

Temperature oscillations near natural nuclear reactor cores and the potential for prebiotic oligomer synthesis

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Abstract Geologic settings capable of driving prebiotic oligomer synthesis reactions remain a relatively unexplored aspect of origins of life research. Natural nuclear reactors are an example of Precambrian energy sources that produced unique temperature fluctuations. Heat transfer models indicate that water-moderated, convectively-cooled natural fission reactors in porous host rocks create temperature oscillations that resemble those employed in polymerase chain reaction (PCR) devices to artificially amplify oligonucleotides. This temperature profile is characterized by short-duration pulses up to 70–100 °C, followed by a sustained period of temperatures in the range of 30–70 °C, and finally a period of relaxation to ambient temperatures until the cycle is restarted by a fresh influx of pore water. For a given reactor configuration, temperature maxima and the time required to relax to ambient temperatures depend most strongly on the aggregate effect of host rock permeability in decreasing the thermal expansion and increasing the viscosity and evaporation temperature of the pore fluids. Once formed, fission-fueled reactors can sustain multi-kilowatt-level power production for 10^5 – 10^6 years, ensuring microenvironmental longevity and chemical output. The model outputs indicate that organic synthesis on young planetary bodies with a sizeable reservoir of fissile material can involve more sophisticated energy dissipation pathways than modern terrestrial analog settings alone would suggest.

Keywords Polymerization · Radiolysis · Oligomerization · Phosphate · Nucleoside

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Introduction

The early Earth environment differed substantially from modern settings; the relative nearness of the moon, the thickness and composition of the Earth's crust and the composition and temperature variation of the Earth's atmosphere are poorly constrained geophysical variables that likely drove the diversity and intensity of naturally-occurring energy dissipation pathways far from recent norms. Prebiotic laboratory experiments often use proxies for ancient energy dissipation pathways that are likely to have been widespread on the early Earth (as inferred from the geological or astronomical record) even if those sources of energy are no longer widespread under modern Earth conditions. Impact records from the Moon indicate that the Earth experienced a period of heavy bombardment shortly after its formation (Chyba and Sagan 1997; Cockell 2006) and hydrothermal vents result from the interaction of water and reduced mantle and lower crustal minerals that make up a significant percentage of protoplanetary materials (Baross and Hoffman 1985; Miller and Bada 1988). These and other geologic phenomena form the heart of a multidisciplinary research agenda that has greatly advanced our understanding of the conditions in which inorganic reactants can be made into organic monomers (Orgel 1998). The same agenda has also usefully highlighted how difficult it is to create abiotic polymers of sufficient complexity and specificity to become 'living' systems without sophisticated intervention (Shapiro 1984).

Chemical processes that can drive prebiotic oligomerization have been intensively studied (Oró and Stephen-Sherwood 1974), but the diversity of natural settings that can host or promote the formation of organic polymers remain a relatively unexplored aspect of prebiotic synthesis (Deamer and Weber 2010). Energy sources, catalysts and chemical potential of simple carbohydrates have all been investigated as drivers for condensation reactions, but placing these processes into a plausible, naturally-occurring environment without invoking or relying upon unrealistic mechanisms of concentration, heating, transport or co-occurrence of synthesized monomers and key inputs such as phosphate has proven challenging (Baaske et al. 2007; Patel et al. 2015; Powner et al. 2009). Regardless of the chemical mechanism(s) invoked, or the particular historical circumstances that formed life on Earth, it is clear that only by understanding the physics and chemistry that enable a transition between polymers and 'living' systems will it be possible to explore the full potential for life in the universe (Ruiz-Mirazo et al. 2014).

Natural nuclear reactors create a unique energy dissipation environment that may help to explore this transition as it may have occurred in Earth's past, or to engineer such a transition for laboratory experiments. Nuclear reactors are known from the geologic record (Gauthier-Lafaye et al. 1996) and a case has long been made for their consideration as an energy source that could have promoted the synthesis of organic materials (Draganić et al. 1980; Draganić et al. 1985). Fissile fuels existed in much greater quantities at the time of the Earth's formation relative to the present (Adam 2007; Coogan and Cullen 2009). This means that smaller concentrations of fissile elements such as uranium were required to create naturally occurring reactors immediately following Earth's formation. The diverse processes of dissipation of fission energy act as a compact proxy for many different forms of energy transfer that would have been present on the early Earth, including the direct and indirect creation of free radicals, ionization, convective heating and condensation or phase change reactions.

The physics of natural reactor formation on the prebiotic Earth have been modeled (Draganić et al. 1993), but there are no reported models that have been constructed to estimate how heat production by reactors may or may not be conducive to generating complex organic

compounds. To more accurately assess the organic polymer synthesis productivity of natural nuclear reactors, temperature predictions were created using models of heat transfer based on known examples of natural reactor zone formation from the geologic record. Heat transfer characteristics predicted by these models are cross-compared with organic monomer synthesis products from gamma ray bombardment facilities. Finally, the reactor zone temperature profiles, mineral content and gamma radiolysis products are compared to the temperature profiles, chemical reactants and organic products of polymerase chain reaction (PCR) devices. These disparate pieces of evidence indicate that natural nuclear reactors exhibit many unique thermochemical properties that could have promoted the formation of oligomeric compounds on the early Earth, or on exoplanets comparably endowed with fissile isotopes.

The Geologic History of Natural Nuclear Reactors

Natural nuclear reactors were predicted to exist almost 20 years before they were discovered in the Francevillian basin near Oklo in Gabon (Kuroda 1960). The Oklo reactors formed when uranium dissolved in pore waters precipitated at a redox front created by buried organic matter in subsurface sandstones around 2.0 Ga (Gauthier-Lafaye et al. 1996). The reactors were buried under 2000 m of rock and operated under ambient conditions of about 150 °C and a hydrostatic pressure of about 200 bars (Openshaw et al. 1977). At least 16 reactor core zones have been identified in the region, separated by distances of about 30 km throughout the Francevillian basin (Bentridi et al. 2011).

At Oklo, it is estimated that the reactor operated on a steady power on-power off cycle for hundreds of thousands of years (Meshik et al. 2004). The upper limit of power productivity and maximum temperature within the core was ultimately regulated by the boiling temperature of the water; after 30 mins of power-on reactor core conditions, water was heated into supercritical steam with peak core temperatures reaching 300–500 °C (Gauthier-Lafaye et al. 1996). The steam left the reactor core, condensed within the surrounding host rock, and slowly percolated back into the core to begin the cycle again after about 2.5 h. About half of the reactors contained abundant biologically-derived organic material that was hydrothermally and radiolytically altered by the radiation environment within their cores (Nagy et al. 1993). The organic material encased and immobilized the uranium oxides, further stabilizing the reactor core configuration.

