INTERPLAY BETWEEN RAPID AND SLOW QUENCHING IN PREBIOTIC EVOLUTION

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(Abstract)

Prebiotic evolution on the primitive Earth could have proceeded through the interplay between the two modes of quenching, rapid and slow, of the synthesized products. The rapid quenching instrumental to stabilizing the synthesized products occurring near the surface of the Earth materializes as traversing from the high temperature specific to the energy source driving synthetic reactions, such as the photons from the sun or the magmatic heat from the core mantle of the Earth, to the normal ambient temperature near the surface. In contrast, the slow quenching as a necessary vehicle for disintegrating the synthesized products into the raw materials for the subsequent synthetic reactions to successively follow materializes as traversing from the normal ambient temperature near the surface of the Earth to the extremely low temperature characterizing deep outer space. A means of reaching out to deep outer space from the Earth is through the emission of the microwave photons. The microwave photons can be emitted in the process of orientational polarization of electric dipole moments intrinsic to the synthesized oligomeric products.

(Keywords)
cosmic microwave background; dielectric dipole; heat reservoirs; hot vents; outer space; quenching

1. Introduction

Chemical evolution is cosmological in its scale. When an inter-stellar dust particle is irradiated by a ultra-violet photon emitted from a remote star, the particle would suddenly be warmed up and start synthetic reactions among the small molecules, such as methane, nitrogen, carbon mono-oxide and water among others, adhered on its surface. The synthesized products including the precursors of amino acid molecule could then be stabilized through the rapid quenching due to the subsequent direct contact with deep outer space. The temperature of deep outer space to be measured as referring to the microwave spectrum is about 2.725K imputed to the cosmic microwave background if the inter-stellar cloud nearby is not dense enough.

Heating up of the reactants and the subsequent rapid quenching of the synthesized products in the cosmological scale are quite suggestive to experimental studies on simulating prebiotic synthesis proceeding on the primitive Earth (e.g., see the appendix in Japanese). Miller's gas discharge experiment [1] was equipped with both energy supply in the form of gas discharge and rapid quenching of the effluent products in the attached condenser. What is more, recent re-examination of the products saved in vials from Miller's other experiments [2], though not reported previously, reveals that when an aspirating nozzle from which a jet of steam and gas was injected into the spark chamber was further attached to the water-containing flask, 22 different kinds of amino acid and five amines were identified. This result makes a marked contrast to the original result Miller reported, especially in the respect of the enhanced diversity of the products. Use of an aspirator or an orifice can more explicitly signify the act of adiabatic expansion which is in turn aptly capable of inducing adiabatic cooling or rapid quenching [3].

Functional competence of rapid quenching in the simulated prebiotic evolution is widespread and ubiquitous [4-8]. Nonetheless, one methodological limitation remains inescapable in the framework of experiments in the laboratory. Implementing the process of quenching requires at least two separate heat reservoirs at different temperatures. The products whose synthesis is activated by the heat energy available from the reservoir at the higher temperature can be quenched and stabilized when they suddenly come to contact with another reservoir at the lower temperature. In fact, preparing two heat reservoirs at different temperatures is technically feasible in the laboratory. However, once the decomposition of the synthesized products comes to be focused upon, participation of a third heat reservoir whose temperature is further lower than those of the former two would have to be called for. Otherwise the proper continuous operation of prebiotic evolution would be jeopardized because of facing the stalemate frozen in the form of stabilization of the synthesized products.

We shall then try to see how the three different kinds of heat reservoir at three different temperatures could be implemented in the natural setting so as to keep the natural operation of prebiotic evolution sustainable.

2. Slow Quenching

Sustainable prebiotic evolution could proceed through the interplay between the synthesis and the decomposition of oligomeric products. Nonetheless, if the time scale of each synthetic reaction happens to be of the same order of that of each decomposition reaction, the whole combined set of the two sorts of reaction could eventually reach an apparent stationary condition and could not be evolutionary any more over the long time span which is far greater than the time scale measuring each reaction. If the interplay between the synthesis and the decomposition turns out evolutionary altogether by all means, on the other hand, the time scale characterizing the decomposition would have to be far greater than the time scale for the synthesis if the latter remains fixed. A large difference between two time scales, for synthesis and for decomposition, can let the underlying reactions be evolutionary in avoiding easy access to stationary stalemates.

