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Discharge plasma for prebiotic chemistry: Pathways to life's building blocks

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Key Points:

- Different plasma environments for the origin of life are summarized.
- Various prebiotic plasma-origin paths for biomolecules are discussed.
- Further research directions of the intersection of plasma and the origin of life are outlined.

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Abstract: Discharge plasmas, recognized as unique platforms for investigating the origins of chemical life, have garnered extensive interest for their potential to simulate prebiotic conditions. This paper embarks on a comprehensive overview of recent advancements in the plasma-enabled synthesis of life's building blocks, charting the complex environmental parameters believed to have surrounded life's inception. This discussion elaborates on the fundamental mechanisms of discharge plasmas and their likely role in fostering conditions necessary for the origin of life on early Earth. We consider a variety of chemical reactions facilitated by plasma, specifically the synthesis of vital organic molecules — amino acids, nucleobases, sugars, and lipids. Further, we delve into the impact of plasmas on prebiotic chemical evolution. We expect this review to open new horizons for future investigations in plasma-related prebiotic chemistry that could offer valuable insights for unraveling the mysteries of life's origin.

Keywords: origin of life; discharge plasma; prebiotic chemistry; chemical evolution

1. Introduction

The origin of life is an enduring topic. It has been highlighted by the journal *Science* (Ball, 2011) as one of the 125 key scientific questions. It also stands as a central issue globally, intersecting various disciplines including biology, astronomy, Earth science, physics, and chemistry. The prevalent scientific consensus is that life has evolved according to Darwinian principles (Peretó et al., 2009), suggesting a journey primarily from simplicity to complexity. In essence, inorganic substances present on the early Earth underwent a series of transformations to form small organic molecules. Subsequently, these molecules combined through polymerization and self-replicating to create larger organic compounds, which assembled into primitive boundary membranes, constituting an independent system with some mechanisms capable of "correcting" mistakes (Singh et al., 2024). This system further refined and evolved into rudimentary living forms that could adapt to the environment. Thus, the genesis of life traces back to the formation of the initial organic molecules.

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It is widely acknowledged that the origin of the initial organic molecules is inextricably linked to the prebiotic environment, as illustrated in Figure 1. This milieu, embodying the varied and dynamic conditions of early Earth, facilitated the genesis of life. In the early hundreds of millions of years following Earth's formation, the planet's environment was extremely harsh, characterized by intense radiation, high temperatures, and extreme climate conditions. The emergence of life in such formidable circumstances remains a profound mystery. Notably, environments such as volcanic vents offered high-temperature settings conducive to the synthesis of initial biomolecules (Huber and Wächtershäuser, 2006), while intertidal belts provided cyclical wet–dry conditions essential for molecular assembly (Forsythe et al., 2015). Similarly, mild hydrothermal environments (Martin et al., 2008), and high-energy plasma induced by lightning (Bada, 2023) can also have played crucial roles in prebiotic chemistry. Beyond terrestrial

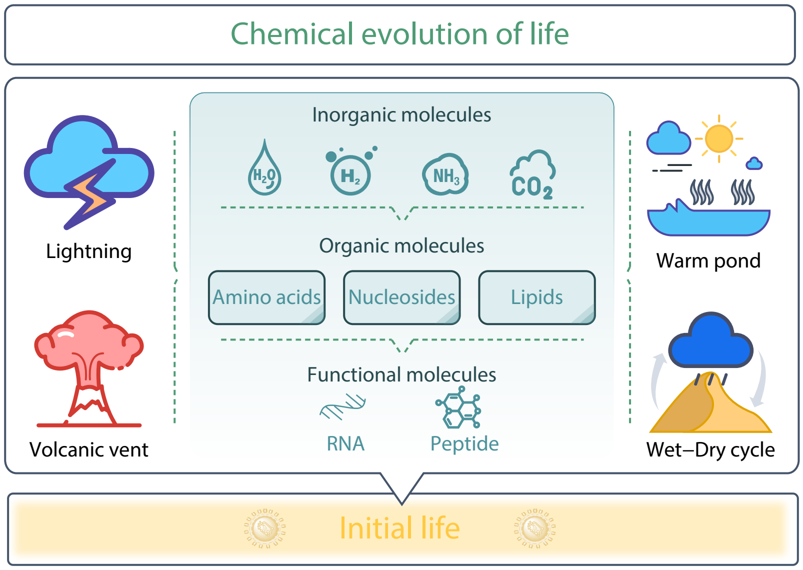

Figure 1. Chemical evolution from simple to complex under prebiotic conditions.

confines, the exploration of life in extraterrestrial environments, such as the vast expanses of planetary space (Nakashima et al., 2018), extends the horizon of today's life-origin research. Recently, discharge plasma has attracted significant interest for its distinctive environmental conditions, catalyzing a burgeoning cross-disciplinary research domain focused on elucidating the origins of life.

The linkage between life genesis and plasma dynamics finds its roots in the seminal "primordial soup" theory proposed independently by Oparin (1924) and Haldane (1929), who suggested that the initial atmosphere, primarily composed of methane, ammonia, free hydrogen, and water vapor, coupled with lightning, could produce plasma with significant energy and temperature to synthesize complex organic compounds such as amino acids and nucleotides. The plasma discharge model highlights the key role that high-energy lightning discharges probably played in the synthesis of complex molecules needed for life (Fry, 2006) and also implies that abiotic organic synthesis may have occurred on the primordial Earth before living organisms appeared.

The landmark experiment by Stanley Miller and Nobel laureate Harold Urey in 1953 stands as a cornerstone in confirmation of the “primordial soup” theory; employing spark discharge in simple reducing molecular gas mixtures of CH_4, NH_3, H_2O, and H_2, they demonstrated synthesis of various amino acids (Miller, 1953). Their work marked the transition of life's-origin research from theoretical conjecture to experimental investigations that have since become extensive and diverse. For instance, discharge has been demonstrated to facilitate the abiotic synthesis of amino acids in a neutral atmosphere with lower concentrations of N_2 and CO_2 (Cleaves et al., 2008). In addition, amino acids and nucleobases may be released on hydrolysis of HCN oligomers (Ferris et al., 1974a). Several other pathways to the formation of nucleobases have been reported, such as the production of purine nucleobases from guanidine and cyano-acetaldehyde (Ferris et al., 1974b), and nucleobases synthesized from high-energy NH_3 and CO plasma discharges (Ferus et al., 2017). Researchers have focused on identifying plausible prebiotic conditions for the synthesis of the initial life molecules, though the quest to fully resolve this question continues.

