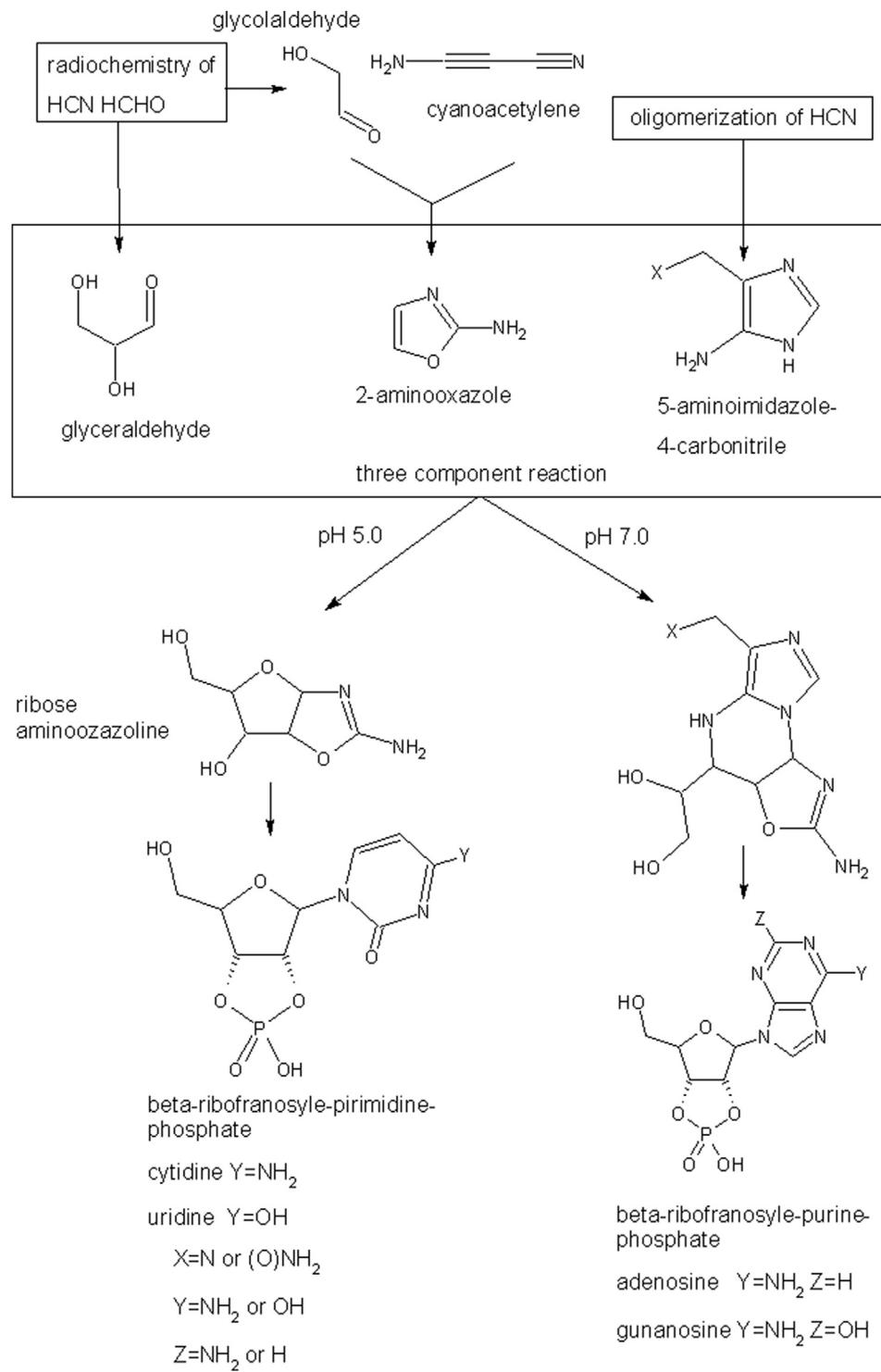


Figure 17. Three-component reaction among 5-aminoimidazole-4-carbonitrile (AlCN), glyceraldehyde, and 2-amino-oxazole ribose aminooazoline in relatively high pH (pH 7) and rac-tetrahydroimidazo[1',3']-2"-aminooxazolo[1',2'-]pyrimidines in relatively low pH (pH 5). The former is likely to lead to the production of pyrimidine nucleotides while the latter to purine nucleotides (Powner and Sutherland, 2010).

generated through ionizing radiation of a natural nuclear reactor driven by a geyser without difficulties, as discussed in Subsection 6.5. We believe that this coincidence is not just by chance but reflects some information of the first metabolism of the primitive life. In other words, we theorize that glycolysis was evolved as the first metabolism of primitive life from the prebiotic reaction network driven by aqueous electrons (ionizing radiation) from a natural nuclear reactor.

7.3. Feasibility of previous models of the birth place of life

As introduced in Section 1, three possible sites of the birth of life have been proposed: (1) tidal flats, (2) submarine hydrothermal vents, and (3) outer space. These models have difficulties to synthesize life in proposed environments, while our Nuclear Geyser model overcomes all of their short comings, which includes enabling continual chemical reaction to form biomolecules such as