There are no older or younger examples of natural nuclear reactors, though measured variations in the ratio of ^{235}U to ^{238}U from uranium deposits around the world provide a means of estimating the maximum amount of uranium that could have been consumed as fission fuel over the history of the Earth. These variations are due to naturally occurring variation (i.e., geochemical fractionation and induced fission) and analytical uncertainty (Brennecka et al. 2010). Assuming that the maximum variation is due to induced fission events in natural reactors enables a calculation of the upper limit of total reactor activity on the early Earth. Naturally occurring uranium contains a $^{238}\text{U}/^{235}\text{U}$ ratio of about 137.78, with variations of about ± 0.1 (Chernyshev et al. 2014). As described by Draganić et al. (1993), the crust has an average concentration of about 3 g of uranium per ton, and the time-averaged fraction of uranium that was composed of ^{235}U was about 0.1 over the span of time from 4.5–1.5Ga. Within these constraints, over 100 million reactor sites with the size, fuel consumption rate and duration of the Oklo reactor cores could have functioned over Earth's history within the envelope of measured isotopic variation.

The decay history of fissile isotopes such as ^{235}U indicates that it was possible for natural reactors to form with smaller amounts of uranium early in Earth's history, thereby opening alternative mechanisms of reactor formation that do not require biologically-derived organic compounds to concentrate uranium (Coogan and Cullen 2009). The reactors at the Oklo site are hosted within a relatively well-preserved Paleoproterozoic sedimentary sequence (Gauthier-Lafaye et al. 1996). The paucity of well-preserved sequences in rocks of older age than the Oklo deposits points to the possibility that the existing geologic record of natural nuclear reactors is an artifact of incomplete preservation of a more widespread geologic phenomenon (Adam 2007; Kuroda 1960; Negrón-Mendoza et al. 1983). An alternative geologic model of reactor formation within placer mineral deposits on the early Earth has been proposed and evaluated using a simple model of reactor criticality for proportions of heavy minerals commonly found in placer beach deposits. This model predicts that around 4.3Ga, uranium exhibited sufficient levels of ^{235}U enrichment that only 1–7 % (by weight) of uraninite was required for a reactor core 10 m in diameter and 0.5 m thick to form (Adam 2007). This is well within the bulk composition of heavy mineral beach sands, which can vary from 15 to 25 wt.% of total heavy minerals (Mahadevan and Sriramadas 1948; Mahadevan et al. 1959; Mohapatra et al. 2015).

Natural Nuclear Reactor Functionality

Nuclear reactors function and behave as complex thermodynamic feedback systems. Fission reactors derive their energy from the dissociation of atomic nuclei in response to neutron bombardment. Reactor criticality is defined as a ratio of daughter neutrons to parent neutrons; for every neutron that enters the core to induce a fission event, a critical reactor contains the dimensions and concentrations of fissile fuel needed to create at least one more neutron that also survives to induce another fission event, maintaining a chain reaction of fission events and producing a steady amount of energy. Hydrogen (present in molecules of water, deuterium or organic compounds) or other low-molecular-mass elements present within a reactor core moderate neutrons, slowing them down to thermal speeds so that they may induce fission in the reactor fuel atoms. The function of reactors with a simple geometric configuration can be modeled as the interaction of four different factors, each of which describes a physical parameter affecting the likelihood that a neutron entering the core will persist long enough to induce another fission event (Department of Energy 1993).

Reactor behavior changes as the reactor consumes its nuclear fuel, which means that the energy output, radiation profile and chemical environment within the reactor changes over the reactor lifespan. A particularly important factor for natural nuclear reactors is the void coefficient, which describes how well neutrons are moderated to sustain reactor criticality as the internal temperature of the reactor core changes and voids (usually steam bubbles) are created. In most configurations, this factor is negative, meaning that neutron moderation forms a negative feedback loop that links the peak temperature of the reactor core to the temperature that drives neutron-moderating compounds out of the core, i.e., the evaporation temperature of water under prevailing core conditions (Meshik et al. 2004). As reactor water is driven out of the core as steam, neutrons cannot be moderated, and the nuclear cycle shuts down until temperatures have cooled sufficiently that water may re-enter the core (Fig. 1).

The result is a thermodynamically sophisticated, long-lived and high energy density heating system with internal and external temperatures governed by physical processes that limit neutron moderation and power production. Though there are many permutations of reactor

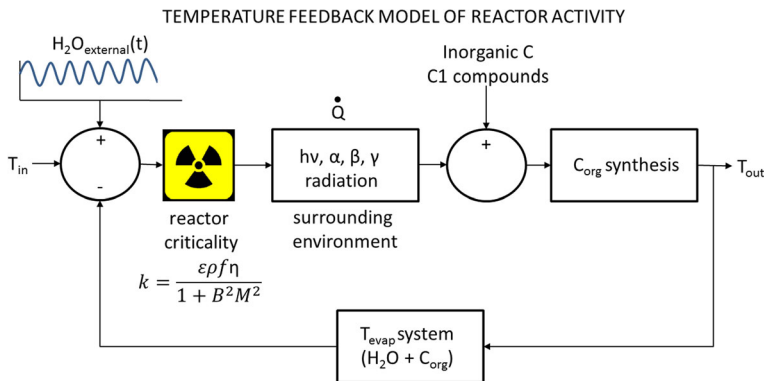


Fig. 1 A simplified temperature feedback model of natural reactor activity. For more details regarding reactor criticality conditions and coupling to evaporation temperature, see Adam 2007

configurations and host rock conditions that can be plausibly imagined for such a system, the temperature-dependency of the feedback loop (specifically, the evaporation temperature of the neutron moderating fluid) inherently limits the periodicity and peak temperatures produced by the core. These limits constrain the temperature profiles of reactors to a relatively narrow set of behaviors. The question becomes whether the temperatures reached around the periphery of a typical reactor core, at distances beyond the destructive effects of intense radiation within the core itself (a few mm for alpha particles, about 20 cm for beta particles and exponentially-decaying values with distance for gamma rays and neutrons), are sufficient to drive oligomer synthesis reactions of interest to the prebiotic community.

Methods

The Energy2D thermal simulation program was used to model a cylindrical reactor zone 10 m in diameter and 0.5 m thick. The 10 m zone was broken into 1.5 m length fragments separated by 0.5 m distances to facilitate simulated coolant flow through the reactor zone. Conduction and convection cases are evaluated as model endmembers to constrain temperature maxima and minima at varying distances from the reactor core. The model was built to approximate a reactor zone that consists of a mix of uraninite and quartz sand in a fine sandstone placer beach deposit. In this model, the periodicity of reactor activation is assumed to be driven by influx of water caused by lunar tides (Adam 2007). Consistent with deposition of placer minerals along high tide margins of a beach, low-tide periods are assumed to coincide with dry periods for the reactor, which would cause the reactor to enter a quiescent, subcritical phase, in which the reactor core is heated by residual daughter radionuclides. Lunar tide periodicity of the Hadean and early Archean Earth is not constrained by geologic measurements; however, most astrophysical models of moon formation and subsequent evolution of the Earth-Moon system indicate that the Moon was nearer the Earth than today, and that the angular rotation speed of the Earth was faster than modern values. Both effects would result in a shortened periodicity of lunar tides.