Direct investigation of Earth and cosmic conditions preceding the emergence of life is challenging. However, leveraging a multidisciplinary approach enables the simulation and reconstruction of various plausible ancient environments, shedding light on potential pathways through which biomolecules may have originated.

This paper highlights the role of discharge plasmas in prebiotic chemistry, emphasizing various mechanisms by which they may have facilitated the synthesis of life's precursor molecules. We review recent advances, both theoretical and experimental, relevant to the significance of plasma in chemical evolution, illustrating plausible scenarios in which plasma could have promoted the emergence of biomolecules on early Earth and perhaps elsewhere.

2. Characteristics of Discharge Plasma

Plasmas, distinguished from solids, liquids, and gases, constitute a fourth state of matter characterized by its unique role in a plethora of astrophysical processes. These processes include movement of interstellar material, nucleation and dispersion of interstellar dust, and nucleosynthesis and evolutionary trajectories of stellar bodies. The prevalence of plasmas, in which matter exists predominantly in ionized states, extends from the ionosphere to the vast expanses of the universe. It is well-recognized that plasmas are a highly reactive environment capable of producing complex organics, which can be transported and accumulated. For example, in the case of Titan, complex organic molecules formed in the upper atmosphere can condense and rain down onto the surface, where they accumulate over time (Ehrenfreund and Charnley, 2000; Hörst, 2017). Plasma phenomena were common in the early Earth environment, manifesting in extreme conditions like lightning and cosmic-ray-induced discharges that, as mentioned above, have been shown capable of synthesizing essential precursors to biotic chemistry. This primitive plasma-rich environment might have furnished the requisite external conditions for the genesis of the earliest life forms.

It is established that plasma, characterized by its quasi-neutrality, can drive chemical reactions through the interaction of diverse reactive species, including molecules, free radicals, metastable species, and energetic electrons (Conrads and Schmidt, 2000) (Figure 2). Plasma discharge into such a chemical "soup" breaks chemical bonds allowing novel compounds to form. Plasmas with unique thermally non-equilibrium characteristics allow exotic reactions to occur under ambient conditions. Previous studies have utilized plasma discharges, such as spark, glow, and jet discharges, to mimic early Earth conditions and to explore the origins of organic molecules. *Spark discharge*, a transient high-energy gas discharge, is marked by an instantaneous flash of light and sound, resulting from a rapid connection across a high-voltage gap between two charged surfaces (Zhang ZH et al., 2014). In contrast, a *glow discharge* operates under low-pressure conditions, typically below 10 mbar (hPa); it is not transient, noted instead for its ability to be sustained as a uniform glow (Bogaerts, 1999). *Jet discharge*, however, involves ionization of gas into a plasma that is subsequently ejected at high velocity, often resulting in rapid gas-flow dynamics (Schutze et al., 1998). Different laboratory discharge configurations can simulate different natural plasma environments, exhibiting distinct physio-chemical characteristics — in terms of energy levels, reactive species profiles, and influences on chemical processes.

On early Earth — the first billion years of our planet, various plasma environments are thought to have been likely, including: (1) Lightning, a common form of electrical discharge, typically occurring between regions of opposite electrical charge within thunderstorms. Lightning discharges are powerful and can ionize the surrounding air, creating a transient plasma channel. However, the exact frequency and intensity of lightning discharges on the early Earth would depend on factors such as temperature and atmospheric composition, particularly the presence (and amount) of water vapor (Hess et al., 2021). (2) Auroras, which are due to interactions between solar wind particles and the Earth's magnetosphere and now occur primarily at high latitudes near the poles, could have occurred at lower latitudes on the early Earth. Auroral ionization and emission of light result from collisions of charged particles with the Earth's atmosphere. The frequency and intensity of auroras on early Earth would depend on the strength of the Earth's magnetic field and on solar activity levels at that time (Maris and Hulburt, 1929). (3) Geomagnetic Storms arise from intense solar activity events, such as coronal mass ejections (CMEs). Today these storms result in enhanced plasma influx into the Earth's magnetosphere, leading to increased auroral activity and possible disruptions to electrical systems on the planet's surface. The flux of plasma during geomagnetic storms can vary greatly depending on the strength and duration of the solar event (Gonzalez et al., 1999).

Plasma environments exist not only on Earth, but also on other planetary bodies. For example, gas giants like Jupiter exhibit intense auroral activity. Jupiter's auroras are much more powerful than those on Earth and can produce highly energetic plasma discharges (Dessler, 1967). The flux of plasma in Jovian auroras is significant, contributing to the complex dynamics of Jupiter's magnetosphere. In addition, Io, one of Jupiter's moons, experiences frequent volcanic eruptions due to tidal forces from Jupiter's gravity. These eruptions can generate volcanic lightning discharges, similar to terrestrial lightning but occurring within

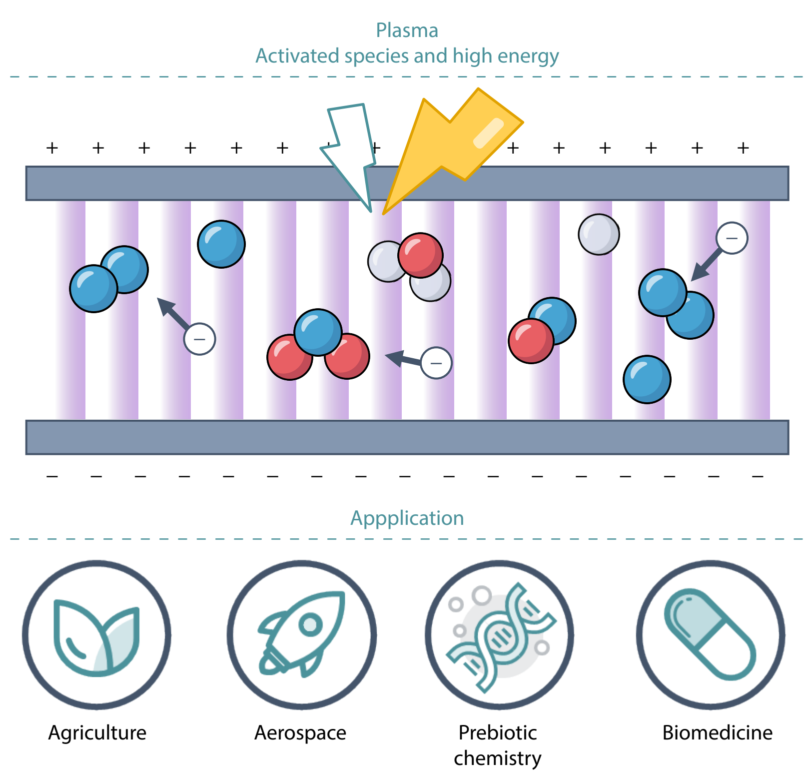

Figure 2. Features and applications of plasma.