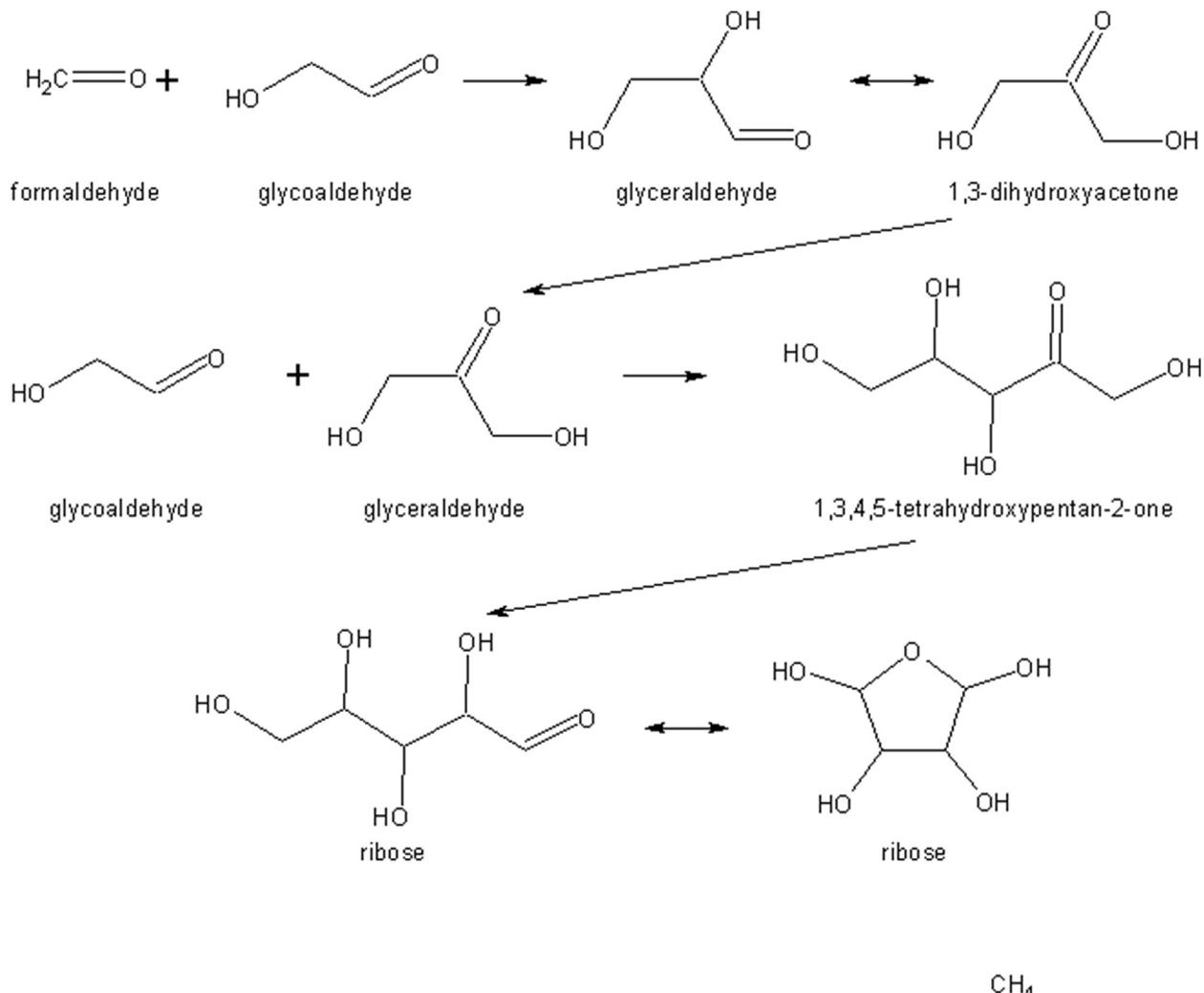


Figure 18. Formose reaction initiates from formaldehyde attaching glycoaldehyde and glyceraldehyde to produce ribose. Glycoaldehyde and glyceraldehyde are produced in a reaction promoted by hydrated electrons (see Fig. 16).

amino acids, nucleotides, ribose, and fatty acids from abiotic process. The important factors are summarized as follows: (1) high-density ionizing radiation to promote chemical chain reactions even for tar, (2) system to maintain material and energy circulation and cyclic nature (warm/cool etc) to enable the production of more complex organic compounds, (3) lower temperature than 100 °C not to break down macromolecular organic compounds, (4) locally reductive environments depending on rock types exposed along the geyser wall, and (5) a container to confine and accumulate volatile chemicals (Fig. 12).

Based on these five factors, we test the feasibility of each model shown in Fig. 21. First, at the tidal flat, UV photons generated by the Sun are the only available source of high-energy electrons to promote continuous chemical reaction. However, UV photons at the surface of the Earth is expected to be extremely low, even less than that of the modern Earth because of thicker CO₂ atmosphere with H₂O. It is too low to sustain the primitive life, as estimated by Chyba and Sagan (1992). Secondly, it lacks the mechanism to create locally reductive environments to give important reductive compounds to synthesize organic compounds such as amino acids. In addition, the concentration of compounds including volatile gas (HCN and HCHO) is impossible in open space without any containers. However, a tidal flat provides a wet/dry cyclic environment which is critical to synthesize membrane.

Submarine hydrothermal vents are also difficult to bear life. It enables material/energy circulation and also yields reductive gas such as H₂ or H₂S depending on the geological situation. However, it does not lead to the synthesis of biomolecules for the following reasons. First, there are no non-thermal radiations in hydrothermal vents. Although Yamamoto et al. (2013) found that chemical gradient between inside and outside of the hydrothermal vent can produce electric potential, the available electric power was as low as 1 W m⁻² (=10⁻⁴ W cm⁻²), even when they used a carefully designed fuel cell. In a purely natural situation, the available electric power must be far less compared with idealized cases that they tried. Second, it has an insufficient supply of necessary elements like N, P, or K as nutrients. In addition, due to almost infinite dilution by sea water, the concentration of chemical compounds is extremely difficult. Furthermore, according to Maruyama et al. (2013), the Hadean ocean was highly toxic, because of very low pH (~1) and high salinity (>10% weight). Therefore, it seems very difficult for primitive biological organisms to survive in such a harsh environment even if they had a sophisticated membrane.

In outer space, galactic cosmic rays are available as an alternative energy source of ionizing radiation, so that many organic materials, such as amino acids and nucleobases, are synthesized as observed in the astronomical observations (e.g. Snow and Bierbaum, 2005). However, in outer space, liquid water is not available,