The model assumes a lunar tide baseline periodicity of 2 h, and tide periodicity is varied to constrain its effect on model outputs. The baseline heating period is 30 min of reactor-on operation, wherein the reactor zone fragments are set at a constant temperature of 100 °C or

150 °C. The upper temperature limit is derived from assuming a shallow buried reactor core, ranging from 0 to 20 m depth, with 0.2 bar/m pore pressure gradient, which in turn places an upper limit on the maximum temperature of the reactor core due to a negative void coefficient. The thermal properties of the background medium during the reactor-on phase are an average of those of water and wet sandstone, diffusivity out of the system is set to that of water, and the fluid properties of the medium during the reactor-on phase are set to those of water with the thermal expansion and viscosity offset by factors of 10^2 to account for the aggregate effect of the pore channel permeability of an unconsolidated, well-sorted sandstone. During the reactor-off phase, the thermal properties of the background medium are an average of those of air and wet sandstone, diffusivity out of the system is set to that of air, and the fluid properties are set to those of air but with the thermal expansion and viscosity offset by factors of 10^2 to account for the aggregate effect of the pore channel permeability of an unconsolidated, well-sorted sandstone. Appendix A summarizes all model inputs.

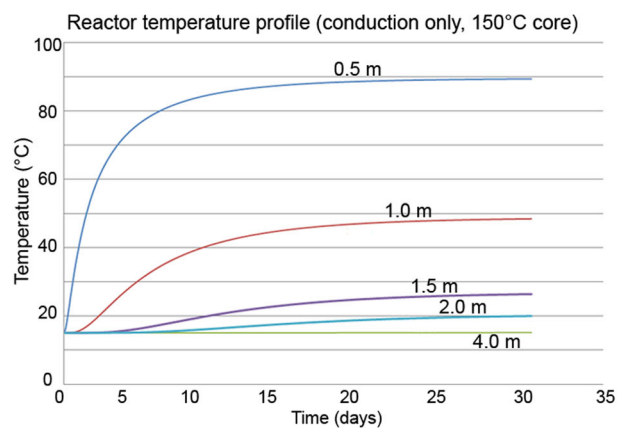
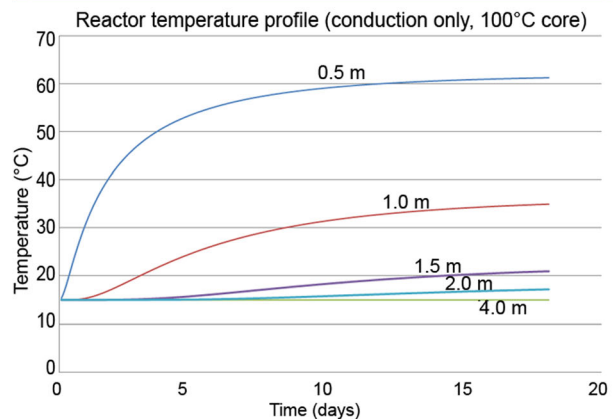
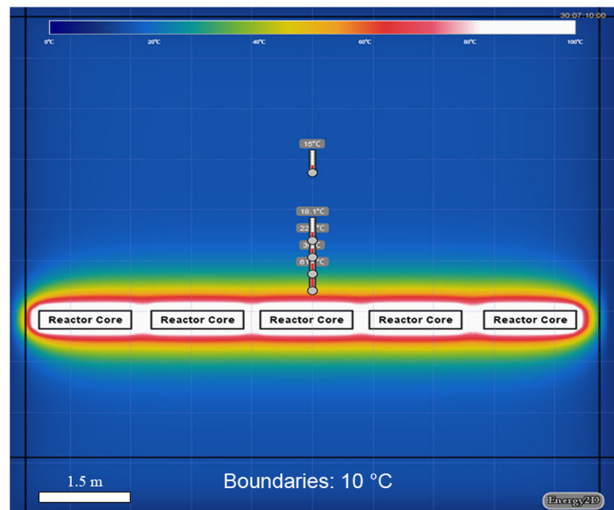
Model Outputs

The conduction-only heat transfer case represents an end-member model of reactor formation within a host rock that is impervious to porous fluid flow (Fig. 2). Heat output from the reactor core slowly raises the ambient temperature of the surrounding material at varying distances from the core. The steady-state temperature maximum for a general location about 0.5 m from the core is about 60 °C when the core temperature is limited to 100 °C, and about 90 °C when the core temperature is limited to 150 °C. There is essentially no variation in temperature over time once steady-state conditions are reached after about 15 days of cumulative reactor-on time.

The temperature profiles for convective heat transfer exhibits greater variation and a more complex structure over time than the conduction-only models (Fig. 3). The formation of convective plumes near the core-background fluid interface facilitates much more rapid transfer of heat energy away from the reactor core, and causes the formation of random temperature fluctuations over time at varying locations relative to the reactor core. The location and intensity of individual convective plumes is stochastic, but there are common features of each temperature cycle that is driven by, and therefore coincident with, the timing of reactor-on/reactor-off cycle of reactor criticality.

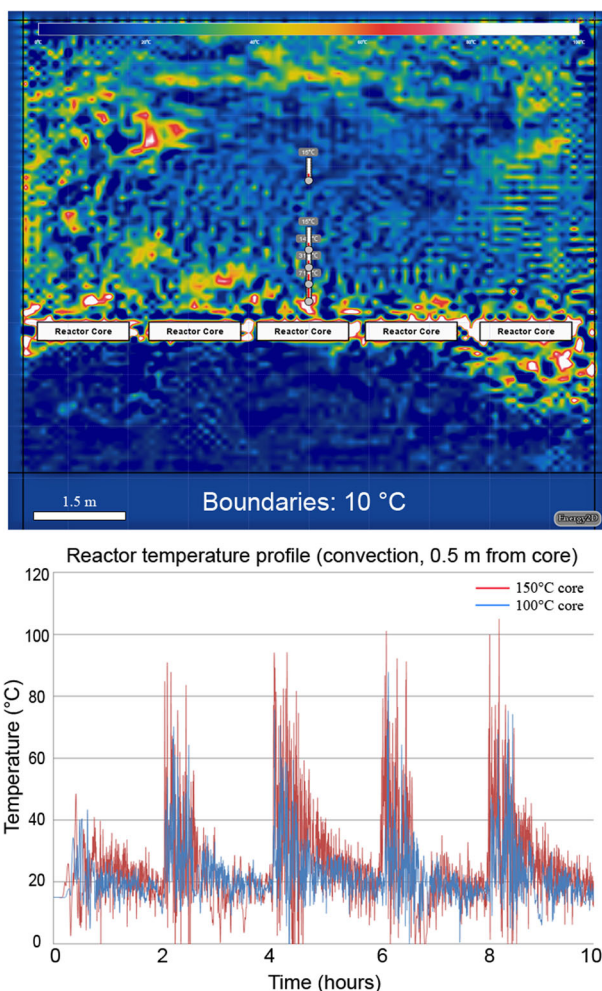
A typical temperature cycle (Fig. 4) begins with 1–3 spikes ranging from 65 to 90 °C maximum temperatures (slightly higher values for a 150 °C core temperature), each lasting 1–2 min, immediately following reactor activation. The number, timing and maximum temperature of the spikes vary slightly from cycle to cycle. These temperature spikes are followed by a period of about 10–20 min of temperatures ranging from 25 to 70 °C as the volume immediately above the reactor dissipates the heat from the reactor. Following reactor de-activation, temperatures relax to the background (ambient) temperature within 15–20 min until the reactor is once again activated, completing the temperature cycle. Shorter or longer periods of reactor-on/reactor-off configurations do not generally alter the progression or maxima of temperatures reached throughout the cycle. However, the T_{\max} reached by the temperature spikes is generally reduced if the temperature has not relaxed to near-background levels before the next cycle begins. Relaxation to background temperatures takes approximately 20–30 min. Since most models of lunar proximity and day length for the early Earth