volcanic plumes. The flux of plasma during volcanic lightning events on Io is obviously a function of the frequency and intensity of Io's volcanic activity (Bagenal and Sullivan, 1981; Queinnec and Zarka, 1998). It is worth noting that Mars, with its thin atmosphere and weak magnetic field, experiences direct interactions with the solar wind. These interactions can lead to the formation of plasma sheaths around the planet, especially during periods of increased solar activity. The flux of plasma around Mars depends on the strength of the solar wind and the efficiency of the planet's magnetic shielding, which is minimal compared to Earth's (Queinnec and Zarka, 1998; Harrison et al., 2016).

Plasma conditions vary widely throughout the universe. The plasma discharge process induces reactive plasma environments conducive to the synthesis of cocktails of life's molecular precursors, mediated through distinct physicochemical mechanisms: 1) High temperatures and the presence of high-energy, ionized particles and molecules in plasma provide an exceptional setting for chemical synthesis. Ionization in this energetic environment can trigger a variety of chemical reactions, leading to the creation of complex organic molecules; 2) Plasma discharges can influence molecular self-assembly by altering molecules' charge states and forming specialized reaction centers, crucial for the initial stages of life formation. Self-assembly, a critical step in the origin of life, involves molecular interactions and the development of complex structures. Previous studies have suggested that the molecules of life may have originated from prebiotic plasma conditions, such as lightning in the ancient atmospheric (Miller, 1955, 1974; Miller and Urey, 1959; Miller et al., 1976; Miller and Bada, 1988), high-energy plasma impacts of extraterrestrial meteorites (Managadze, 2007), and interstellar charged dust particles (Wickramasinghe and Hoyle, 1999; Stark et al., 2014). These conditions can be replicated through plasma discharge simulations in the laboratory (Chernavskii et al., 1995; Desai et al., 2017; Ferus et al., 2017; Lingam et al., 2018; Longo et al., 2019; Kobayashi, 2019; Meijer et al., 2019; Köhn et al., 2022).

3. Synthesis of Amino Acids by Discharge Plasma

Proteins and nucleic acids, as critical components of contemporary life forms, play essential roles in the origin of life (Joyce and Orgel, 1993; Plankensteiner et al., 2005; Robertson and Joyce, 2012; Higgs and Lehman, 2015). Investigating the synthesis of these molecules in prebiotic conditions is vital to understanding life genesis. The initial step towards forming peptides and proteins is the generation of amino acids via diverse prebiotic mechanisms. It is widely accepted that, before life emerged on Earth, amino acids accumulated in various regions and forms across the Earth's atmosphere, hydrosphere, and lithosphere, as well as in extraterrestrial settings, facilitated by numerous natural energy sources.

Although lightning was a prevalent environmental phenomenon on early Earth, some studies claim that lighting may have been a relatively minor source of amino acids, compared to other sources, such as cometary delivery (Chyba and Sagan, 1991); however, the possibly important role of a lighting-based pathway to amino acid synthesis on early Earth cannot be ignored (Chyba and Sagan, 1992). Similarly, plasma elsewhere in the universe likely catalyzes formation of amino acids. Hence, laboratory plasma discharges, simulating primordial plasma milieus found in the cosmos, are useful ways to investigate the genesis of primitive biomolecules.

A significant body of research has emerged in this area, demonstrating the feasibility of amino acid formation under prebiotic plasma conditions. Table 1 summarizes representative studies of this sort.

Gas discharges have been shown to be capable of producing amino acids and their analogues, serving as precursor materials for the further chemical evolution of life. The underlying reaction mechanisms have been extensively studied (Miller, 1953; Anders, 1989; Ferus et al., 2014; Longo et al., 2021). Stanley Miller pioneered experimental research into the abiotic synthesis of amino acids via gas discharges in an atmosphere mixture of CH_4,

Table 1. Discharge plasma-enabled synthesis of amino acids.

Principal investigator	Discharge object	Discharge modes	Primary product	Ref.
Miller	Reducing atmosphere (H_2, CH_4, NH_3, and H_2O)	Spark	Multi-amino acids	(Miller, 1953)
Rode	Neutral atmosphere (N_2, CO_2, and H_2O)	Spark	Alanine, glycine	(Plankensteiner et al., 2004)
Ring	CH_4 and N_2	Spark	Multi-amino acids	(Ring et al., 1972)
Saladino	CH_4, N_2, and NH_3	Spark	Multi-amino acids	(Saladino et al., 2013)
Wang	H_2S, PH_3, CH_4, N_2, and H_2O	Spark	Multi-amino acids (including phosphorus and sulfur containing amino acids)	(Wang WQ et al., 1984)
Janda	CO_2, N_2, and H_2O	Spark	Multi-amino acids	(Janda et al., 2008)
Goto	Gly and H_2O	Pulse	Glycine Oligopeptide	(Hayashi et al., 2018)
Abelson	Martian atmosphere (N_2, H_2, CO, and CO_2)	Spark	Glycine	(Abelson, 1966)
Hörst	Titan atmosphere (N_2, CH_4, and CO)	Radio-frequency	Amino acids and Nucleobases	(Hörst et al., 2012)
Sagan and Khare	Titan atmosphere (N_2, CH_4, and CO)	Spark	Tholins	(Sagan and Khare, 1979)

NH_3, H_2O and H_2 (Miller, 1953). This mechanism, hypothesized to involve hydrolysis of nitriles into amino acids — a process integral to the Strecker synthesis — marked a seminal contribution to our understanding of life's chemical origins (Figure 3a). Miller and Magrino et al. provided critical experimental and theoretical insights into the thermodynamics and kinetics of the Strecker synthesis of glycine (Miller and Van Trump, 1981; Magrino et al., 2021). Notably, Wang and colleagues expanded on Miller's experimental setup by introducing phosphine (PH_3) and hydrogen sulfide (H_2S) into the discharge environment, observing the formation of amino acids containing phosphorus and sulfur (Wang WQ et al., 1984), thereby offering a broader perspective on the possible diversity of prebiotic chemistry.