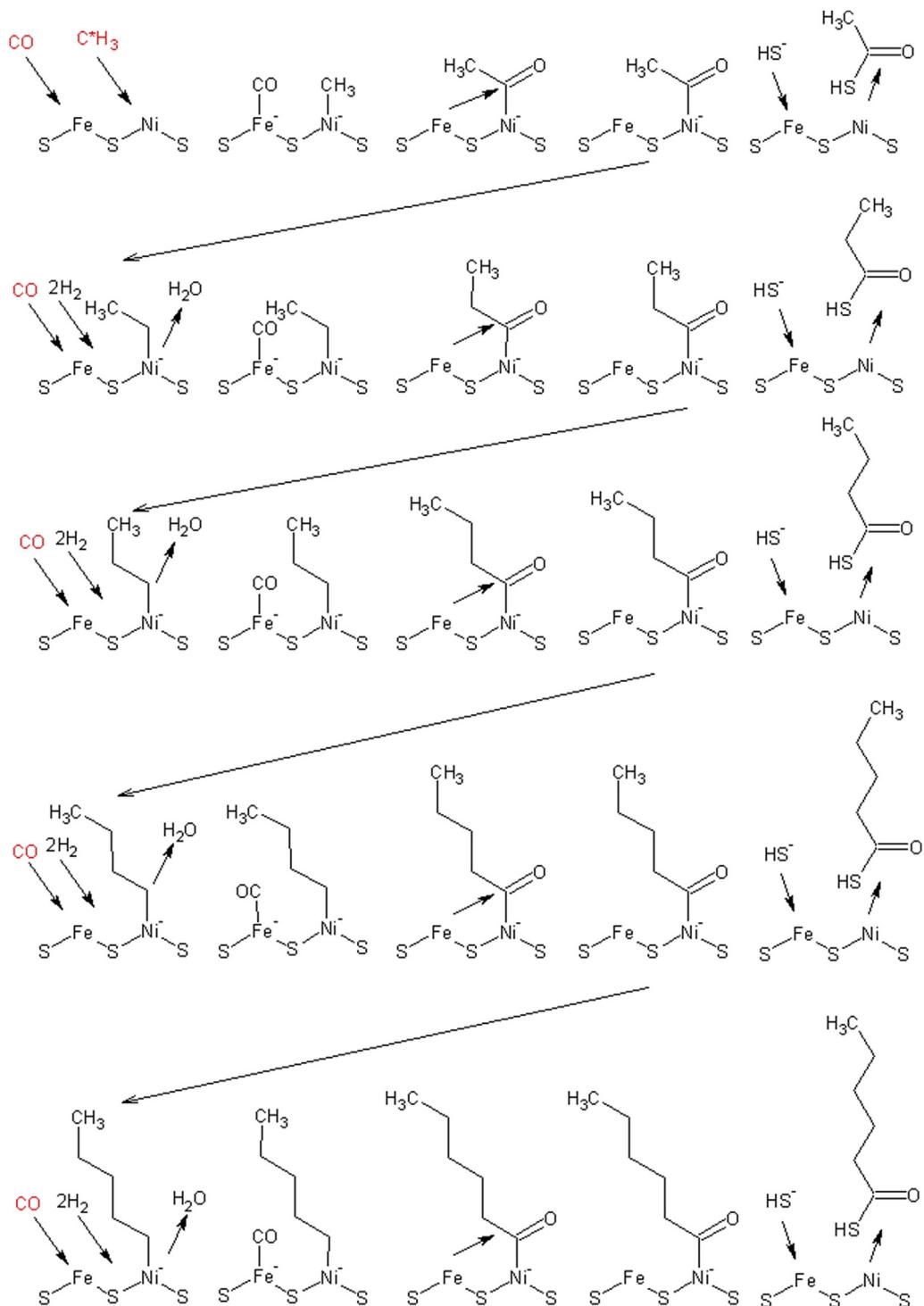


Figure 19. Fatty Acid formation on the surface of FeS_2 (Davis, 2001; Cody, 2005).

and thus it is impossible to synthesize other building blocks of life such as a membrane. In addition, the delivery process to the surface of the Earth is problematic, since most of organic materials are expected to be destroyed by the high temperature of the impacts of asteroids or comets, and possibly remaining as H_2O and CO_2 following the impact events (Hashimoto et al., 2007).

In summary, none of the three previous models can meet the five conditions to bear life. Only nuclear geyser can meet all of them.

7.4. Research for the origin of life and next step

One of the most remarkable contribution of this paper to unravel the origin of life is to conclude that nuclear geyser is the most potential and powerful energy source to promote continuous chemical reaction from inorganic matter into complex organic compounds, which is based on the understanding of physics in addition to biology, chemistry, and geology. It was devised through