Fig. 2 Temperature profiles at varying distances from a shallow buried reactor core for conduction-only cases of heat transfer. Top: visual representation of the 2D temperature profile and placement of temperature sensors at varying distances from the reactor. Middle: Variation of temperature over time with 100 °C core temperature. Bottom: Variation of temperature over time with 150 °C core temperature



imply lunar tidal periods in excess of at least 8–9 h (Williams 1997; Zahnle and Walker 1987). the modeled T_{\max} values are expected to be reflective of actual conditions for a reactor formed on the early Earth.

Fig. 3 Temperature profiles at varying distances from a shallow buried reactor core for convection cases of heat transfer. Top: visual representation of the Energy2D temperature profile and placement of temperature sensors at varying distances from the reactor. Bottom: Variation of temperature over time 50 cm from a reactor core with 100 °C (blue) and 150 °C (red) core temperatures

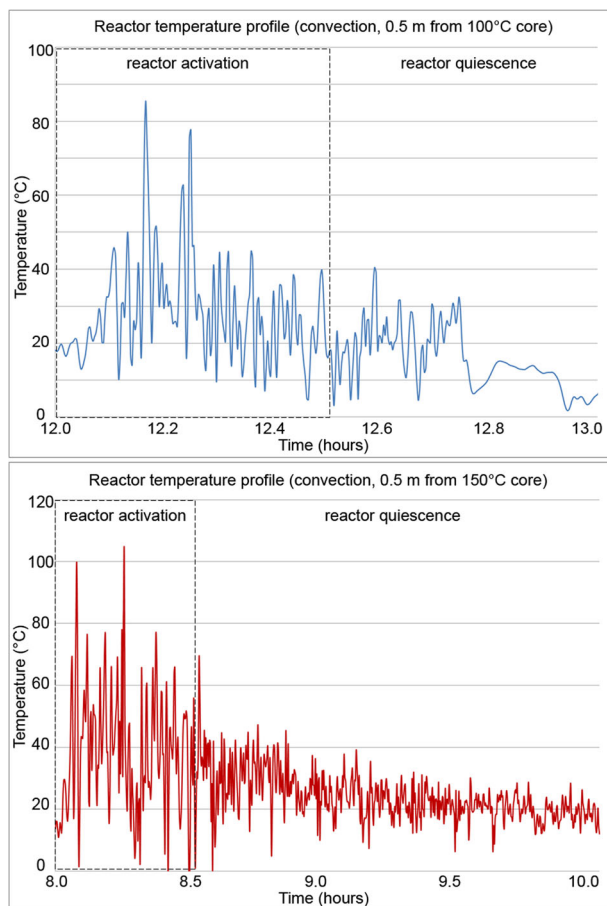


Discussion

The temperature profiles calculated for the conduction-only heat transfer cases exhibit almost no stochastic variation over time; shallow buried reactors in host rocks exhibiting this form of heat transfer are unlikely to serve as a source of heat that can drive interesting prebiotic chemical reactions. However, heat transfer by convection creates a stochastic but structured temperature profile around the margins of the reactor core that exhibits the potential to drive organic synthesis reactions of interest to the origins of life community, most notably heating/cooling and wetting/drying cycles that drive oligomerization reactions (Lahav et al. 1978; Mamajanov et al. 2014; Oró and Stephen-Sherwood 1974).

The convective temperature profile of short-duration temperature spikes that reach maxima just below boiling temperatures, followed by a prolonged period of moderate heating, and concluded by an extended period of low-temperatures until the cycle is repeated strongly resembles artificial heating profiles used in polymerase chain reaction (PCR) devices (Hadidi

Fig. 4 Typical temperature cycle under convective flow conditions, core maximum temperature 100 °C (top) and 150 °C (bottom). Temperature maximum spikes last about 1–2 min in duration, followed by temperatures above ambient for about 15 mins, and relaxation to background temperatures over about 20 mins before returning to oscillation near the background temperature until the cycle is restarted



and Candresse 2003). In a PCR cycle, an oligomer such as DNA is heated to around 95 °C for a few minutes to separate the two DNA strands from their bound state as a helix. The temperature is then dropped to around 70 °C to allow a replicative enzyme and activated nucleotides to promote the formation of respective strand copies. Finally, the temperature falls to around 5–15 °C to preserve the newly replicated strands until the next PCR cycle may begin with a fresh input of nucleotides. This process is repeated many times, resulting in rapid sequence replication in just a few hours.

An engineered PCR device can only function with pre-existing, biologically-derived replicative enzymes, and the continued input of activated nucleotides that have been artificially or biologically produced. Under prebiotic conditions, an alternative source for these components proximal to the reactor would be required to drive oligomer synthesis reactions to obtain similar chemical products. Gamma radiolysis experiments have been conducted to explore the synthesis of prebiotic compounds via gamma irradiation (Dondi et al. 2011; Draganić et al. 1980; Draganić et al. 1985; Negrón-Mendoza et al. 1983; Ramirez et al. 2001). In these experiments, gaseous compounds simulating primitive atmospheres or simple mixtures of aqueous carbon compounds such as acetonitrile and methanol were irradiated with gamma rays. The result was a mix of pyrimidines, purines and amino acids. The production of adenine

(Dondi et al. 2011) from relatively simple precursors that may have been present on the early Earth is one of the most interesting findings of these studies, given that it is a compound central to information transmission, cellular respiration and protein synthesis in all forms of life. The convective dissipation of heat can cause chemical species such as adenine produced within the reactor core to be carried out to the reactor margins, where they can cool and interact with other radiolytic synthesis products.

