Prebiotic Gels as the Cradle of Life

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Abstract: We present the "prebiotic gel-first" framework, which considers how the origin of life (OoL) could have potentially emerged within surface-attached gel matrices. Drawing on concepts from soft-matter chemistry and using modern microbial biofilms as a framing device, we review the physicochemical features of prebiotic gels, and discuss how prebiotic gels could have provided the means for localized environments conducive to chemical complexification and evolutionary potential well before cellularization.

Such prebiotic gels may have allowed primitive chemical systems to overcome key barriers in prebiotic chemistry by enabling molecular concentration, selective retention, reaction efficiency, and environmental buffering. Furthermore, we explore how gel matrices could have supported proto-metabolic activity through redox chemistry, light-driven processes, chemo-mechanical coupling—and proto-replication *via* autocatalytic networks or template-directed synthesis.

We then briefly extend this model into the domain of extraterrestrial life detection, discussing the potential existence of "Xeno-films", *i.e.*, alien biofilm-like structures composed of non-terrestrial (or with some terrestrial) building blocks, and emphasize the relevance of agnostic life-detection strategies in the search for life as we know it, and *don't* know it.

1. Introduction

Scientific inquiry into the origins of life (OoL) often draws on both reductionist and modular approaches. Reductionism seeks to understand systems by breaking them down into their simplest components, while modularity focuses on functional units, such as the *cell*, *i.e.*, the basic unit of biology[1]. The cell theory sets the foundation of modern terrestrial biology and implicitly assumes the basic unit of universal biology — whether on earth or extraterrestrial — is also cellular by nature[2–4].

Building on this cell-centric foundation, protocells, *i.e.*, cellular models bridging chemistry and life are typically defined as minimal and primitive entities that could ideally integrate metabolism and replication within a containe[5,6]. Many protocell types have been proposed (*e.g.*,[7–10], but membranous protocells (*e.g.*, lipid vesicles) are most intensively studied due to their closer resemblance to modern cells, which themselves are composed of a lipid membrane[5].

However, the concept of an idealized, free-living (*i.e.*, planktonic) and autonomous membranous protocell still remains largely theoretical. While many protocell experiments demonstrate some life-like features and partial functionalities (*e.g.*, selective permeability, growth)[11–15], the protocell is still simply a modular concept. Modularity offers a practical scientific framework for isolating and testing individual functions, but when applied to the OoL, it risks oversimplification, neglecting the emergent (and often undefinable or intractable) properties and interdependencies that likely characterized early life[16–19].

This tension highlights a broader epistemological issue in OoL research. While protocell models are useful—and may even be correct[20]—the study of OoL may benefit more from a continuous, integrative narrative that reflects the chemical and environmental messiness of early Earth, rather than relying on overly tidy, cell-like frameworks.

As such, rather than a linear, stepwise process, the OoL likely involved overlapping chemical systems interacting in unpredictable and intractable ways[21–24]. For example, life may have emerged from tightly interdependent components whose boundaries blurred over time, suggesting a continuum of transitions rather than a modular construction or development[25,26]. In this view, features such as informational molecules, compartmentalization, and proto-metabolism likely arose contemporaneously along contiguous pathways before merging into more integrated, cell-like systems. This particular perspective broadens OoL research by encouraging exploration of intermediate, non-cellular assemblies that may have carried out life-like functions well before modern cells existed[18,25,27,28].

To extend this continuum-based approach, we synthesize ideas from published literature in various fields showing that the prebiotic gel framework, which are an underexplored construct in the context of OoL, suggests that these gels are structurally and functionally analogous to biofilms and could have provided distinct localized environments fostering complexity and integration prior to the emergence of protocells. We argue that such prebiotic gel phases are imbued with valuable physicochemical properties capable of supporting the eventual emergence of cellular life, and, later, for the evolution of biofilms as we know them today.

In the following sections, we review the structure and characteristics of modern biofilms, using them as a framing device to explore the plausibility of prebiotic gels as conceptual platforms for the OoL, and to consider broader implications, including the potential for gel-based alien life.

2. Microbial Biofilms

Biofilms are communities of different microorganisms adhered to a surface and enveloped by a polymeric substance produced extracellularly by the microorganisms themselves[29,30]. Far from being random collections of cells, biofilms behave as coordinated, multicellular-like organisms[31,32]. It is estimated that up to ~ 80% of prokaryotic cells[32], and some unicellular eukaryotes, including amoebae, flagellates, diatoms, fungi, and certain algae reside within biofilms[32].

Because they form wherever moisture meets a surface, they are ubiquitous. They are found in environments ranging from coastal lagoons and hot springs to high-altitude lakes, hypersaline waters, and man-made structures like ships, pipelines, and drilling rigs[33–36]. These examples, along with their role in persistent human infections[37], highlight their adaptability to colonize across diverse chemical and physical conditions.