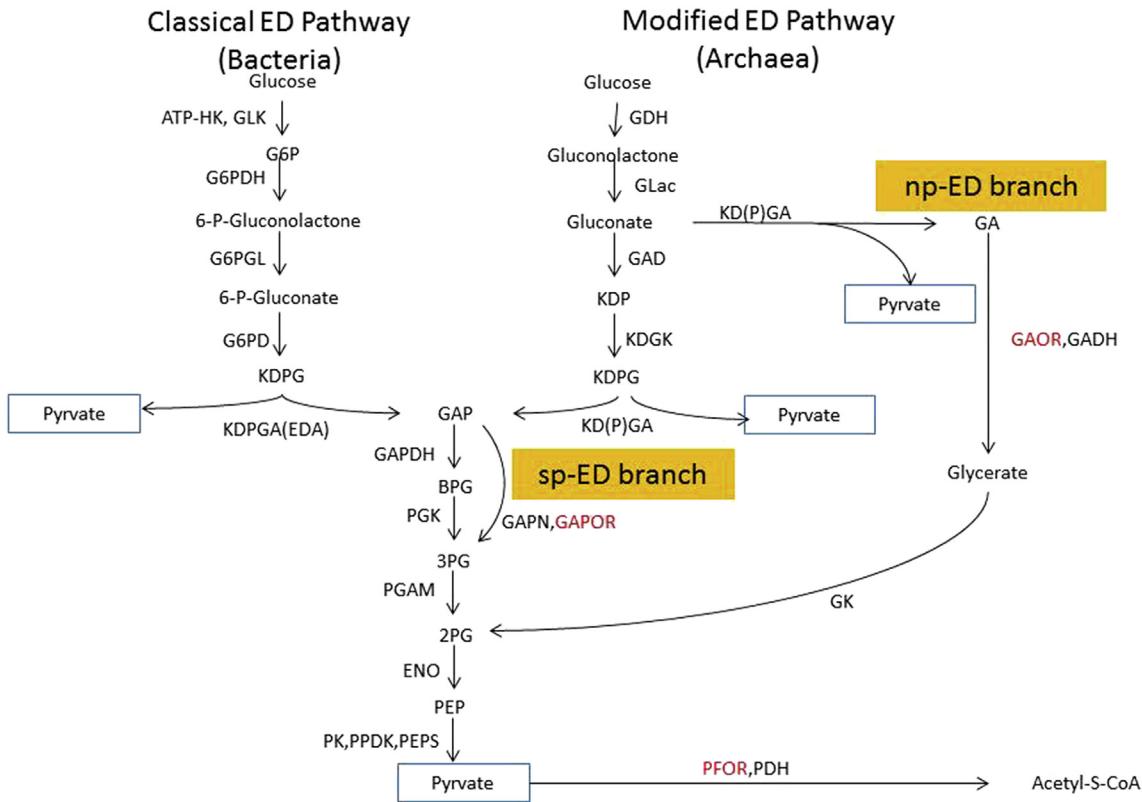


Figure 20. Glycolysis through the Entner-Doudoroff (ED) pathways known for Bacteria (classical) and the modified branched versions reported for Archaea: The non-phosphorylative ED (npED) and the semiphosphorylative ED (spED) branches in Archaea are also shown. Glycolysis branch produce two pyruvate molecules from one glucose molecule as well as free energy to be used in high energy compounds, such as ATP and NADH. In npED branch, GA (glyceraldehyde) appears as an intermediate compound instead of GAP (glyceraldehyde 3-phosphate) in spED branch and classical ED pathway. The pyruvates are transformed to Acetyl CoA by PFOR (pyruvate-Ferredoxin Oxidoreductase) or PDH (pyruvate dehydrogenase). Compound abbreviations: G6P, glyceraldehyde 3-phosphate; KDPG, 2-keto-3-deoxy-6-phosphogluconate; GAP: glyceraldehyde 3-phosphate; BPG, 1,3-bisphosphoglycerate; 3PG, 3-phosphoglycerate; 2PG, 2-phosphoglycerate; PEP, phosphoenolpyruvate; KDG, 2-keto-3-deoxygluconate; KDPG, 2-keto-3-deoxy-6-phosphogluconate. Enzyme abbreviations: ATP-HK, ATP-dependent hexokinase; GLK, glucokinase; G6PDH, glucose-6-phosphate dehydrogenase; 6PGL, 6-phosphoglucono-1,4-lactonase; 6PGD, gluconate-6-phosphate dehydratase; KDPGA, 2-keto-3-deoxy-6-phosphogluconate aldolase; GAPDH, glyceraldehyde-3-phosphate dehydrogenase; PGK, phosphoglycerate kinase; PGAM, phosphoglycerate mutase; ENO, enolase; PK, pyruvate kinase; PPDK, pyruvate: phosphate dikinase; PEPS, PEP synthetase; GDH, glucose dehydrogenase; GLac, gluconolactonase; GAD, gluconate dehydratase; KDGK, 2-keto-3-deoxygluconate kinase; KD(P)GA, 2-keto-3-deoxy-(6-phospho) gluconate aldolase; GAPN, nonphosphorylating; GAPDH, glyceraldehyde-3-phosphate dehydrogenase; GAPOR, GAP:Fd oxidoreductase; GAOR, glyceraldehyde: ferredoxin oxidoreductase; GK, glycerate kinase; PFOR, pyruvate-Ferredoxin Oxidoreductase; PDH, pyruvate dehydrogenase.

Comparison between models	Tidal flats	Hydrothermal vents	Outer space	Nuclear geyser
Ionizing radiation (energy density)	No	No	Yes	Yes
Material/energy circulation	Yes/No	Yes	No	Yes
Temperature <100°C	Yes	Yes	Yes/No	Yes
Locally reductive environment	No	Yes	Yes	Yes
Concentration of gasses	No	No	No	Yes

Figure 21. Five necessary conditions for bearing the first life. Only Nuclear geyser mode can meet all of five conditions.

extensive interdisciplinary researches combining all related subjects to overcome difficulties to synthesize life.

One of the next steps of research is quantitative experimental measurements of the reaction yields, taking into account the Hadean conditions. This includes the flux and energies of ionizing radiation, pressure, temperature, and chemical compositions. This data will be utilized in the detailed numerical simulations of a natural nuclear reactor as well as chemical reaction networks driven by ionizing radiation.

Second, the signature or the evolutional process of primitive metabolism in the Hadean nuclear geyser might be unraveled. Such researches will be feasible by the comparative studies of variations of glycolysis seen in extant microorganisms, as discussed in Subsection 7.2 and Fig. 19. Distributions and molecular phylogenetics of genes used in nonphosphorylative and semi-phosphorylative branches of archaea can be compared to those of classical ED (Entner–Doudoroff) pathway to figure out the evolution of the primitive life.

Another important target of studies would be the transformation from nuclear energy dependent life in the Hadean Earth to the modern solar energy dependent life. Sophisticated membrane systems for the photon harvesting (conversion of photon energy to aqueous electrons) and the storage of chemical energy have to be innovated to utilize visible photons, which is abundantly but with low density available from the solar radiation on the surface of the Earth. The emergence of photosynthetic system I and II with chlorophylls and photon dependent pumps (rhodopsins) may be considered as a results of the necessary adaptation to the surface environment outside of the nuclear geyser.

Finally, it will be necessary to demonstrate a series of synthesis of life from inorganic to organic matters as consecutive chemical reaction by laboratory experiments centered on a simulated nuclear geyser. Strong ionizing radiation from a nuclear geyser ionizes or excites N₂, CO₂, H₂O into highly reactive compounds or radicals which can actively react with other chemical compounds. Near the core of the reactor, the radiation flux may rise too high so that organic materials are destroyed completely. However, in the regions surrounding the reactor core, the situation is much favorable for the production of chemical compounds because of the rather moderate radiation field and temperature. We therefore believe that the birth of life is closely related to a nuclear geyser and associated radiation chemistry. But to emerge life, the process is not so simple. It should have followed some steps to evolve into first life. Working hypothesis to explain how first life was born with specific Hadean surface environment will be required for further research to unveil the origin of life.

8. Conclusions

We proposed the Nuclear Geyser model, with a nuclear geyser being an optimal site to lead to the emergence of first life on the Earth. A nuclear geyser system, driven by the chain reaction of ²³⁵U of natural a nuclear reactor provides the followings: (1) high-density ionizing radiation to promote chemical chain reactions that even tar can restart the chemical reaction, (2) system to maintain material and energy circulation and cyclic nature (warm/cool, etc.) to enable the production of more complex organic compounds, (3) lower temperature than 100 °C not to break down macromolecular organic compounds, (4) locally reductive environments depending on rock types exposed along the geyser wall, and (5) a container to confine and accumulate volatile chemicals. These five conditions must be satisfied to be the birth place of life, and only a nuclear geyser system can meet all of them, in contrast to the previously proposed birth sites, such as a tidal flat, a submarine hydrothermal vent, and outer space. Within a nuclear

geyser system, numerous kinds of chemical reactions to synthesize complex organic compounds progress continuously with the energy of ionizing radiation, where the most primitive metabolism could be generated.

Acknowledgement

We thank Prof. Ken Kurokawa for his encouraging discussions, Ms. Reiko Hattori for technical assistance to complete the paper, Dr. James M. Dohm for the improvement of English, and Ms. Shio Watanabe for illustrations. This work was partially supported by Grant-in-Aid for Scientific Research on Innovative Areas (Grant Nos. 26106002 and 26106006).