This observation then raises a serious question on whether and how, if ever possible, the time scale characterizing the decomposition reactions could turn out far greater than the time scale measuring the synthetic reactions.

Indicative to the extraordinary enhancement of the time scale of the decomposition reactions on the basis of factual observation is an enzymatic reaction met in the practice of biochemistry. Take, for instance, an ATP hydrolysis with the help of a myosin molecule serving as an ATPase enzyme. A myosin molecule helps hydrolyzing an ATP molecule and releasing the energy of order of 30kJ/mol over 10 milli-seconds. If energy release as much as 30kJ/mol by breaking a single phosphate bond within an ATP molecule takes place as emitting a single photon, the energy of the photon could roughly be of order of 5×10^{-20}J and its emission would be completed within 10^{-14}s. However, the actual energy release takes as long as 10 milli-seconds. Such an enormous elongation of the time scale for an ATP hydrolysis is equivalent to releasing the energy of 5×10^{-20}J by emitting a train of many low-energy photons. If the emission of those low-energy photons over 10 milli-seconds is uniform in a continuous fashion, each photon would turn out to carry energy as much as 10^{-26}J and the total number of the low-energy photons emitted over 10 milli-seconds would reach about 10^{6}. The frequency of each emitted photon could be about 100MHz in the microwave range [9, 10].

The present survey, though specific to the already fully developed biological organisms, is quite suggestive in calling our attention to a possible scheme of enhancing the time scale of decomposition reactions in prebiotic evolution. A key at this point is a possibility of emitting the microwave photons in the process of decomposition reactions.

Once the prebiotic synthesis of oligopeptides with use of rapid quenching is focused upon, it could be likely to encounter participation of polar amino acids, such as aspartic acid, glutamic acid, arginine and lysine, in the oligomerization process. A polar amino acid in a synthesized oligopeptide then maintains a permanent electric dipole moment, and the resulting oligopeptide is electrically polarized. When the polarized oligopeptide is mechanically disturbed from its outside, it tends to be stabilized through the adjustment of the orientational polarization of the oligomer. Since the movement of the orientational polarization is associated with the acceleration of electrically charged particles in the oligomer, it can radiate an electromagnetic wave as a matter of principle.

Furthermore, the characteristic frequency for the orientational polarization of oligo- or polypeptide can be found in the frequency range of 100MHz~10GHz [11]. Oligopeptides to be synthesized in prebiotic evolution could thus be seen to undergo an extremely slow quenching as releasing the stored energy in the form of the microwave photons. The next question coming up would be how prebiotic evolution could naturally implement such a decomposition scheme accompanied with emission of the microwave photons.

3. Three-Staged Heat Reservoirs

As a matter of principle, a role of heat reservoirs to be involved in prebiotic evolution can be evaluated in terms of the energy flux density from each source [12]. The density of the solar energy flux impinging on the surface of the Earth or the solar constant is about 1370W/m^2. Although the flux density on the surface of the sun maintained at temperature 6000K is estimated about 2.4×10^{6}W/m^2 based upon Planck's law of black body radiation, the density of the impinging solar photons on the Earth is significantly diminished while the energy of each solar photon remains unchanged during the flight from the sun to the Earth. In contrast, the ambient temperature 290K near the surface of the Earth gives the thermal energy flux density of roughly 20W/m^2, which should be contrasted to the basal metabolic rate of 30W/m^2 of an average organism living on the Earth. The present rough coincidence between the energy flux density from the black body radiation and the basal metabolic rate of an average organism, though their origins are totally different, would make the surface of the Earth a habitable zone to the organism in the hindsight. Underlying the coincidence is the slow decomposition of the products synthesized as being subject to the energy influx of 1370W/m^2 while experiencing, at the same time, the thermal energy flux density specific to the ambient only as much as 20~30W/m^2.

In a similar vein, the thermal energy flux density in the hot spring at, say, 573K or 300^{o}C, near hydrothermal vents in the ocean is about 170W/m^2, while the cold surrounding water maintained at 273K or 0^{o}C keeps the nearby energy flux density on the level of 10W/m^2. The rapid quenching from the energy flux density 170W/m^2 near hot vents to 10W/m^2 in the immediate neighborhood of the cold surrounding water could be instrumental to various synthetic reactions as freezing the former thermal energy into the binding energy of various chemical bonds. In addition, the slow decomposition of the products synthesized in the process of rapid quenching would take place as experiencing the thermal environment allowing for the thermal flux density of 10W/m^2.