It is worth noting that Pearce (2024) proposed that organic hazes could act as a source of life’s building blocks in the Hadean Earth period. Pierce used PHAZER, a vacuum flow system and stainless steel chamber, to simulate early organic hazes and haze chemistry in planetary atmospheres. Within the chamber is the option to attach different energy sources. Pearce (2024) attached two electrodes that produced cold plasma discharges and detected several amino acids in the organic hazes resulting from atmospheres with different CH_4 concentrations.

Prebiotic amino acids could also have been formed by the Gabriel method (Gibson and Bradshaw, 1968). The Gabriel synthesis starts with phthalimide reacting with KOH, leading to the formation of 2-isoindoline-1, 3-dione. Subsequent hydrolysis introduces H_2O into the reaction, yielding amino acids and phthalic acid (Figure 3b). While there is currently no evidence of amino acid synthesis by the Gabriel technique in simulated primordial plasma environments, the distinctive chemical routes and feedstocks associated with this process suggest that further investigation is warranted.

3.1 Effects of Different Atmospheres on Amino Acid Production

In 1953, Miller explored plasma synthesis of organic compounds from simple gases consisting of H_2, CH_4, NH_3, and H_2O, mimicking Earth's primordial atmosphere. Using the apparatus depicted in Figure 4a, a total of 20 organic species were generated after a week of discharge, including four natural amino acids, namely glycine, alanine, aspartic acid, and glutamic acid. This finding suggested the necessity of a reducing environment, rich in prebiotic materials and diverse energy sources, for the abiotic synthesis of life’s building blocks (Miller, 1953). Subsequently, Miller refined his hypothesis about Earth’s early atmosphere, proposing a gas mixture of CH_4, N_2, traces of NH_3, and H_2O. This adjustment was based on the realization that NH_3 would have been scarce in the early atmosphere due to its solubility in seawater. In 1972, further experiments with this revised mixture generated 35 organic species. Among them, 10 natural amino acids were detected, with the following yields: glycine (440 mM, hereinafter referred to as the same unit), alanine (790), valine (19.5), leucine (11.3), isoleucine (4.8), proline (1.5), aspartic acid (34), glutamic acid (7.7), serine (5.0), and threonine (~0.8), achieving a total amino acid

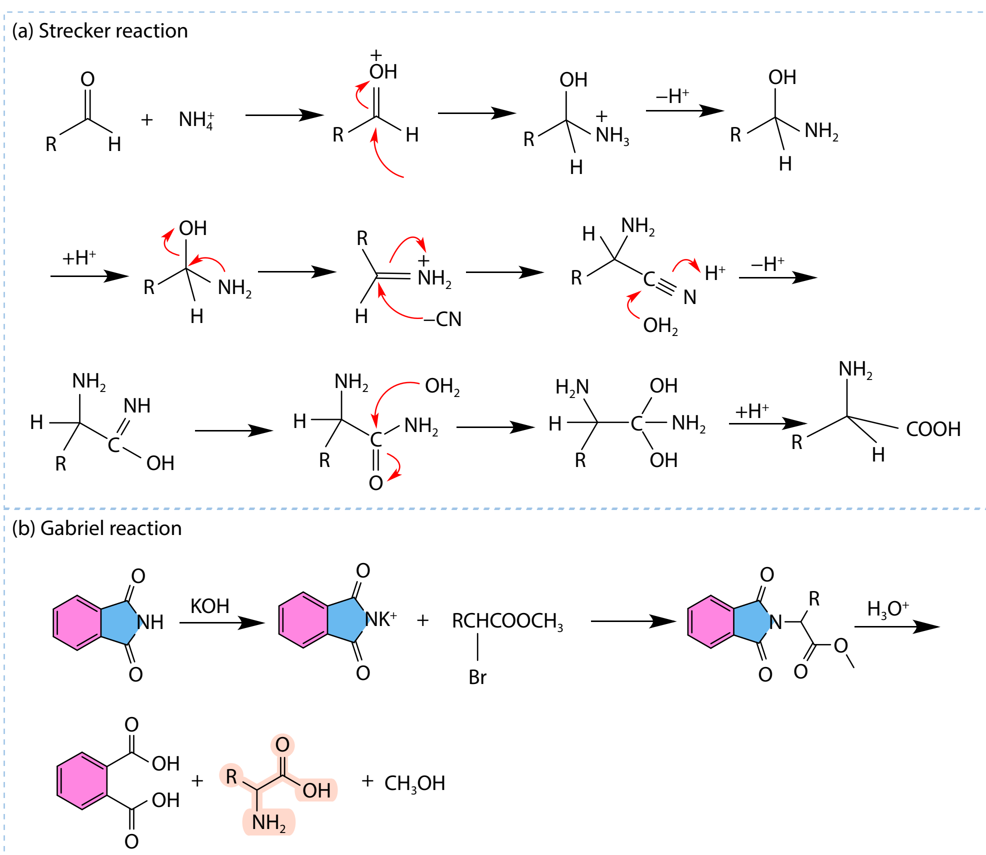

Figure 3. Mechanisms of abiotic synthesis of amino acids. (a) Strecker reaction to form amino acids, redrawn from Miller and Van Trump (1981). (b) Gabriel reaction to form amino acids, redrawn from Gibson and Bradshaw (1968).