References

- Abrajano, T.A., Sturchio, N.C., Bolke, J.K., Lyon, G.L., Poreda, R.J., Stevens, C.M., 1988. Methane-hydrogen gas seeps, Zambales ophiolite, Philippines: deeper shallow origin? *Chemical Geology* 71, 211–222.
- Abe, Y., Matsui, T., 1986. Early evolution of the Earth - Accretion, atmosphere formation, and thermal history. *Journal of Geophysical Research-Solid Earth and Planets* 91, E291–E302.
- Adam, Z., 2007. Actinides and life's origins. *Astrobiology* 7, 852–872.
- Albarède, F., 2009. Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* 461, 1228–1233.
- Anderson, R.B., 1984. *The Fischer-Tropsch Reaction*. Academic Press, London.
- Arrhenius, G., Sales, B., Mojzsis, S., Lee, T., 1997. Entropy and charge in molecular evolution—the case of phosphate. *Journal of Theoretical Biology* 187, 503–522.
- Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., Meurer, W.P., Humphris, S.E., 2006. Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP leg 209, Site 1274). *Geophysical Research Letters* 33, L13306.
- Benner, S.A., Kim, H.-J., Kim, M.-J., Ricard, A., 2010. Planetary organic chemistry and the origins of biomolecules. *Cold Spring Harbor Perspectives in Biology* 2, a003467.
- Bentridi, S., Gall, B., Gauthier-Lafaye, F., Seghour, A., Pape, A., Medjadi, D., 2013. Criticality of Oklo natural reactors: realistic model of reaction zone 9. *IEEE Transactions on Nuclear Science* 60, 278–283.
- Bodu, R., Bouzigue, H., Morin, N., Pfiffelm, J.P., 1972. Sur L'existence d'anomalies isotropiques rencontrées dans l'uranium du Gabon. *Comptes Rendus de l'Académie des Sciences Paris* 275, 1731–1734.
- Bockelée-Morvan, D., Lis, D.C., Wink, J.E., Despois, D., Crovisier, J., Bachiller, R., Benford, D.J., Biver, N., Colom, P., Davis, J.K., 2000. New molecules found in comet C/1995 O1 (Hale Bopp)- Investigating the link between cometary and interstellar material. *Astronomy and Astrophysics* 353, 1101–1114.
- Boussard, A., Toupance, G., 1981. In: Wolman, Y. (Ed.), *Origins of Life*. D. Dorrecht, Holand, p.93.
- Brasen, C., Esser, D., Rauch, B., Siebers, B., 2014. Carbohydrate metabolism in Archaea: current insight into unusual enzymes and pathways and their regulation. *Miclobiology and Molecular Biology reviews* 78, 89–175.
- Briner, E., Baerfus, A., 1919. On nitrogen fixation in the form of hydrocyanic acid by means of electric arc. *Helvetica Chimica Acta* 2, 663–666.
- Briner, E., Hoefer, H., 1940. Research on the chemical effect of electrical discharges XIX the production of cyanhydric acid and ammoniac by the electrical arc in high and low frequencies sending out in nitrogen-oxide mixtures of carbon hydrogen at ordinary pressure and at low pressure. *Helvetica Chimica Acta* 23, 826–831.
- Briner, E., Desbaillets, J., Wertheim, M., 1938. Research on the chemical effects of electrical discharge. XVI the production of cyanhydric acid by the electric arc, at different frequencies, spouting in vapor hydrocarbon-azote-hydrogen mixes. *Helvetica Chimica Acta* 21, 859–862.
- Bryant, D.E., Kee, T.P., 2006. Direct evidence for the availability of reactive, water soluble phosphorus on the early Earth. H-Phosphinic acid from the Nantan meteorite. *Chemical Communications* 22, 2344–2346.
- Bryant, D.E., Greenfield, D., Walshaw, R.D., Evans, S.M., Nimmo, A.E., Smith, C.L., Wang, L.M., Pasek, M.A., Kee, T.P., 2009. Electrochemical studies of iron meteolite. Phosphorous redox chemistry on the early Earth. *International Journal Astrobiology* 8, 27–36.
- Bujdak, J., Fayzikova, K., Eder, A., Yangyi, Y., Rode, B.M., 1995. Peptide-chain elongation – a possible role of montmorillonite in prebiotic synthesis of protein precursors. *Origin of Life and Evolution of Biospheres* 25, 431–441.
- Bujdak, J., LeSon, H., Yongyi, Y., Rode, B.M., 1996. The effect of reaction conditions on montmorillonite-catalysed peptide formation. *Catalysis Letters* 37, 267–272.
- Capezzutti, P., Cramarossa, F., Ferraro, G., Maione, P., Molinari, E., 1973. Gas discharges at radiofrequency as chemical reactors .1. synthesis of HCN from nitrogen and methane at moderate pressure. *I. Gazzetta Chimica Italiana* 103, 1169–1188.
- Catling, D.C., Zahnle, K.J., McKay, C.P., 2001. Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Science* 293, 839–843.

- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., Holm, N., 2002. Geochemistry of high H(2) and CH(4) vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36 degrees 14' N, MAR). *Chemical Geology* 191, 345–359.
- Chyba, C., Sagan, C., 1992. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origin of life. *Nature* 355, 125–132.
- Chyba, C., Thomas, P.J., Brookshaw, L., Sagan, C., 1990. Cometary delivery of organic molecules to the early Earth. *Science* 249, 366–373.
- Cody, G.D., 2005. Geochemical connections to primitive metabolism. *Elements* 1, 139–143.
- Cody, G.D., Boctor, N.Z., Filley, T.R., Hazen, R.M., Scott, J.H., Sharma, A., Yoder, H.S., 2000. Primordial carboxylated iron sulfur compounds and synthesis of pyruvate. *Science* 289, 1337–1340.
- Cortial, F., Gauthier-Lafaye, F., Lacrampe-Coulombe, G., Oberlin, A., Weber, F., 1990. Characterization of organic-matter associated with uranium deposits in the Francevillian formation of Gabon (lower Proterozoic). *Organic Geochemistry* 15, 73–85.
- Davis, B.H., 2001. Fischer-Tropsch synthesis: current mechanism and futuristic needs. *Fuel Processing Technology* 71, 157–166.
- Dohm, J.M., Maruyama, S., 2014. Habitable trinity. *Geoscience Frontiers* 6, 95–101.
- Dubessy, J., Pagel, M., Beny, J.M., Cristensen, H., Hicek, B., Kosztolanyi, C., Poty, B., 1988. Radiolysis evidence by H2-O2 and H2-bearing fluid inclusions in three uranium deposits. *Geochimica et Cosmochimica Acta* 52, 1152–1167.
- Dyson, F., 1985. *Origin of Life*. Cambridge University Press.
- Engel, A., Macko, S.A., Silfer, J.A., 1997. Carbon isotope composition of individual amino-acids in the Murchison meteorite. *Nature* 348, 47–49.
- Etiope, G., 2011. Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. *Earth and Planetary Science Letters* 310, 96–104.
- Etiope, G., Lollar, B.S., 2013. Abiotic methane on Earth. *Review of Geophysics* 51, 276–299.
- Etiope, G., Tsikouras, B., Kordella, S., Ifandi, E., Christodoulou, D., Papatheodorou, G., 2013. Methane flux and origin in the Othrys ophiolite hyperalkaline springs, Greece. *Chemical Geology* 347, 161–174.
- Ferris, J.P., 1984. The chemistry of life's origin. *Chemical and Engineering News* 62, 22–35.
- Ferris, J.P., 2005. Catalysis and prebiotic synthesis. *Reviews in Mineralogy and Geochemistry* 59, 187–210.
- Ferris, J.P., Orgel, L.E., 1966a. An unusual photochemical rearrangement in the synthesis of adenin from hydrogen cyanide. *Journal of the American Chemical Society* 88, 1074.
- Ferris, J.P., Orgel, L.E., 1966b. Studies in prebiotic synthesis. I. Aminomalononitrile and 4-amino-5-cyanoimidazole. *Journal of the American Chemical Society* 88, 3829.
- Foustoukos, D.I., Seyfried, W.E., 2004. Hydrocarbons in hydrothermal vent fluids: the role of chromium-bearing catalysis. *Science* 304, 1002–1005.
- Frost, B.R., Berad, J.S., 2007. On silica activity and serpentinization. *Journal of Petrology* 48, 1351–1368.
- Fuchida, S., Mizuno, Y., Masuda, H., Toki, T., Makita, H., 2014. Concentrations and distributions of amino acids in black and white smoker fluids at temperature over 200 °C. *Organic Geochemistry* 66, 98–106.
- Gabel, M.W., Ponnamperuma, C., 1967. Model for origin of monosaccharides. *Nature* 216, 453–455.
- Galimov, E.M., 2006. Phenomenon of life: between equilibrium and non-linearity. *Origin and Principles of Evolution*. *Geochemistry International* 44 (Suppl. 1), S1–S95.
- Gauthier-Lafaye, F., 1986. Les gisements d'uranium du Gabon et les reactor d'Oklo. *Modele metallogenique de gites a fortes teneurs du Proterozoique inferieur. Memoire Science Geologiques* 78, 206.
- Gauthier-Lafaye, F., Weber, 1981. Les concentration uranifères du Francevillian du Gabon: Leur association avec des gites a hydrocarbures fossiles du Proterozoïque inférieur. *Comptes Rendus Académie of Science Paris* 292, 69–74.
- Gauthier-Lafaye, F., Weber, F., 1989. The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon. *Economic Geology* 84, 2267–2285.
- Gauthier-Lafaye, F., Weber, F., 2003. Natural nuclear fission reactors: time constraints for occurrence, and their relation to uranium and manganese deposits and to the evolution of the atmosphere. *Precambrian Research* 120, 81–100.
- Getoff, N., 1994. Possibilities on the radiation-induced incorporation of CO₂ and CO into organic compounds. *International Journal of Hydrogen Energy* 19, 667–672.
- Grassia, G.S., Mclean, K.M., Glenat, P., Bauld, J., Sheehy, J., 1996. Asystematic survey for thermophilic fermentative bacteria and archaea in high-temperature petroleum reservoirs. *FEMS Microbiology Ecology* 21, 47–58.
- Handschohu, G.J., Orgel, L.E., 1973. Struvite and prebiotic phosphorylation. *Science* 179, 463–484.
- Hart, E.G., Boag, J.W., 1962. Absorption spectrum of hydrated electron in water in aqueous solutions. 84, 4090–4095.
- Hashimoto, G.L., Abe, Y., Sugita, S., 2007. The chemical composition of early terrestrial atmosphere: formation of a reducing atmosphere from Cl-like material. *Journal of Geophysical Research* 112, E05010.
- Heinen, W., Lanwers, A.M., 1996. Organic sulfur compounds resulting from interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an aqueous environment. *Origins of Life and Evolution of Biospheres* 26, 1–20.
- Hidaka, H., Kikuchi, M., 2010. SHRIMP in situ isotopic analyses of REE, Pb and U in micro-minerals bearing fission products in the Oklo and Bangombe natural reactors A review of a natural analogue study for the migration of fission products. *Precambrian Research* 183 (SI), 158–165.