The likelihood of slow decomposition of the synthesized products, which may be indispensible for both prebiotic and biotic evolution, now comes to face a serious challenge. In any case, thermodynamic constraints are inescapable. The temporary stabilization of the evolving products to be synthesized and their slow decomposition cannot proceed as experiencing one and the same environment in thermal equilibrium, in the latter of which there is no likelihood of evolution. The slow decomposition requires one more heat reservoir, in addition to the reservoir at a higher temperature driving various synthetic reactions and another one at the normal ambient temperature for saving and stabilizing the synthesized products at least temporarily. The third reservoir must be the one being capable of absorbing the microwave photons of their frequency around 100MHz. As a matter of fact, the black body radiation whose peak frequency is around 100MHz is to maintain its temperature as low as 1 milli-Kelvin.

An empirical likelihood of the heat reservoir that can absorb the microwave radiations is in fact guaranteed by the present big-bang cosmology. Although deep outer space is filled with the cosmic microwave background whose black-body radiation is centered around its frequency 100GHz or at 2.725K in terms of the black-body radiation temperature, it is quite transparent to the microwaves whose frequency is far less than 100GHz. Deep outer space can serve as a heat reservoir maintained at an extremely low temperature even compared to 2.725K due to the cosmic microwave background, and it can be reached out by means of the emission of the microwave photons even from the surface of the Earth.

The cosmic microwave transparency being infinitely absorptive towards the microwave disposals without suffering the risk of being struck back on the part of the emitter now function as the third heat reservoir positioned at an extremely low temperature [13]. Such a natural implementation of the heat reservoir maintained at an extremely low temperature can make the slow decomposition of the synthesized products proceeding in the normal thermal environment, thermodynamically comprehensible. When one considers the slow decomposition as following the scheme of a heat engine operating between the normal ambient temperature and the extremely low temperature characterizing the cosmic microwave transparency, the efficiency of the work to be done by processing the transfer of heat energy would approach almost unity because of the extreme smallness of the lower temperature. Most of the heat energy fed from the heat reservoir at the higher temperature can be transferred into work. The relative amount of the heat energy transferred into the heat reservoir maintained at the extremely low temperature in the form of the microwave photons directly reaching out to deep outer space could be minute, though substantial at the same time, compared to the one transformed into various modes of work, the latter of which could eventually be dissipated as heat energy into the normal thermal environment.

The present minute, nonetheless indispensible, amount of energy flow in the form of the microwave photons, directly reaching out to deep outer space, can thus provide a solid physical means for an almost complete coincidence of both the temporary stabilization of the synthesized products and their slow decomposition in sharing the one and the same thermal environment maintained at the normal temperature without offending thermodynamic principles. Prebiotic synthesis is found to proceed through the operation of at least two different kinds of heat engine implemented in a tandem manner. One is to operate between the higher temperature unique to the energy sources for driving synthetic reactions and the normal lower temperature characterizing the ambient for the temporary stabilization of the synthesized products. Another one is between the normal ambient temperature and the extremely low temperature intrinsic to the cosmic microwave transparency for supporting the slow decomposition of the synthesized products. The environment near the surface of the Earth maintained at the normal ambient temperature serves as the low temperature heat reservoir for the prebiotic synthetic reactions, while it also serves as the high temperature heat reservoir for the slow decomposition of the synthesized products.

4. Prebiotic Enzymatic Reactions

Actual implementation of three-staged heat reservoirs could be made feasible even in prebiotic evolution if some oligomers functioning like an enzyme appear in a prebiotic synthesis. An experimental candidate for suggesting the emergence of a prebiotic enzyme can be seen in the synthesis of oligopeptides in the solution of even only glycine and alanine in the flow reactor simulating a submarine hydrothermal system [14, 15]. We observed the buildup of glycylalanine followed then by the synthesis of alanylglycine while dissecting the pre-existing glycylalanine. The sequence of emergence was always glycylalanine first and then followed by alanylglycine, and by no means vice versa. Alternation of glycylalanine by alanylglycine going along with dissecting glycylalanine suggests participation of enzymatic oligomers being capable of dissecting glycylalanine. A likelihood of such enzymatic oligomers to emerge could be seen in the wide variety of oligopeptides available in the flow reactor experiment.