Placer mineral settings also indicate a plausible source of phosphate for the creation of activated nucleotides on the early Earth. Phosphate-bearing molecules are central to energy metabolism, genetic information storage and chemical synthesis intermediates throughout all forms of life (Westheimer 1987), and identifying a plausible mechanism for its incorporation into prebiotic chemistry remains an important problem. Common placer components include the radioactive thorium-uranium-phosphate minerals monazite and apatite, which are found in placer beach deposits in India, Australia and elsewhere in the world (Mahadevan et al. 1959; Mallik et al. 1987; Prasad and Asher 2001; Roy 1999). Monazite was also a probable source mineral for the uranium that formed the Oklo natural nuclear reactors (Cuney and Mathieu 2000). The presence of apatite within sands that host nuclear reactors opens the possibility for phosphate-mineral catalyzed reactions. Apatite has been shown to catalyze the phosphorylation of adenosine and other nucleosides when mixed with pyrophosphate under drying conditions and elevated temperatures up to 100 °C, and adenosine 5'-phosphate may be further phosphorylated to ADP and ATP with relatively high yield (Neuman et al. 1970a; b). Dissolved phosphate also plays multiple roles as an acid/base catalyst, a nucleophilic catalyst, a pH buffer and a chemical buffer in controlling synthetic reactions that lead to the production of activated ribonucleotides (Powner et al. 2009).

The observed interaction between radiolysis, thermal heating and reactor functionality at the Oklo reactors provide independent indications that the reactor environment is suitable for driving sustained organic synthesis. Of the sixteen known natural fission reactor cores, six reactors contain only traces of organic matter, but the others are rich in organic substances. Though biologically-derived organic matter helped to concentrate the quantities of uranium sufficient to initiate the nuclear chain reactions, the sustained operation of the reactor further altered this initial amount of carbon hydrothermally. Specifically, liquid bitumen generated by hydrothermal reactions became a solid, consisting of polycyclic aromatic hydrocarbons and a mixture of cryptocrystalline graphite, which enclosed and immobilized the uraninite fuel and the fission-generated isotopes entrapped within the uraninite (Nagy et al. 1991). This mechanism prevented major loss of uranium and fission products from the natural nuclear reactors and may have stabilized reactor functionality over hundreds of thousands of years (Nagy et al. 1993; Naudet 1991).

Direct radiolysis of organic compounds is not the only energy dissipation pathway at the periphery of reactor cores; ionization by beta particles and Cerenkov radiation can create proton gradients localized to organic-filled micropores (Fig. 5). In this process, the volume near the core contains some pore spaces that have higher (green) and lower (blue) concentrations of buffering organic compounds. These organic-rich microvolumes may have accumulated and become concentrated over many cycles of reactor activation or tidal flux. Upon irradiation, protons are buffered more effectively within the microvolume containing organic compounds, and a proton gradient is formed along the edges of the microvolume. This mechanism has already been demonstrated to drive the reduction of the high-energy charge carrier NADPH by β - and X-rays (Chan et al. 1975) and phosphorylation of the low-energy charge carrier ATP by longer wavelength photons (Gould et al. 1979) in the presence of

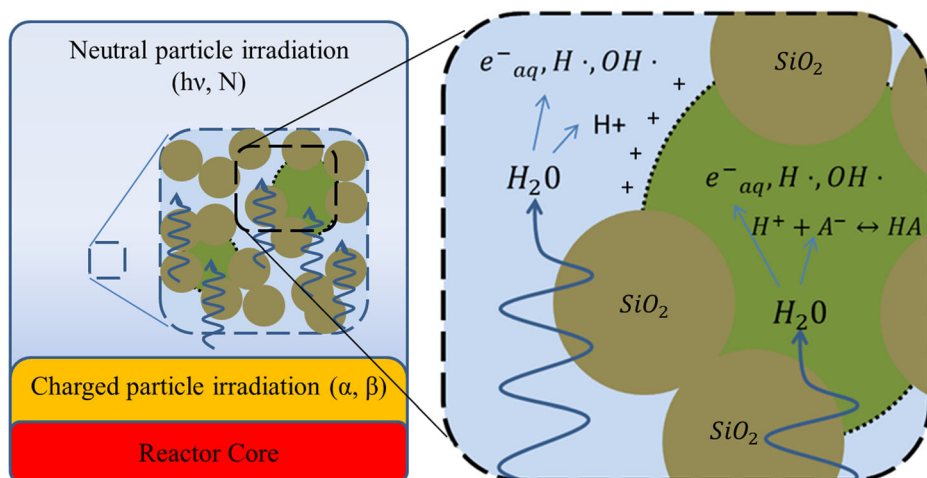


Fig. 5 Depiction of proton gradient formation arising across micropores created between sand grains (brown) containing slightly more organic buffering compounds (green) and slightly fewer organic compounds (blue) within an ionization field

respective functional proteins and buffer solutions. The pervasiveness of the proton motive force across all domains of life has been used to infer that the creation and exploitation of a proton gradient was a feature of the last universal common ancestor (Lane et al. 2010; Lane and Martin 2012), thus indicating its energetic presence at the origins of life (Herschy et al. 2014). The advantage of a proton gradient generated by ionization is that the gradient is localized to the organic-filled microvolumes, thus removing the need to tune physical and chemical parameters of the system (i.e., the thickness and composition of the barriers between alkaline vent effluent and an acidic external environment) to create the gradient at sites that contain reactive organic molecules.

The complexity, diversity and co-location of energy dissipation pathways associated with reactor cores enables the construction of a conceptual model linking monomer formation to the emergence of polymer synthesis in this environment (Pascal et al. 2013). Simple carbon reactants were already present in waters near the primitive oceanic air/water interface as dissolved atmospheric gases or as remnants of meteoritic or cometary influx (Chyba and Sagan 1997; Pasek and Lauretta 2008), radiolysis of the atmosphere (Kobayashi et al. 1998; Ramirez et al. 2001) or heavy mineral catalysis of atmospheric gases (Schrauzer and Guth 1977). Near reactor cores, direct radiolysis of organic compounds by charged particles produces monomers near the reactor core that are transported outward from the core by convective currents. During transport, these monomers are heated and cooled while they are brought into contact with different groups of monomers generated by neutral particle irradiation (neutrons, gamma rays and Cerenkov radiation) farther from the core. More specifically, these monomers are transported through a halo of Cerenkov radiation (UV light with a spectrum ranging from about 300–450 nm) up to 20 cm from the core created by the slowing of beta particles, which is known to drive the formation of ribonucleotide and amino acid precursors (Ritson and Sutherland 2012). Temperature fluctuations at the periphery of reactor cores occur in phase with influxes of fresh monomers. This is a physicochemical characteristic that distinguishes natural reactors from hydrothermal vents or other cyclic phenomena such as day/night cycles or tides. The convective dispersal of monomers away from the reactor core

would be an efficient mechanism for dispersing reactive metabolic substrates to volumes where long-chained compounds may persist.