- Horiuchi, T., Takano, Y., Ishibashi, J., Marumo, K., Kobayashi, K., 2004. Amino acids in water samples from deep sea hydrothermal vents at Suiyo Seamount, Izu-Bonin Arc. *Pacific Ocean, Organic Geochemistry* 35, 1121–1128.
- Huber, C., Wachtershauser, G., 1997. Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* 276, 245–247.
- Huber, C., Kraus, F., Hanzlik, M., Eisenreich, W., 2012. Elements of metabolic evolution. *Chemistry – A European Journal* 18, 2063–2080.
- Janeczek, J., 1999. Mineralogy and geochemistry of natural fission reactors in Gabon, in: "Uranium Mineralogy, Geochemistry, and the Environment". In: Burns, P.C., Finch, R. (Eds.), *Reviews in Mineralogy, Mineralogy Society of America*, vol. 38. ISSN 0275-0279.
- Joyce, G.F., 1989. RNA evolution and the origin of life. *Nature* 338, 217–224.
- Kehew, A.E., 2001. *Applied Chemical Hydrogeology*. Prentice Hall.
- Kelley, D.S., Karson, J.A., Blackman, D.K., Früh-Green, G.L., David, A., Butterfield, D.A., Lilley, M.D., Olson, E.J., Schrenk, M.O., Roe, K.K., Lebon, G.T., Rivizzigno, P., the AT3-60 Shipboard Party, 2001. An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N. *Nature* 412, 145–149.
- Klevenz, V., Sumoondur, A., Ostertag-Henning, C., Koschinsky, A., 2010. Concentrations and distributions of dissolved amino acids in fluids from Mid-Atlantic Ridge hydrothermal vents. *Geochimical Journal* 44, 387–397.
- Kugler, E.L., Steffgen, F.W., 1979. Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen. *American Chemical Society, Advances in Chemistry Series* 178, Washington, D.C.
- Kuroda, P.F., 1956. On the nuclear physical stability of the uranium minerals. *The Journal of Chemical Physics* 25, 781–782.
- Kvenvolden, K., Lawless, J., Pering, P., Peterson, E., Flores, J., Ponnampe, C., Kaplan, I.R., Moore, C., 1970. Evidence for extraterrestrial amino-acids and hydrocarbons in Murchison meteorite. *Nature* 228, 923–926.
- L'Haridon, S.L., Reysenbach, A.-L., Glenat, P., Prieru, D., Jeanthon, C., 1995. Hot subterranean biosphere in continental reservoir. *Nature* 337, 223–224.
- Lahav, N., White, D., Chang, S., 1978. Peptide formation in prebiotic era-thermal condensation of glycine in fluctuating clay environments. *Science* 201, 67–69.
- Lahav, N., Nir, S., Elitzer, A.C., 2001. The emergence of life on Earth. *Progress in Biophysics and Molecular Biology* 75, 75–120.
- Lam, P., Cowen, J.P., Jones, R.D., 2004. Autotrophic ammonia oxidation in a deep-sea hydrothermal plume. *FEMS Microbiology* 47, 191–206.
- Lang, R.S., 1980. *Astrophysical Formulae, Second Corrected and Enlarged Edition*. Springer-Verlag, Berlin Heidelberg, New York, pp. 465–471.
- Lang, S.Q., Früh-Green, G.L., Bernasconi, S.M., Butterfield, D.A., 2013. Sources of organic nitrogen at the serpentinite-hosted Lost City hydrothermal field. *Geobiology* 11, 154–169.
- Lilley, M.D., Butterfield, D.A., Olson, E.J., Lupton, J.E., Macko, S.A., McDuff, R.E., 1993. Anomalous CH₄ and NH₄⁺ concentration at an unsedimented mid-ocean-ridge hydrothermal system. *Nature* 364, 45–47.
- Lowe, C.U., Rees, M.W., Markham, F.R.S., 1963. Synthesis of complex organic compounds from simple precursors: formation of amino acids, amino acid polymers, fatty acids and purines from ammonium cyanide. *Nature* 199, 219–222.
- Martin, W., Russell, M.J., 2003. On the origins of cells: a hypothesis for the evolutionary transitions from abiotic geochemistry to chemoautotrophic prokaryotes, and from prokaryotes to nucleated cells. *Philosophical Transactions of the Royal Society of London series B-Biological Sciences* 358, 59–83.
- Maruyama, S., Ebisuzaki, T., 2017. Origin of the Earth: a proposal of new model called ABEL. *Geoscience Frontiers* 8, 253–274.
- Maruyama, S., Ikoma, M., Genda, H., Hirose, K., Yokoyama, T., Santosh, M., 2013. The naked planet Earth: most essential pre-requisite for the origin and evolution of life. *Geoscience Frontiers* 4, 141–165.
- Mathieu, R., Zetterstrom, L., Cuney, M., Gauthier-Lafaye, F., Hidaka, H., 2001. Alteration of monazite and zircon and lead migration as geochemical tracers of fluid paleocirculations around the Oklo-Okelobondo and Bangombe natural nuclear reaction zones (Franceville basin, Gabon). *Chemical Geology* 171, 147–171.
- McCollom, T.M., Bach, W., 2009. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta* 73, 856–875.
- Meshik, A.P., Hohenberg, C.M., Pravdivsteva, Q.V., 2004. Record of cycling operation of the natural nuclear reactor in the Oklo/Okelobondo area in Gabon. *Physical Review Letters* 93, 182302-1–4.
- Miller, S.L., 1953. A production of amino acid under possible primitive Earth conditions. *Science* 117, 528–529.
- Miller, S.L., Urey, H.C., 1959. Organic compound synthesis on the primitive Earth. *Science* 130, 245–251.
- Mossman, D.J., Gauthier-Lafaye, F., Jackson, S.E., 2001. Carboneous substances associated with the Paleoproterozoic natural nuclear fission reactors of Oklo, Gabon: paragenesis, thermal maturation and carbon isotopic and trace element compositions. *Precambrian Research* 106, 135–148.
- Mourey, D., Raulin, F., Toupane, G., 1981. In: Wolman, Y. (Ed.), *Origins of Life*. Reidel Publ. Co., Dordrecht, Holland, p. 135.
- Mukhin, L.M., Tishchenko, A.I., Pomarev, V.V., Bondarev, V.B., Kalinichenko, V.I., Safonova, E.N., 1976. Organic-Compounds in hydrothermal system of Koshelevsky volcano. *Doklady Akademii Nauk, SSSR* 226, 1463–1464.