The synthesis of glycylalanine is endergonic in freezing some of the heat energy supplied from the heat source maintained at a high temperature into the form of peptide bond, while the decomposition of the synthesized glycylalanine is exergonic in releasing the stored energy. The involved enzymatic reaction could change the molecular configuration of the substrate through the tactile interaction which may be extremely slow compared to electronic movements as being epitomized in the mechanical adjustment of a key-lock relation. More specifically, the ongoing tactile interaction can mechanically disturb the directional movement of electric dipole moments latent in the participating oligopeptides. Oligomers made of glycine and alanine can in fact maintain in their inside electric dipole moments even though both amino acids are non-polar, since the electric charge distribution is not uniform along the peptide chain. Consequently, the tactile deformation of the substrate caused by the thermal disturbances expected at the normal ambient temperature could be reacted upon by emitting a train of the microwave photons. The energy source compensating for the emission of the microwave photons could be attributed to the exergonic reaction for dissecting the synthesized oligomers.

5. Concluding Remarks

Prebiotic evolution proceeding on primitive planets including the primitive Earth requires both the energy sources and sinks as its necessary ingredients. Chemical synthesis of oligomers from the smaller organic molecules in the primitive environments on the Earth could be endergonic as being fed by either the photon energy from the sun or the heat energy from the core mantle of the Earth. The synthesized oligomers can freeze and store the supplied energy internally in the form of chemical bonds through the process of rapid quenching. Sustainable chemical evolution could then be made possible by constantly disintegrating and converting the synthesized oligomers into the smaller molecules to be taken in again as the necessary material resources for the subsequent synthetic reactions in an alternating manner. Such disintegration reaction is exergonic as releasing the energy acquired in the preceding synthetic reactions, extremely slowly.

The slow quenching characterizing such exergonic reactions makes the thermodynamic framework available to the likelihood of prebiotic evolution proceeding near the surface of the Earth maintained at temperature roughly 290K, to be multi-staged or at least three-staged. The effective temperature of the energy source driving the endergonic reactions is far high above 290K while the accompanied heat sink for stabilizing the synthesized products is maintained near at 290K. In contrast, the temperature of the energy source driving the exergonic reactions is near at 290K while the temperature of the intended heat sink for the disintegration reactions must be far below 290K. The candidate of the lower temperature heat sink is deep outer space itself, and the means of taking advantage of and reaching out to the sink is the microwave photons to be emitted in the process of the intervening disintegration reactions. The prebiotic material vehicle for reaching out to deep outer space maintained at an extremely low temperature could be the emission of the microwave photons from dielectrically polarizable oligomers that can also function as prebiotic enzymes.

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Appendix

起原にかかわる実験で可能なこと
－なにが問題なのか？－

生命の起原を積極的に意識した化学実験はオパーリンに端を発します。その流れに沿って現れた画期的な成果が、1953年に報告されたミラー、ユーリーによる還元性大気での放電実験です。アミノ酸の生成が確認されました。それから半世紀あまりを経て現在に至っております。その間、ミラー・ユーリーの枠組みに従って多彩な成果が生み出されてきました。しかし、判明してきたのは、目指す起原がますます遠のいて行った、とする皮肉な事態です。このことは、相反する二つのことを示唆します。一つは、起原はわれわれの手に負えるような代物ではない、とする覚めた悲観論です。もう一つは、現在に至るまでの半世紀の間、賢明かつ真面目に起原を手中に収めようと多数の関係者が心がけながら、心ならずも的をはずしてきたのではないか、との反省に基づく楽観論です。ここで、私がお話しようと思うのは、この楽観論の方です。

生命の起原を目指した化学実験は手段としてはまともであり、それに対抗できる新たな手段を思い浮かべることは困難です。コンピュータとそのディスプレーは強力な武器でありながら、それが有効となるのはあくまでも、ある程度的が絞り込まれてからです。求められているのは、漠とした起原の問題を技術的に処置可能な問題にまで絞り込むことです。少なくともわれわれの原始地球は、当初さまざまな漠とした問題を