The periodic heating of the core, combined with tidal outflow, causes random permutations of monomeric compounds to become isolated in micropores within the host sandstone surrounding the reactor core as water leaves the system at low tide and the system cools. The monomers interact with one another and with adjacent mineral surfaces within these micropores, which undergo a mix of condensation- and carbohydrate-driven oligomer synthesis processes driven by heating/cooling and wetting/drying reactions (Forsythe et al. 2015). Throughout the period of reactor quiescence, some of these oligomers persist while others are broken down due to weathering or residual radiation bombardment. With the next influx of tidal waters, the cycle begins again. Reactor criticality brings a fresh influx of newly synthesized monomers created near the core boundary into contact with the micropores containing newly synthesized oligomer substances. New permutations of monomers and oligomers are created, some of which are better able to persist throughout successive reactor cycles. The resulting physicochemical system has the potential to explore a relatively large parameter space of peptide formation (Rodriguez-Garcia et al. 2015). The success of some permutations of organic materials at persisting between periods of reactor operation and tide-driven desiccation leads to their successive accumulation and increased incorporation into polymers of greater length that are effectively ‘imprinted’ by the chemical selection effects of the environment. As some micropores persist over longer periods of time, they are more likely to accumulate polymers that can take advantage of the ephemeral proton gradient created between the organic-rich micropore volume and the surrounding interstitial pore water.

The details of the environment invoked to construct this framework lead to extended predictions that link monomer and polymer synthesis, monomer/polymer interactions and the emergence of the last universal common ancestor. The temperature and radiolysis profiles associated with the periphery of reactor cores should promote the formation of intermediate, oligomer-sized compounds that are able to dissipate transient energy and chemical gradients and can also persist in a high-radiation-dose environment. Many of these intermediates may not leave a direct trace in the genomes of extant organisms, and may be formed of reactive organometallic complexes with functions that were eventually replaced by gene-encoded proteins. However, there may remain evidence for ancestral versions of highly specialized, extant proteins (such as ATP synthase or NADP reductase) that are better able to carry out their enzymatic functions under detrimental environmental conditions such as high radiation dose, variable temperature and periodic desiccation. Ionization of heterogeneously distributed pore volumes should simultaneously create proton gradients and give rise to conditions of prebiotic selection for oligomers capable of directing proton gradient formation into organic synthesis. Finally, synthesis of monomers and oligomers should be coupled to chemically degrading conditions associated with convection-driven exchange and diffusion, reactor-driven irradiation and environmental weathering of the chemical products by ambient environmental conditions. The coupling between synthesis and degradation reactions should cause only those monomers and oligomers that are amplified through interactions with other chemical species produced within and adjacent to the reactor to persist over long periods of time.

Though the available evidence indicates that fission-driven temperature oscillations may assist abiological synthesis of oligomeric compounds, there are many outstanding questions regarding the efficacy of this process to bridge the transition between oligomers and complex

systems with ‘living’ attributes. There are no reported experiments examining whether gamma radiolysis of simple carbon precursors can be coupled to apatite-catalyzed phosphorylation or sugar production to create activated nucleosides and nucleotides. Nor are there experiments constraining whether any non-biological agents present within a natural reactor (i.e., dissolved metal ions such as Mg or Fe, organometallic complexes, mineral surfaces or low-molecular weight organic compounds) are effective in catalyzing the formation of oligomers or polymers when subjected to the temperature profiles and radiation doses predicted by these models. It is also unclear exactly how heat production will impact oligomerization- though the temperature fluctuations may indeed induce non-enzymatic separation of some oligonucleotide strands, increased temperatures may also increase the rate of degrading chemical reactions and it will likely alter the equilibrium concentrations of both reactants and products. There are also heat transfer model limitations that should be validated prior to prebiotic synthesis experimentation; the ENERGY2D model does not incorporate changing fluid and thermal properties of phase transitions near the freezing or boiling points of water, thus there are likely to be fewer or lower intensity low- or high-temperature maxima than predicted by the model. These limitations restrict the interpretation of model outputs to semi-qualitative indicators of the temperature profile expected to arise from the modeled reactor settings. A more sophisticated modeling tool, or validation with an experimental setup, would be required to derive more rigorous statistical values describing temperature excursions beyond ambient values.

Conclusions

Natural nuclear reactors illustrate how energy dissipation pathways on the early Earth may have been more complex than extant analog environments suggest. The dynamics of radiolysis, heat transfer and organic synthesis in actual and modeled natural nuclear reactors point to the possibility of overlapping heating/cooling and wetting/drying cycles in microenvironments located just beneath the surface of any young planet with a suitable stock of fissile elements. Comparable variations in engineered laboratory conditions have demonstrated the efficacy of creating oligomeric compounds with relatively simple starting compounds (Forsythe et al. 2015; Rodriguez-Garcia et al. 2015). Natural reactors thus provide a geologically plausible setting for exploring the prebiotic synthesis potential of these and similarly driven reactions that bridge gaps between monomer synthesis, polymer synthesis and the emergence of complex chemical reaction networks that resemble metabolic and chemosynthetic pathways. The geologic record of natural reactor functionality at Oklo demonstrates that periodicity may be an emergent property for shallowly-buried reactor cores reliant upon pore water to serve as both neutron moderator and coolant. Beyond the dynamics of fission criticality and feedback, intense lunar tides in conjunction with shortened daily cycles of insolation could also have driven wetting cycles over large tidal areas along protocontinental margins containing radioactive or catalytic heavy minerals such as apatite or rutile, regardless of whether the fissile isotope content of the crust was sufficient to create critical reactor cores. These inferences bolster the plausibility of incorporating complex heating and drying cycles and catalytic minerals into prebiotic synthesis experiments to increase chemical productivity.

Acknowledgments Zachary Adam was supported by a postdoctoral fellowship from the Agouron Institute.

Appendix A Model parameters

PARAMETER	VALUE	UNITS	SOURCE/JUSTIFICATION
Reactor power	3000	W	Adam 2007; comparison to Oklo reactor zones
Reactor width	10	m	Adam 2007; comparison to Oklo reactor zones
Reactor height	0.5	m	Adam 2007; comparison to Oklo reactor zones
Reactor volume	39.26988	m ³	
Power density	76.39444	W/m ³	
Initial rock temp	15	C	
Initial air temp	10	C	
WATER (300 K)			
Conductivity	0.6	W/mK	http://www.engineeringtoolbox.com/thermal-conductivity-d_429.html
Specific heat	4180	J/kgK	http://www.engineeringtoolbox.com/water-thermal-properties-d_162.html
Density	990	kg/m ³	http://www.engineeringtoolbox.com/water-thermal-properties-d_162.html
Kinematic viscosity	1.00E-06	m ² /s	http://www.engineeringtoolbox.com/water-dynamic-kinematic-viscosity-d_596.html
Thermal expansion	0.0003	1/K	http://www.engineeringtoolbox.com/volumetric-temperature-expansion-d_315.html
Thermal diffusivity	1.00E-06		http://en.wikipedia.org/wiki/Thermal_diffusivity
AIR (300 K)			
Conductivity	2.62E-02	W/mK	http://www.engineeringtoolbox.com/dry-air-properties-d_973.html
Specific heat	1004	J/kgK	http://www.engineeringtoolbox.com/dry-air-properties-d_973.html
Density	1.2	kg/m ³	http://www.engineeringtoolbox.com/dry-air-properties-d_973.html
Kinematic viscosity	1.57E-05	m ² /s	http://www.engineeringtoolbox.com/dry-air-properties-d_973.html
Thermal expansion	3.40E-03	1/K	http://www.engineeringtoolbox.com/air-properties-d_156.html
Thermal diffusivity	2.20E-05	m ² /s	http://www.engineeringtoolbox.com/dry-air-properties-d_973.html
WET SANDSTONE			
Conductivity	2	W/mK	http://hydrologydays.colostate.edu/papers_2009/smits_paper.pdf
Specific heat	830	J/kgK	http://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html
Density	1922	kg/m ³	
Kinematic viscosity	N/A		
Thermal expansion	N/A		
Thermal diffusivity	1.15E-06	m ² /s	http://en.wikipedia.org/wiki/Thermal_diffusivity
URANIUM			
Conductivity	27.5	W/mK	http://en.wikipedia.org/wiki/Uranium
Specific heat	116	J/kgK	http://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html
Density	10,970	kg/m ³	http://en.wikipedia.org/wiki/Uranium_dioxide
Kinematic viscosity	N/A		