- Nagy, B., Gauthier-Lafaye, F., Holliger, P., David, D.W., Mossman, D.J., Leventhal, J.S., Rigali, M.J., Parnell, J., 1991. Role of organic matter containment of uranium and fissogenic isotopes at the Oklo natural reactors. *Nature* 354, 472–475.
- Nagy, B., Gauthier-Lafaye, F., Holliger, P., David, D.W., Mossman, D.J., Leventhal, J.S., Rigali, M.J., 1993. Role of organic matter in the Proterozoic Oklo natural fission reactors. *Gabon, Africa. Geology* 21, 655–658.
- Ndongo, A., Guiraud, M., Vennin, E., Mbina, M., Buoncristiani, J.-F., Thomazo, C., Flotté, N., 2016. Control of fluid-pressure on early deformation structures in the Paleoproterozoic extensional Franceville Basin (SE Gabon). *Precambrian Research* 277, 1–25.
- Neubeck, A., Duc, N.T., Bastviken, D., Crill, P., Holm, N.G., 2011. Formation of H₂ and CH₄ by weathering of Olivine at temperatures between 30 and 70 °C. *Geochemical Transactions* 12, 6–11.
- Neuilly, M., Nief, G., Vendryes, G., Yvon, J., Bussac, J., Frejacqu, C., 1972. Sur l'existenc dans un passé reculé d'une réaction en chaîne naturelle de fission, dans le gisement d'uranium d'Oklo (Gabon). *C.R. Académie de Science, Paris* 275, 1847–1849.
- Oparin, A.I., 1924. *Proishozhdenie zhizni* (Origin of Life). Moscow, Izd. Moskoviih Rabochi.
- Orgel, L.E., 2004. Prebiotic chemistry and the origin of the RNA world. *Critical Reviews in Biochemistry and Molecular Biology* 39, 99–123.
- Orgel, L.E., Lohrmann, R., 1974. Prebiotic chemistry and nucleic acid replication. *Accounts of Chemical Research* 7, 368–377.
- Oro, J., 1960. Synthesis of adenine from ammonium cyanide. *Biochemical and Biophysical Research Communications* 2, 407–412.
- Pant, C.K., Lata, H., Pathak, H.D., Mehata, M.S., 2009. Heat-initiated prebiotic formation of peptides from glycine/aspartic acid and glycine/valine in aqueous environment and clay suspension. *International Journal of Astrobiology* 8, 107–115.
- Pasek, M.A., Lauretta, D.S., 2005. Aquous corrosion of phosphate minerals from iron meteorites, A highly reactive source of prebiotic phosphorous on the surface of the early Earth. *Astrobiology* 5, 515–535.
- Pasek, Lauretta, 2008. Extraterrestrial flux of potentially prebiotic C, N, and P to the early Earth. *Origins of Life and Evolution of Biospheres* 38, 5–21.
- Pasek, M.A., et al., 2007. A radical pathway for organic phosphorylation during schreibersites corrosion with implication for the origin of life. *Geochimica et Cosmochimica Acta* 71, 1721–1736.
- Pasek, M.A., Dworkin, J.P., Lauretta, D.S., 2008. Rethinking early Earth phosphorous, geochemistry. *Proceedings of the National Academy of Sciences* 105, 853–858.
- Pech, H., Henry, A., Khachikian, C.S., Salamassi, T.M., Hanrahan, G., Foster, K.L., 2009. Detection of geothermal phosphite using high performance liquid chromatography. *Environmental Science and Technology* 43, 7671–7675.
- Powner, M.W., Sutherland, J.D., 2010. Phosphate-mediated interconversion of Ribonucleotides and Arabino-configured prebiotic nucleotide intermediates. *Angewandte Chemie International Edition* 49, 4641–4643.
- Powner, M.W., Gerland, B., Sutherland, D., 2009. Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* 459, 239–242.
- Proskurowski, G., Lilley, M.D., Kelley, D.S., Olson, E.J., 2006. Low temperature volatile production at the Lost City hydrothermal field, evidence from a hydrogen stable isotope geothermometer. *Chemical Geology* 229, 331–343.
- Proskurowski, G., Lilley, M.D., Seewald, J.S., Früh-Green, G.L., Olson, E.J., Lupton, J.E., Sylva, S.P., Kelley, D.S., 2008. Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* 319, 604–607.
- Reid, C., Orgel, L.E., 1967. Synthesis of sugars in potentially prebiotic conditions. *Nature* 216, 455.
- Ritson, Sutherland, 2012. Prebiotic synthesis of simple sugars by photoredox systems chemistry. *Nature Chemistry* 4, 895–899.
- Ritson, D.J., Sutherland, J.D., 2013. Synthesis of aldehydic ribonucleotide and amino acid precursors by photoredox chemistry. *Angewandte Chemie-International Edition* 52, 5845–5847.
- Ritson, J., Sutherland, J., 2014. Conversion of biosynthetic precursors of RNA to those of DNA by photoredox chemistry. *Journal of Molecular Evolution* 78, 245–250.
- Russel, M.J., Hall, A.J., 1997. The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *Journal of the Geological Society, London* 154, 377–402.
- Sales, B.C., Chakoumakos, B.C., Boatner, L.A., Ramey, J.O., 1993. Structural properties of the amorphous phases produced by heating crystalline MgHPO₄·3H₂O. *Journal of Non-crystalline Solids* 159, 121–139.
- Sanchez, R.A., Ferris, J.P., Orgel, L.E., 1967. Studies in prebiotic synthesis .2. synthesis of purine precursors and amino acids from aqueous hydrogen cyanide. *Journal of Molecular Biology* 30, 223–253.
- Schmitt-Kopplin, P., Gabelica, Z., Gougeon, R.D., Fekete, A., Kanawati, B., Harir, M., Gebefuegi, I., Eckel, G., Herkorn, N., 2010. *Proceedings of the National Academy of Science of the United States of America* 107, 2673–2768.
- Siouri, F., Boldissar, S., Ligare, M., Nachtigallova, D., de Vries, M.S., 2015. Nucleobase Photochemistry: a Search for Prebiotic Molecular Fossils. *Astrobiology Science Conference, Chicago*.
- Schimpl, A., Lemmon, R.M., Calvin, M., 1965. *Science* 147, 149–150.
- Shanker, U., Bhushan, B., Bhattacharjee, kamaluddin, G., 2012. Oligomerization of Glycine and alanine catalyzed by iron oxides: implications for prebiotic chemistry. *Origins of Life and Evolution of Biospheres* 42, 31–45.
- Sleep, N.H., Meibom, A., Fridriksson, Th., Coleman, R.G., Bird, D.K., 2004. H₂-rich fluids from serpentinization: geochemical and biotic implications. *Proceedings of the National Academy of Sciences* 101 (35), 12818–12823.
- Strazzulla, G., Baratta, G.A., Johnson, R.E., Donn, B., 1991. Primordial comet mantle-irradiation production of a stable, organic crust. *Icarus* 91, 101–104.
- Snow, T., Bierbaum, V.M., 2008. Ion chemistry in the interstellar medium. *Annual Review of Analytical Chemistry* 1, 229–259.
- Stribling, R., Miller, S.L., 1987. Energy yields for hydrogen-cyanide and formamide synthesis – The HCN and amino-acid-concentration in the primitive ocean. *Origins of life and Evolution of Biosphere* 17, 261–273.
- Sutherland, J.D., Whitfield, J.N., 1997a. Studies and potentially prebiotic synthesis of RNA. *Tetrahedron* 53, 11595–11626.
- Sutherland, J.D., Whitfield, J.N., 1997b. Synthesis of potentially prebiotic RNA precursors, cytosine and guanine derivatives. *Tetrahedron Letter* 38, 1451–1454.
- Svetov, S.A., Svetova, A.I., Huhma, H., 1999. Geochemistry of the Komatiite–Tholeiite Rock Association in the Vedlozero–Segozero Archean Greenstone Belt, Central Karelia. *Geochemistry International* 39 (Suppl. 1), S24–S38.
- Takano, Y., Kobayashi, K., Yamanaka, T., Marumo, K., Urabe, T., 2004. Amino acids in the 308 °C deep sea hydrothermal system of the Suiyo Seamount. Izu-Bonin Arc. *Pacific Ocean. Earth and Planetary Science Letters* 219, 147–153.
- Tassi, F., Fiebig, J., Vaselli, O., Nocentini, M., 2012. Origins of methane discharging from volcanic-hydrothermal, geothermal and cold emissions in Italy. *Chemical Geology* 310–311, 36–48.
- Thornton, J., Sergio, R., 1967. Synthesis of Formaldehyde from methane in electric discharges. *Nature* 213, 590–591.
- Toupance, G., Raulin, F., Buvet, R., 1975. Formation of prebiochemical composition in models of primitive Earth's atmosphere I: CH₄–NH₃ and CH₄–N₂ atmospheres. *Origin of Life* 6, 83–90.
- Wetherill, G., Inghram, M., 1953. In: *Proceedings of the Conference on Nuclear Processes in Geological Settings, USA, September 1953*, p. 30.
- Xu, P., Ge, X., Chen, L., Wang, X., Dou, Y., Xu, J.Z., Patel, J.R., Stone, V., Trinh, M., Evans, K., Kitten, T., Bonchev, D., Buck, G.A., 2011. Genome-wide essential gene identification in *Streptococcus sanguinis*. *Scientific Reports* 1, 125.
- Yamamoto, M., Nakamura, R., Oguri, K., Kawaguchi, S., Suzuki, K., Hashimoto, K., Takai, K., 2013. Generation of electricity and illumination by an environmental fuel cell in Deep-Sea Hydrothermal Vents. *Angewandte Chemie International Edition* 52, 10758–10761.
- Zahnle, K., Nick, A., Cockell, C.S., Halliday, A., Nisbet, E., Sleep, N.H., 2007. Emergence of a habitable planet. *Space Science Reviews* 129, 35–78.
- Zang, X.V., Martin, S.T., 2006. Driving parts of Krebs Cycle in reverse through mineral photochemistry. *Journal of the American Chemical Society* 128, 16032–16033.
- Zel'dovich, Y.B., Khariton, Y.B., 1940a. On a chain decay of uranium under the action of slow neutrons. *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 10, 29–36.
- Zel'dovich, Y.B., Khariton, Y.B., 1940b. Fission and chain decay of uranium, *Usp. Fiz. Nauk* 23, 329–357.