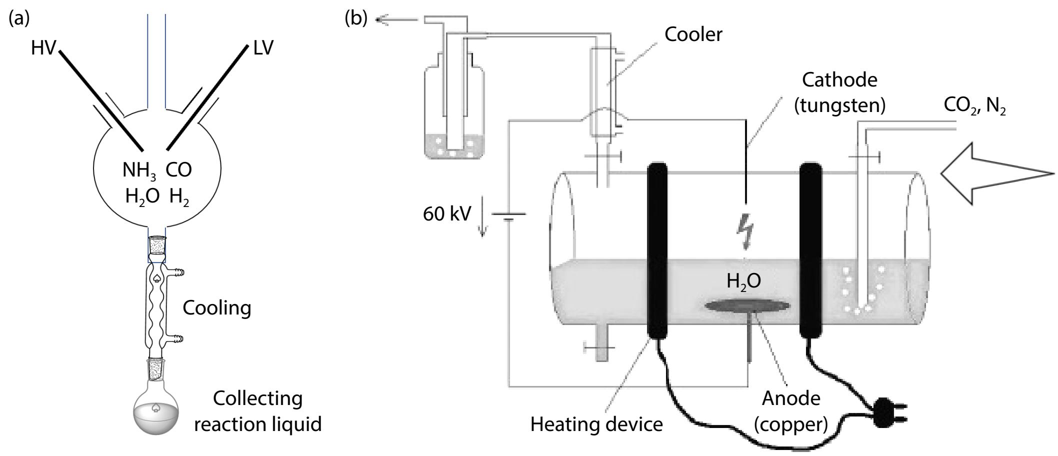

Figure 4. Diagram for the discharge experiment. (a) Miller discharge experiment, redrawn from the Ref. (Miller, 1953). (b) Rode discharge experiment, redrawn from the Ref. (Plankensteiner et al., 2004).

yield of 1.55% (Ring et al., 1972).

While Miller's pioneering work marked a seminal advancement in the field of life origin research, the question of how life began remained open. Holland and Kasting challenged the reducing atmosphere hypothesis, suggesting that the early atmosphere was likely neutral, moderately reducing, or slightly oxidizing (Holland, 1978; Kasting and Ackerman, 1986), a perspective that has since guided subsequent studies. In 2004, Rode et al. conducted discharges on neutral atmospheres of N_2, CO_2, and H_2O (Plankensteiner et al., 2004) (Figure 4b) over a water surface at a rate of 20 times per second (60 kV and 30 mA). After 2 weeks of sustained discharge, O_2 was judged to have been produced during the reaction, based on the oxidation of the copper electrodes; also detected were small amounts of alanine and glycine (HPLC spectra of the standards were used for comparison).

In 2008, Janda conducted an experiment on the plasma chemical reaction of gas mixtures (CO_2, N_2, and H_2O) with DC power (70 kV, 20 mA, discharge duration of 3 weeks, 8 h per day). Fourier infrared absorption spectroscopy was employed to identify the formation of organic molecules. Janda hypothesized that the CO generated during the reaction may play a significant role in the production of organic molecules by interacting with plasma-generated reactive species, such as H or N radicals, thus serving as initial steps for these syntheses (Janda et al., 2008).

Further exploring the conditions of early Earth, Kobayashi and Ponnamperuma (1985) investigated spark discharge synthesis in CH_4, N_2, and H_2O vapor, simulating conditions less reliant on NH_3 due to the vulnerability of NH_3 to UV decomposition. Amino acids including glycine, alanine, valine, and leucine, among others were detected. In addition, their experiments showed enhanced organic production in the presence of trace metal ions, with the total yield of amino acids increasing from 0.25 to 1.1%, suggesting the potential importance of these metals in prebiotic chemistry .

3.2 Effects of Solution pH on Amino Acid Production

The influence of aqueous solution pH on the efficacy of gas discharges in synthesizing organic molecules underscores a nuanced aspect of prebiotic chemistry. For example, Hayashi et al. (2018) demonstrated that pulsed-discharge plasma could polymerize glycine into peptides in aqueous solutions, with a conversion rate of 73.1% at 18.6 kV over 250 s of discharge. It was found that the oligopeptide production is dependent on the pH of the glycine solution (optimum at pH 4–8) rather than on conductivity. In a complementary study, Criado-Reyes et al. (2021) explored the effects on amino acid synthesis of solution pH and the presence of borosilicates under discharges (30 kV) in CH_4, N_2, and NH_3 atmospheres. They found enhanced amino acid yields in solutions with pH around 11 compared to those around 8.7, and identified borosilicates as beneficial contributors to both amino acid diversity and yield.

While the above studies reveal that solution pH in gas-liquid discharge can significantly affect the production of biomolecules, the underlying mechanisms — potentially involving reactive particles and free radicals in varying pH environments — remain to be further elucidated. Next-step studies, possibly leveraging computational chemistry alongside experimental approaches, may advance our understanding of these complex reaction dynamics.

3.3 Exploration of Amino Acid Synthesis in Extraterrestrial Plasma Environments

Some investigators have speculated that amino acids may have been formed in extraterrestrial cosmic space and then brought to Earth by meteorites or asteroids (Cockell et al., 2003; Marchi et al., 2014). Numerous studies have been conducted to simulate extraterrestrial space in order to investigate that possibility. Abelson was a pioneer in combining geological evidence of a weakly oxidizing atmosphere on the early Earth with experiments, first investigating the production of glycine from spark discharges into an atmosphere of N_2, H_2, CO, and CO_2, chosen to mimic that of today's Mars (Abelson, 1965), and then production of HCN in an atmosphere of N_2, CO, and H_2 (Abelson, 1966). Hörst et al. (2012) efficiently synthesized amino acids by the action of cold plasma generated by radio frequency discharges into a simulated Titan atmosphere. Sagan and Kharev (1979) synthesized complex organic aerosols, which they named *tholins*, by plasma discharge into a simulated Titan atmosphere. Further studies showed that amino acids are formed after the hydrolysis of tholins (Khare et al., 1986). Stark et al. (2014) investigated plasma energization in atmospheres of sub-stellar objects such as gas giants and the role of the plasma electron temperature, reporting that a moderate electron temperature of ≈1 eV (≈104 K) is sufficient to accelerate the ions to energies in excess of the activation energies required for the formation of formaldehyde, ammonia, hydrogen cyanide, and the amino acid glycine.

The studies described above investigated amino acid formation by simulating different extraterrestrial plasma environments, suggesting that plasma may have played an important role in the extraterrestrial origin of amino acids, crucial raw materials for protein synthesis. We suggest that further experimentaton of this sort, under other, perhaps earlier plasma conditions, such as two-phase interfaces, such as charged droplets in the ancient atmosphere (the interface between a liquid phase and a gas phase), could provide further evidence of the advantages of gas-liquid interface effect. Those advantages include high stability, interface carrying charge, easy generation of free radicals, and high mass transfer efficiency, all of which might effectively promote complex chemical reactions to produce a variety of complex organic molecules (Yan X et al., 2016; Nam et al., 2018). Furthermore, these approaches would be assisted if a more comprehensive chemical mechanism could be proposed, based on theoretical calculations.