かかえ込みながら、その一部を生命の出現という仕方で問題を絞りこむことに成功してきました。実験科学者としてのわれわれもそれにあやかりたく思っています。ここで、状況が少し明らかになってきます。起原を取り巻く問題とは一体どのような種類の問題であって、それを解決可能な問題にまで絞り込むための技術的手段に、なにがあったのか、との状況分析が、関心を寄せるに足る的として浮かびあがってきます。

起原を特徴づける現象は持続する化学反応の出現です。原始地球上を想定したとき、反応分子とその反応を駆動するエネルギー源がなんであったか、については凡そ目安が立ちます。エネルギー源を担うのは原子核の分裂、あるいは核融合反応であって、地熱、太陽光あるいは宇宙線を介してエネルギーが反応分子に提供されます。その原始地球を巨大な一つの化学反応炉とみなしたとき、そこで発生することになる厄介な問題に次の二つがあります。反応分子が十分に用意されていながら、反応を駆動するエネルギーが欠けているのがそのひとつ目です。もう一つの問題は、エネルギーが十分に用意されていながら、反応分子を欠いている場合です。この二つが問題になるのは、いずれの場合も極めて不安定だからです。反応分子が用意されていながらエネルギーを欠いている場合には、エネルギーがわずかでも外から新たに加えられると、新たな反応が進行します。また、エネルギーが用意されていながら反応分子を欠いている場合には、反応分子がわずかでも外から新たに加えられると、同じく新たな反応が進行します。この巨大化学反応炉が熱平衡にあれば、エネルギーと反応分子の間に安定した平衡状態が期待されますが、原始地球を取り巻く巨大化学反応炉は決して熱平衡に達してはいません。

エネルギーと反応分子との間で安定した釣り合いを欠いたまま化学反応炉の運転が開始されたとき、どのような道筋を経て、比較的安定した運転状況に移り行くことができるのか？これが、化学反応炉としての原始地球の遭遇した問題であったはずです。この比較的安定した運転状況のうちに含まれるのが、生命の出現と呼ばれる現象です。生命の出現が比較的安定した現象である、との表明には二重の意味がこめられています。比較的安定であるとは、外部から少々の揺さぶりを受けてもそれに動じない頑健さを備えている、ということです。この頑健さがなければ、生命の出現にあたかも敵対するかのような苛酷な周囲状況のなかからその出現を期待することは甚だしい的はずれになります。さらに、生命の出現がまったくの気まぐれによるものとするならば、その出現を実験科学の対象にするのはそれこそ正気の沙汰ではなくなります。

そこで巨大化学反応炉としての原始地球に提供されたと思われる反応分子とエネルギーの素性を、もう少し具体的に見てみることにします。反応分子としては、アミノ酸分子を例としてとりあげます。エネルギー源としては原始海洋での熱水口近傍で利用可能となる熱エネルギーを考えてみます。熱水口からの熱エネルギーはその近くのアミノ酸の重合を促進します。しかし水中の重合反応であるため、加水分解も同時に生じます。この中にあって、利用済み熱エネルギーは周りの冷海水中に廃棄されます。ここで進行する熱重合反応と加水分解反応には、熱平衡反応において認めることのできない、一つの特徴が備わっているのがわかります。重合反応の各々がそれとは逆方向に進む分解反応と個別に釣り合っていることはない、とする特徴です。この個別反応での釣り合いの欠如は、熱平衡反応では決して想定することのできなかった状況です。

熱平衡系では、定義により、順方向に進む反応は、それぞれ、それを反転させた逆方向に進む反応と個別に釣り合う、との詳細釣り合いが成立しています。この詳細釣り合いを熱水口近傍での反応には適用することができません。われわれは実験によってこのことを実際に確かめました。熱平衡ではアミノ酸モノマーの重合によってダイマーが生じる反応は必ずダイマーがモノマーに分解する反応と釣り合い、それによって熱平衡反応の安定性が保たれています。ところが熱水口近傍での反応では、モノマーの重合によってダイマーが生成され、そのダイマーが新たなモノマーと重合してトライマーを生成し、そのトライマーがさらに新たなモノマーと重合してテトラマーを生成し、そのテトラマーが加水分解を受けて二つのダイマーに分解される経路があることがわかりました。化学反応系が比較的安定に実現するためには、重合と分解の釣り合いが求められながら、ここで実現したのは熱平衡系を想定した詳細釣り合いではなく、迂回路を経由した迂回路釣り合いです。ダイマーの安定性を評価するには、それと直結したモノマー、トライマーとの反応に加えて、テトラマーからダイマーに戻る迂回路経由分も加える必要がでてきます。