Appendix A (continued)

PARAMETER	VALUE	UNITS	SOURCE/JUSTIFICATION
Thermal expansion	N/A		
Thermal diffusivity	N/A		
REACTOR ON - medium			
Thermal diffusivity	1.08E-06	m ² /s	water and wet sandstone average
Conductivity	1.3	W/mK	water and wet sandstone average
Specific heat	2505	J/kgK	water and wet sandstone average
Density	1456	kg/m ³	water and wet sandstone average
Kinematic viscosity	1.00E-04	m ² /s	Water *100; permeability for well-sorted, fine sand is typically differs by 10 ⁻² compared to open flow conditions
Thermal expansion	0.000003	1/K	Water/100; permeability for well-sorted, fine sand is typically differs by 10 ⁻² compared to open flow conditions
REACTOR OFF - medium			
Thermal diffusivity	1.16E-05	m ² /s	air and wet sandstone average
Conductivity	1.01312	W/mK	air and wet sandstone average
Specific heat	917	J/kgK	air and wet sandstone average
Density	961.6	kg/m ³	air and wet sandstone average
Kinematic viscosity	1.57E-03	m ² /s	air *100; permeability for well-sorted, fine sand is typically differs by 10 ⁻² compared to open flow conditions
Thermal expansion	3.40E-05	1/K	air/100; permeability for well-sorted, fine sand is typically differs by 10 ⁻² compared to open flow conditions
REACTOR OFF - core			
Constant temp	20	C	residual heating- daughter nuclides

References

- Adam Z (2007) Actinides and life's origins. *Astrobiology* 7(6):852–872
- Baaske P, Weinert FM, Duhr S, Lemke KH, Russell MJ, Braun D (2007) Extreme accumulation of nucleotides in simulated hydrothermal pore systems. *Proc Natl Acad Sci* 104(22):9346–9351
- Baross JA, Hoffman SE (1985) Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life. *Orig Life Evol Biosph* 15(4):327–345
- Bentridi S-E, Gall B, Gauthier-Lafaye F, Seghour A, Medjadi D-E (2011) Inception and evolution of Oklo Natural nuclear Reactors. *Compt Rendus Geosci* 343(11):738–748
- Brennecke GA, Borg LE, Hutcheon ID, Sharp MA, Anbar AD (2010) Natural variations in uranium isotope ratios of uranium ore concentrates: understanding the 238 U/235 U fractionation mechanism. *Earth Planet Sci Lett* 291(1):228–233
- Chan S, Nordlund T, Frauenfelder H, Harrison J, Gunsalus I (1975) Enzymatic reduction of nicotinamide adenine dinucleotide phosphate induced by radiolysis. *J Biol Chem* 250(2):716–719
- Chernyshev IV, Golubev VN, Chugaev AV, Baranova AN (2014) 238 U/235 U isotope ratio variations in minerals from hydrothermal uranium deposits. *Geochem Int* 52(12):1013–1029
- Chyba CF, Sagan C (1997) Comets as a source of prebiotic organic molecules for the early earth. *Comets and the Origin and Evolution of Life*, New York, Springer, pp. 147–173
- Cockell CS (2006) The origin and emergence of life under impact bombardment: *Philosophical Transactions of the Royal Society B. Biological Sciences* 361(1474):1845–1856