Whether the synthesis of amino acids is carried out by simulating a lightning environment on Earth or a plasma discharge environment in the extraterrestrial universe, a common fundamental aspect is the first generation of a batch of excited and radical substances and ions, which subsequently enter a number of chemical reaction pathways to form biomolecules of prebiotic origin. It is important to mention that while theoretical and experimental studies highlight the significance of plasma discharge in the formation of prebiotic biomolecules during the origin of life and are supported by solid geological, biochemical, physical, and other scientific principles, there are still unresolved questions. One such question is the low yield of amino acids and uncrtainty regarding their ability to persist in the plasma discharge environment and contribute to subsequent chemical evolution. Furthermore, there is ongoing debate on the precise method by which certain catalytic chemicals, which were quite prevalent in the early stages, contribute to the synthesis of amino acids in the plasma discharge environment.

4. Synthesis of Nucleobases by Plasma Discharge

Besides amino acids, which are the building blocks of proteins, nucleic acids are the second key component of modern living organisms (Benner, 2004; Minchin and Lodge, 2019). Gilbert (1986) proposed the "RNA world", which hypothesized that, in the initial stages of life on Earth, the first type of molecule that encoded protein synthesis was RNA, which emphasized the importance of the nucleobase origin. Thus, the investigation of the prebiotic origin of nucleobases in the plasma environment is also of great significance to the exploration of the origin of life. It is well known that the primitive Earth was a harsh environment, in which lightning (Chameides and Walker, 1981; Bada, 2004), thunderstorms (Woese, 1979), and even meteorite impacts frequently occurred (Chapman, 2004). Numerous simulations have been conducted to investigate plasma discharge circumstances pertaining to the synthesis of nucleobases.

Between 4 and 3.85 billion years ago, the Earth observed a significant influx of meteorites, potentially resulting in the creation of biomolecular precursors. Ferus et al. (2015) used high-power lasers to simulate plasma discharge breakdown resulting from meteorite impacts in the primitive atmosphere to form RNA-nucleobases (A, U, C, G). Remarkably, the plasma irradiation of 2, 3-diaminomaleononitrile (DAMN) also produced four RNA-nucleobases (Ferus et al., 2015; Civiš et al., 2016a). In addition, high energy density events were common during the Plutonic period and may have played an important role in HCN synthesis. RNA-nucleobases were also synthesized by Ferus and his team from the same gases (NH_3 and CO) that the Miller-Urey experiment used (Ferus et al., 2017). Further, their team demonstrated that ultrafast impact plasma can induce synthesis of all typical nucleobases via formamide, isocyanate, HNCO, or formaldehyde (Ferus et al., 2018, 2019); they also proposed a mechanism for prebiotic nucleobase formation, based on formamide via plasma discharges. To form nucleobases, formamide is first decomposed into reactive radicals and simple gaseous molecules; among them, CN- and NH- were identified as the most abundant radicals in the plasma, which then react with the formamide parent molecule to produce nucleobases (Ferus et al., 2014, 2015) (Figure 5).

Aside from the presence of primordial nucleobases on Earth, astrobiological research has demonstrated that other planets and moons, such as Titan and Europa, have ice that may contain simple organic compounds. Biomolecules, such as nucleobases, can be formed when a freezing urea solution is exposed to high-energy methane/nitrogen plasma discharge (Menor-Salván et al., 2009). Hörst et al. (2012) have reported qualitative detection of RNA nucleobases and a variety of amino acids generated in a mixture of N_2, CH_4, and CO (the atmosphere of Titan) during discharge. These experimental results and theoretical calculations by others (Chyba and Sagan, 1992) suggest that a reduced and relatively active atmosphere may be more efficient for biomolecule synthesis (Chyba et al., 1990). Miyakawa et al. (2000) also reported abiotic synthesis of guanine by irradiating mixtures of N_2, CO and H_2O gases with a simulated high-temperature extraterrestrial plasma.

All of these studies have used either high-energy or low-energy plasmas to act on small, simple molecules to synthesize key life-giving molecules. The following mechanisms are proposed: (1) high-energy-density plasmas generate large numbers of high-energy electrons and ions as well as highly reactive radicals, which are able to break chemical bonds between molecules by collision or oxidation, resulting in complex organic molecules; (2) low-energy-density plasmas promote cross-linking of small organic molecules, which is critical in the polymerisation of simple organic molecules to produce more complex organic molecules. For example, previous work by Zhou RW et al. (2018) has verified that plasma discharge can cross-link small organic molecules and can promote CO_2 to form small molecular organic acids; in particular, underwater plasma bubbles were used for highly selective synthesis of oxalic acid from CO_2 (Zhang TQ et al., 2023), and

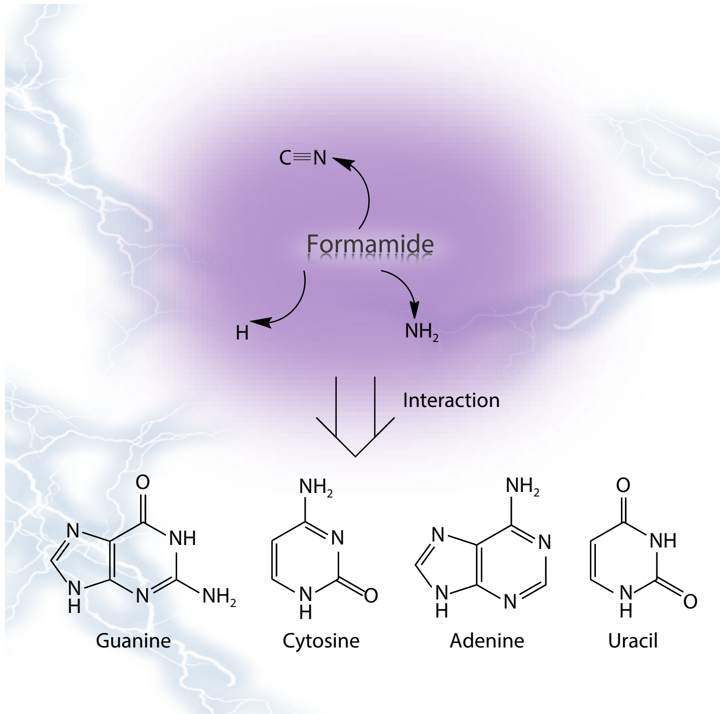

Figure 5. Formamide-based plasma discharge synthesis mechanism for prebioltic nucleobase synthesis.

demonstrated that long-chain organics could be formed in CO_2 and CH_4 plasma bubbles (Knezevic et al., 2024).