熱水口近傍では、迂回路釣り合いを介してそこでの化学反応系の安定性を実現するものがあります。このことが実験によって確認されました。迂回路釣り合いによる、安定した化学反応系の実現とは、安定した化学反応回路に実現に他なりません。加えて、ひとたび、化学反応回路が実現されますと、それを特徴づける一つの定量的な指標が登場してきます。化学反応経路の下流から上流に向けての還流があるため、その寄与は自己触媒的となり、回路を構成する分子は、ある限られた時間内ではありますが、時間の経過とともにその個数を指数関数的に増加させます。このことも、実験によって確かめることができました。

要約します。熱水口近傍において化学反応回路を実現することが可能となります。これまで、安定した、自律的な化学反応回路の実現は生化学の独壇場でした。ところが、実験という手段に訴えるならば、生物、あるいは生命の出現するはるか以前から、原始地球上の海洋中の熱水口近傍で比較的安定な仕方で、化学反応回路が出現し得た、とする見方が新たに浮かび上がってきます。物質現象としての生命の特徴は、それが保有する化学反応回路にあります。原始地球がエネルギーと反応分子とをいかに釣り合わせるかとの問題を抱え、それを解決可能な問題に絞り込もうとしていたとき、熱水口由来の化学反応回路は得難い助け舟の一つになり得たは

ずです。仮に原始酵素の出現が偶然に由来するできごとであっても、それの定着を熱水口由来の、比較的安定した化学反応回路に委ねる、とする道がここに開かれてきます。原始酵素と化学反応回路のいずれもが、特異的である、という点において共通しているからです。もちろん、お互いに助けにならなければ、それを参照する必要は毛頭ありません。

生命の出現に向けて問題状況を絞り込むことができたとは、生命の出現以前に既に自然選択が働いていた、ということです。複製分子が出現する以前でも、自然由来の選択は可能です。海底熱水口の近くでは確かに、前生物的自然選択が可能となる一つの条件を満足しています。高温で重合した反応物が周りの冷海水に抛り出され、それが分解される以前に急冷されますと、分解の抑制により、重合の方が熱平衡での反応に比較して選択的に、かつ一方的に強調されることになります。さらに、熱水口を繰り返し訪れることにより、この選択性の寄与は掛け算の仕方でその効果を拡大して行きます。原始地球にとっての海底熱水口は、そこで進行する化学進化に、前生物的自然選択の場を提供した、となります。化学反応回路の出現は、前生物段階での自然選択が働いた一例です。

この前生物的自然選択は、分割することのできない資源の消費を司る法則、たとえば、ポテンシャルとしての温度差に対するフーリエの熱伝達則や電位差に対するオームの法則の内に、すでに含まれています。資源は一方的に消費される対象であるため、それを貫くのは、独り占めによる早もの勝ち、の原則です。資源の消費を司るのは消費者であり、消費者の中で支配的になるのは消費速度を最大とするものです。ある一定の消費速度を伴った消費者の中により小さな速度で消費するものが現われても消費者の交代は起こりません。しかし、より大きな速度で消費するものが現われた場合には旧来のものに代わってそれが定着し、消費者の交代が生じます。フーリエの熱伝達則、あるいは、オームの法則が安定した物理法則であると信頼されているのは、最大速度での資源消費を保証する、前生物的な自然選択のためです。

始めに、ミラー・ユーリーの枠組みの生産的な点とその限界について触れました。この枠組みの歴史的な意義を認めた上で、さらに求められるのは、起原にかかわる問題の一層の絞り込です。その絞り込み先の候補として、ここで申し上げたく思っていたのが、生物あるいは生化学に由来しない化学反応回路の活用です。実験に基づくかぎり、原始海洋の海底熱水口近傍では、生命を前提とすることなく、化学反応回路の運転が可能となりえたはずです。