- Coogan L, Cullen JT (2009) Did natural reactors form as a consequence of the emergence of oxygenic photosynthesis during the Archean. *GSA Today* 19(10):5
- Cuney M, Mathieu R (2000) Extreme light rare earth element mobilization by diagenetic fluids in the geological environment of the oklo natural reactor zones, franceville basin, Gabon. *Geology* 28(8):743–746
- Deamer D, Weber AL (2010) Bioenergetics and life's origins. *Cold Spring Harb Perspect Biol*, 2(2):a004929
- Department of Energy (1993) DOE fundamentals handbook: nuclear physics and reactor theory: Washington. D. C, U.S. Department of Energy
- Dondi D, Merli D, Pretali L, Buttafava A, Faucitano A (2011) Detailed analytical study of radiolysis products of simple organic compounds as a methodological approach to investigate prebiotic chemistry—part I. *Radiat Phys Chem* 80(3):403–407
- Draganić I, Jovanović S, Niketić V, Draganić Z (1980) The radiolysis of aqueous acetonitrile: compounds of interest to chemical evolution studies. *J Mol Evol* 15(3):261–275
- Draganić Z, Niketić V, Vujošević S (1985) Radiation chemistry of an aqueous solution of glycine: compounds of interest to chemical evolution studies. *J Mol Evol* 22(1):82–90
- Draganić I, Draganić Z, Adloff J (1993) Radiation and radioactivity on earth and beyond. CRC press, Boca Raton, FL, p. 349
- Forsythe JG, Yu SS, Mamajanov I, Grover MA, Krishnamurthy R, Fernández FM, Hud NV (2015) Ester-mediated amide bond formation driven by wet–dry cycles: a possible path to polypeptides on the prebiotic earth. *Angew Chem Int Ed* 54(34):9871–9875
- Gauthier-Lafaye F, Holliger P, Blanc P-L (1996) Natural fission reactors in the franceville basin, gabon: a review of the conditions and results of a “critical event” in a geologic system. *Geochimica et Cosmochimica Acta* 60(23):4831–4852
- Gould JM, Patterson LK, Ling E, Winget GD (1979) Phosphorylation in a simple system of lipids and chloroplast ATP synthetase driven by pulsed ionising radiation. *Nature* 380:607–609
- Hadidi A, Candresse T (2003) Polymerase chain reaction. In: Hadidi A, Flores R, Randles JW, and Semancik JS (eds), *Viroids: Properties, detection, diseases and their control*: Australia, Csiro Publishing, p. 115–122
- Herschby B, Whicher A, Campubri E, Watson C, Dartnell L, Ward J, Evans JR, Lane N (2014) An origin-of-life reactor to simulate alkaline hydrothermal vents. *J Mol Evol* 79(5–6):213–227
- Kobayashi K, Kaneko T, Saito T, Oshima T (1998) Amino acid formation in gas mixtures by high energy particle irradiation. *Orig Life Evol Biosph* 28(2):155–165
- Kuroda P (1960) Nuclear fission in the early history of the earth: *Nature*, v 187.
- Lahav N, White D, Chang S (1978) Peptide formation in the prebiotic era: thermal condensation of glycine in fluctuating clay environments. *Science* 201(4350):67–69
- Lane N, Martin WF (2012) The origin of membrane bioenergetics. *Cell* 151(7):1406–1416
- Lane N, Allen JF, Martin W (2010) How did LUCA make a living? *Chemiosmosis in the Origin of Life: BioEssays* 32(4):271–280
- Mahadevan C, Sriramadas A (1948) Monazite in the beach sands of Vizagapatam district. *Proceedings Proceedings of the Indian Academy of Sciences, Section A* 1948 27(4):275–278
- Mahadevan V, Das GN, Rao NN (1959) Prospecting and evaluation of beach placers along the coastal belt of India. Dept. of Atomic Energy, India
- Mallik T, Vasudevan V, Verghese PA, Machado T (1987) The black sand placer deposits of Kerala Beach, southwest India. *Mar Geol* 77(1):129–150
- Mamajanov I, MacDonald PJ, Ying J, Duncanson DM, Dowdy GR, Walker CA, Engelhart AE, Fernández FM, Grover MA, Hud NV, Schork FJ (2014) Ester formation and hydrolysis during wet–dry cycles: generation of far-from-equilibrium polymers in a model prebiotic reaction. *Macromolecules* 47(4):1334–1343
- Meshik A, Hohenberg C, Pravdivtseva O (2004) Record of cycling operation of the natural nuclear reactor in the Oklo/Okelobondo area in Gabon. *Phys Rev Lett* 93(18):182302
- Miller SL, Bada JL (1988) Submarine hot springs and the origin of life. *Nature* 334:609–611
- Mohapatra S, Behera P, Das SK (2015) Heavy mineral potentiality and alteration studies for ilmenite in astaranga beach sands, District Puri, Odisha, India. *J Geosci Environ Prot* 3:31–37
- Nagy B, Gauthier-Lafaye F, Holliger P, Davis D, Mossman DJ, Leventhal JS, Rigali MJ, Parnell J (1991) Organic matter and containment of uranium and fissionogenic isotopes at the oklo natural reactors. *Nature* 354:472–475
- Nagy B, Gauthier-Lafaye F, Holliger P, Mossman DJ, Leventhal JS, Rigali MJ (1993) Role of organic matter in the Proterozoic oklo natural fission reactors, Gabon Africa. *Geology* 21(7):655–658
- Naudet R (1991) Des réacteurs nucléaires fossiles, Paris, France. le Commissariat a l'Energie Atomique, Eyrolles, p. 695
- Negrón-Mendoza A, Draganić Z, Navarro-González R, Draganić I (1983) Aldehydes, ketones, and carboxylic acids formed radiolytically in aqueous solutions of cyanides and simple nitriles. *Radiat Res* 95(2):248–261
- Neuman M, Neuman W, Lane K (1970a) On the possible role of crystals in the origins of life IV. The Phosphorylation of Nucleotides: *Biosystems* 3(3):277–283

- Neuman M, Neuman W, Lane K (1970b) On the possible role of crystals in the origins of life.(III) the phosphorylation of adenosine to amp by apatite. *Biosystems* 3(3):253–259
- Openshaw R, Pagel M, Poty B (1977) Fluid phases contemporaneous with sandstone diagenesis, tectonic movements and functioning of the Oklo nuclear reactors (Gabon), Natural fission reactors, Volume IAEA Symposium Proceedings, IAEA-TC-119/9, IAEA, p. 267–289
- Orgel LE (1998) The origin of life- a review of facts and speculations. *Trends Biochem Sci* 23(12):491–495
- Oró J, Stephen-Sherwood E (1974) The prebiotic synthesis of oligonucleotides. *Origins of Life* 5(1-2):159–172
- Pascal R, Pross A, Sutherland JD (2013) Towards an evolutionary theory of the origin of life based on kinetics and thermodynamics. *Open Biology* 3(11):130156
- Pasek MA, Lauretta D (2008) Extraterrestrial flux of potentially prebiotic C, N, and P to the Early Earth. *Origins of Life and Evolution of Biospheres* 38(1):5–21
- Patel BH, Percivalle C, Ritson DJ, Duffy CD, Sutherland JD (2015) Common origins of RNA, Protein and Lipid Precursors in a Cyanosulfidic Protometabolism. *Nat Chem* 7(4):301–307
- Powner MW, Gerland B, Sutherland JD (2009) Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* 459(7244):239–242
- Prasad B, Asher R (2001) Acritarch biostratigraphy and lithostratigraphic classification of Proterozoic and Lower Paleozoic sediments (Pre-unconformity sequence) of Ganga Basin, India, Dehra Dun, Geoscience Research Group, Keshava Deva Malaviya Institute of Petroleum Exploration. Oil and Natural Gas Corporation., *Paleontographica Indica*, p. 151
- Ramirez S, Navarro-Gonzalez R, Coll P, Raulin F (2001) Possible contribution of different energy sources to the production of organics in Titan's Atmosphere. *Adv Space Res* 27(2):261–270
- Ritson DJ, Sutherland JD (2012) Prebiotic synthesis of simple sugars by photoredox systems chemistry. *Nat Chem* 4(11):895–899
- Rodriguez-Garcia M, Surman AJ, Cooper GJT, Suárez-Marina I, Hosni Z, Lee MP, Cronin L (2015) Formation of oligopeptides in high yield under simple programmable conditions. *Nat Commun* 6:8385
- Roy PS (1999) Heavy mineral beach placers in southeastern Australia; their nature and genesis. *Econ Geol* 94(4): 567–588
- Ruiz-Mirazo K, Briones C, de la Escosura A (2014) Prebiotic systems chemistry: new perspectives for the origins of life. *Chem Rev* 114(1):285–366
- Schrauzer GN, Guth TD (1977) Photocatalytic reactions. 1. Photolysis of water and photoreduction of nitrogen on titanium dioxide. *J Am Chem Soc* 99(22):7189–7193
- Shapiro R (1984) The improbability of prebiotic nucleic acid synthesis. *Origins of Life* 14(1–4):565–570
- Westheimer FH (1987) Why nature chose phosphates. *Science* 235(4793):1173–1178
- Williams GE (1997) Precambrian length of day and the validity of tidal rhythmite paleotidal values. *Geophys Res Lett* 24(4):421–424
- Zahnle K, Walker JC (1987) A constant daylength during the Precambrian era?.. *Precambrian Res* 37(2):95–105