5. Synthesis of Sugars and Lipids by Plasma Discharge

Sugars, lipids, and fatty acids are also important life-form building blocks and may have been crucial components of the first cell. For example, the encapsulation of genetic polymers inside lipid bilayer compartments (vesicles) is thought to have been a vital step in the emergence of cell-based life (Steller et al., 2022). Folsome et al. (1976) gave a plausible answer in 1976 to how plasma discharges could influence the origin of the first cell. He found that organic microstructures could be produced in quenched spark-discharge reactions within CO, CH_4 and N_2 gases over a water surface. In the quenched spark-discharge reactions, the spark was directed upon the water surface; a yellow-brown film was then observed on the water near the electrode. The properties of the film's microstructures were similar to coacervates, proteinoid microspheres, and archean microfossils, suggesting that such microstructural abiotic organic particles could have been precursors to the first living cell.

It is worth noting that cyanide, peptides, and polysaccharides were synthesized by Simionescu et al. (1976) from water vapor, methane, and ammonia through the cold plasma state at a low temperature of –60 °C. After plasma discharge, gel filtration separated the raw product into eight distinct fractions of different molecular weights. Lowry method determined that the product contains 0.2 mg of protein-like compounds. The same investigators also successfully synthesized lipid-like compounds, starting with simple gas mixtures rich in methane (Simionescu et al., 1981), and found that the CH_4 concentration significantly influenced the lipid-like yield.

Investigation of how lipids and sugars might have been formed abiotically has not been limited to simulating the early Earth plasma environment; influences from the extraterrestrial environment have also been taken into consideration, such as meteorite impacts. Civiš et al. (2016b) demonstrated the synthesis of glycerol and diglycolic acid along with a mixture of pentoses (threose, arabinose, ribose, and xylose) by employing high-energy chemistry (laser-induced dielectric breakdown plasma) combined with a TiO_2 catalyst to simulate meteorite impact into early Earth conditions. Subsequent gas chromatography-mass spectroscopic (GC-MS) analysis, after its derivatization by silylation, confirmed that glycolaldehyde could be added to the list of products mentioned above.

Although plasma synthesis of sugars and lipids has been subjected to only a few studies, their results suggest that plasmas may have played significant roles in abiotic synthesis of lipids and sugars on the early Earth. Many gaps remain to be filled in this research direction, from developing various kinds of plasma discharge to exploring different conditions in which the generated lipids might be further assembled, under plasma conditions, into a closed system similar to a primitive cell membrane structure.

6. Synthesis of Prebiotic Active Phosphorus by Plasma Discharge

The emergence of life was almost certainly not a singular event but rather a result of sequences of prebiotic physicochemical processes. The initial stages in the genesis of life are likely to have involved the emergence of small biological molecules, including amino acids and nucleobases, as well as their incorporation of certain vital elements like phosphorus (Zhao YF et al., 2018). Phosphorus can be used as a "marker" for the exploration of life and is now being popularized for use in the exploration of life on Mars (Zhao YF et al., 2021). Furthermore, it should be noted that soluble phosphates have a significant impact on the development of prebiotic sources of life molecules (Gan DW et al., 2022). If the presence of phosphorus is indeed closely associated with the existence of life, it will be imperative to investigate possible prebiotic syntheses of phosphorus compounds plausibly related to those now seen in living organisms.

Phosphorylated biomolecules are a key component of modern life. There are many types, ranging from nucleic acids, which control heredity and some forms of catalysis, to metabolites, such as nucleotide triphosphates, and structural molecules such as the phospholipids that make up cellular membranes. The fact that these compounds all play important functional roles in life on Earth today suggests that they were formed long ago and have been strongly preserved (Pasek, 2020). However, reactive phosphorus is thought to have been relatively poorly distributed on the early Earth; most phosphorus being in calcium phosphate, whose insolubility would have made phosphate a minimally bioavailable component (Gulick, 1957; Keefe and Miller, 1995; Maciá et al., 1997). The quest for soluble phosphorus is thus of significant importance in the elucidation of how phosphorus-containing nucleic acids, amino acids, and other vital components were first synthesized.

Investigators have suggested that Earth's pre-life environment may have included phosphate minerals other than calcium phosphate, derived from dust, meteorites, and asteroids, that supplied sufficient potentially reactive phosphorus to allow the necessary compounds to appear prior to the emergence of life (Brown and Kornberg, 2004). For instance, Griffith et al. (1977) found that iron(III) phosphate can be reduced by carbon monoxide to produce iron(II) phosphate and carbon dioxide, and that iron(III) phosphate, in the presence of H_2S, can produce pyrophosphate, which spontaneously polymerizes at moderately elevated temperatures to form linear and cyclic multimeric phosphates and orthophosphates. Yamagata and colleagues analyzed volatile condensates from volcanic gases in experiments simulating magmatic conditions and showed that volcanic activity can produce water-soluble polyphosphates, such as trimetaphosphate, through partial hydrolysis of P_4O_{10} (Yamagata et al., 1991); other researchers have detected pyrophosphate and triphosphate in ancient Mount Ussuri volcanic jet condensate (Schwartz, 2006). These pathways provide a plausible source of soluble phosphorus. Next, we review some highlights regarding the importance of plasma discharge in reactions involving soluble phosphorus.

The abundance of plasma on early Earth can be attributed to the elevated temperature and high energy conditions during its formation. It is plausible that lightning strikes and flashes played a significant role in the generation of reactive phosphorus under prebiotic circumstances on the early Earth. Lightning is estimated to have struck the early Earth's surface approximately 44 times per second (Christian et al., 2003). The energy dissipation per lightning flash can be up to 10^9 J (Krider et al., 1968), which is sufficient to heat the surrounding air instantly to 10^5 K (Wang J et al., 2009). Pasek and Block (2009) conducted a study on the impact of lightning on phosphate levels in clinoptilolites, which are glassy compounds derived from soil that are affected by lightning. They found that lightning contributes to reduced phosphorus that is usable to living organisms; they also highlighted the significance of lightning-reduced phosphate in the biogeochemistry of phosphorus. Essene and Fisher (1986) also reported that phosphites can be produced by lightning strikes. Hess et al. (2021) report that lightning strikes on the early Earth may have formed 10−1000 kg of phosphides and 100−10000 kg of phosphites and hypophosphates per year and suggest that reactive phosphorus on early Earth may not have required extraterrestrial sources of phosphate minerals such as dust, meteorites, and asteroids.

Compounds such as phosphite, containing reduced phosphorus, may have been more abundant on the early Earth or in extraterrestrial environments than more oxidized forms such as phosphates (PO_4^{3-}), because reducing conditions such as those prevalent on early Earth could have facilitated the reduction of phosphate to phosphite, which requires modest amounts of energy (Pasek et al., 2013; Herschy et al., 2018). Reduced phosphorus compounds can participate easily in phosphorylation reactions under mild conditions, making them potentially important in the prebiotic synthesis of key biomolecules (Gull, 2014; Gull et al., 2023). It is worth noting that phosphite is more stable than phosphate under certain environmental conditions, particularly in aqueous solutions. This stability could have allowed phosphite to persist in ancient environments where phosphate may have been less available or more prone to hydrolysis or oxidation (Pasek, 2008, 2020). Previous studies have indicated that plasma discharge is likely to have served as a potent and uninterrupted source of reduced phosphorus on land. Given the essentiality of phosphorus for life, lightning is likely to have played a significant role in the origin of life. The connections between lightning and other energy sources on early Earth and the emergence of reactive phosphorus compounds necessary to the life are summarized schematically in Figure 6.

7. Possible Mechanisms of Plasma Discharge in Chemical Reactions

Plasma is characterized as a highly energized gaseous state in which electrons have become unbound from atoms and molecules, resulting in a hot mixture of ions and electrons. Plasmas are very hot and very electrically conductive, capable of facilitating significant roles in chemical reactions. Plasma-mediated chemical reactions exploit the high energy invested in the electrons and positive ions within a plasma (Denes and Manolache, 2004; Capitelli et al., 2012). Free electrons are able to absorb and carry energy, while positive ions can collide with other substances to initiate chemical reactions. These chemical reactions may occur in the plasma or at interfaces where the plasma is in contact with other substances (Pârvulescu et al., 2012).

The role of plasma in promoting chemical reactions includes the following aspects: 1) providing energy to the reactions: high-energy plasma electrons can transfer energy to molecules or atoms, stimulating them to jump from low-energy states to higher-energy states, thus facilitating reactions with each other. 2) providing the reactants themselves: positive ions in plasmas are highly reactive with other chemicals present in or touching the

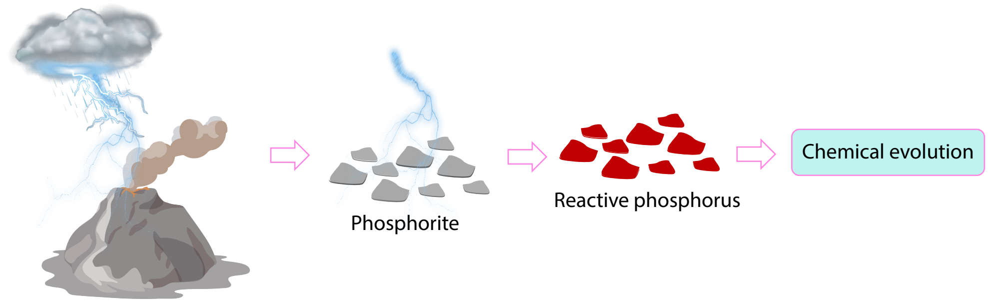

Figure 6. Reactive phosphorus under prebiotic plasma conditions drives its further evolution.

plasma. Electrons and positive ions cannot act as free radicals to participate in the reaction, but they can still play important roles in chemical reactions by participating in ion chemistry, transferring charge, or forming chemical bonds (Yin YX et al., 2021).

In the study of life's origin, a central question is that of the driving forces behind the formation of compounds crucial to life, in other words, the problem of reaction energy (Sakiyama et al., 2012). Researchers have been looking for many years for a variety of possible early conditions and even the existence in today's universe of environments that may simulate those in which known life processes emerged; central to all of these investigations is the determination of environment-specific energy effects essential to the emergence of molecules crucial to life. As one of the most common but also chemically favorable environments in the universe, the plasma environment has almost certainly played an indispensable role in the physicochemical origin of life.

8. Summary and Outlook

The origin of life remains one of the most fascinating and complex enigmas in natural science. Plasma, a ubiquitous form of matter in the universe, appears to be profoundly connected to this fundamental question. Its ability to quickly generate a wide array of reactive species essential to the emergence of life seems well established. Recent years have witnessed a surge in research leveraging plasma technology to probe life's origins. By simulating conditions ranging from Earth's primordial atmosphere to extraterrestrial environments such as those of Mars, interstellar space, and asteroids, experiments employing plasmas have proved to be valuable tools in the field of prebiotic chemistry, a distinct platform for advancing our comprehension of life origins.

Although previous research, exploring the synthesis and interactions of different molecular entities (e.g., amino acids, nucleobases), has clearly established the importance of plasma-based studies of the origin of life, most of these studies have not mentioned the chirality of biomolecules, a crucial detail that needs to be further explored. Other matters that require attention include:

1) Gas-phase environments have been the predominant focus of studies pertaining to plasma-condition origins of biomolecules, but the early Earth environment also included liquids and gas-liquid interfaces; these have received comparatively little attention. In plasma-liquid systems, a plasma discharge can be applied to a liquid to induce various chemical reactions at the liquid-gas interface, leading to the generation of reactive species, such as reactive oxygen species or free radicals, which can in turn react with molecules in the solution. Specific cases in which plasmas can interact with solutions have been identified (Zhou RW et al., 2018).

2) Further experiments are required to elucidate how amino acids form polypeptides inside the plasma milieu, as well as how nucleosides form nucleotides.

3) Metal ions such as Mg^{2+} and Cu^{2+} are known to have been present in the early ocean (Kitadai et al., 2019). However, previous plasma condition studies have rarely taken into account the roles of metal ions and salt ions on the prebiotic formation of small biomolecules (i.e., amino acids and nucleobases) and biomacromolecules (i.e., polypeptides and nucleotides).

In summary, this paper presents a comprehensive examination of research into prebiotic sources of chemicals central to life forms, in the context of plasma discharge circumstances, presenting perspectives that we hope can inform future investigations and advancements in this interdisciplinary field.

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