Biofilms are more than just colonizers, they are active builders of their environments. Through biomineralization, sediment binding, and structural stabilization[38–40], they can alter geological substrates and build layered mineral formations. Stromatolites, *i.e.*, rock-like structures formed by microbial communities, are a relevant example for these processes, where the oldest fossilized stromatolites (dated ~3.5 Ga) suggest that early life may have existed as biofilms[41–43].

Biofilm's structural organization is enabled by their complex 3D architecture, formed by a framework of extracellular polymeric substances (EPS)[44–47]. The EPS comprises an amalgam of proteins, extracellular DNA, lipids, and mono- and poly-saccharides and cellulose, which facilitate bacterial adhesion to non-living/inorganic surfaces, a crucial factor to ensure community stability existing in a crowded setting[48–51].

Given the structural complexity, ecological ubiquity, and geological persistence of biofilms, it is worth asking: what specific advantages does the biofilm mode of life offer compared to free-living, planktonic existence? Moreover, what might this imply about the conditions and constraints that shaped the OoL?

3. Metabolic Efficiency and Resource Sharing and the Protective Role of the EPS Matrix

Biofilms differ significantly from planktonic microbes in terms of physiology and general living. While a range of these differences is summarized in Table 1, one notable example involves microbial metabolism. Biofilms reduce individual metabolic demands through resource sharing, environmental buffering, and cooperative behavior. Unlike planktonic microbes, which expend energy on locomotion and stress responses, biofilm-residing cells prioritize collective survival[52–54]. For example, metabolic tasks are redistributed, allowing cells to specialize in specific functions and conserve energy[53,54]. This communal strategy contrasts with planktonic microbes, which rapidly metabolize osmolytes to cope with fluctuating conditions, diverting resources from reproduction to immediate survival[55,56]. The resulting high energy per-cell demand may come at the cost of reduced reproduction, prioritizing survival over multiplication.

In addition to metabolic advantages, the most significant distinction between biofilms and planktonic microbes is the physical protection provided by the EPS, which shields resident cells from stresses such as desiccation, antimicrobials, mechanical forces, radiation, and toxic metals (see Table 2). EPS also plays a key role in adaptation to extreme environments. In high pH environments, for example, species like biofilms of *P. aeruginosa* and *E. coli* increase alginate (a component of EPS) production [57]. Alginate binds with divalent cations like calcium to form crosslinked gels, leading to enhanced structural integrity [57–62]. In high salinity conditions, such as seawater or brine, biofilms of *Vibrio* spp. maintain their cell activity and overproduce EPS [59]. Such protective measures are further supported by extracellular proteins, eDNA, and water-retaining polysaccharides [60]. And as the EPS can hold water [61], it can maintain hydration around bacterial cells in salty environments. Similarly, some biofilms (such as *Cylindrotheca closterium)* show greater growth and viability in elevated salinities due in part to EPS support [62].

An excellent review of biofilm adaptation in extreme environments and its potential relevance to astrobiology was recently provided by [63].

Table 1. Differences between free-living microorganisms and biofilms.

Free-Living Microbes	Biofilms
Individual cells existing freely	• Attached to a surface and grouped together as a community of cells • EPS components (*e.g.*, curli, fimbriae, and cellulose) facilitate bacterial adhesion to non-living/inorganic surfaces[50]
Protected by the cell wall (or plasma membrane/pellicle for protozoa)	• Protected and interconnected by the EPS
Normal metabolism within each cell and growth takes place as usual/needed	• Cells have altered metabolism to conserve energy and reduce growth rates[53] but remain alive • Cells on the inner and outer regions of the biofilm exchange metabolic molecules (amino acids and fatty acids) for cell repair, tolerance and survival[54]
Must only rely on nutrients in the environment when and where they are available	• While still relying on the environment for nutrients, biofilms generate an internal nutrient reservoir and recycling systems that support the entire community—even when immediately accessible external nutrients are scarce. For example:

	- Voids, channels and regions supply/circulate nutrients, water and oxygen[29, 64, 65] - The EPS facilitates the uptake of trace metals, the sequestration of dissolved organic matter and nutrients, and the production of dissolved and particulate organic matter[66] - Metabolic products such as organic acids can become trapped within the biofilm matrix, contributing to nutrient availability[67], - Dead microbial cells within the community can serve as a nutrient source for surviving members[68]
Gene regulation for cellular benefit, like protein production	• Gene regulation in biofilms governs not only the production of useful molecules but also the maintenance of the community itself. For example, cells within a biofilm communicate using a process called *quorum sensing*, where they release and detect small signaling molecules called autoinducers. As the number of cells increases, the concentration of these signals rises, triggering a coordinated response such as promoting further aggregation or initiating cell dispersal from the biofilm [69–71]

Table 2. Advantages of the biofilm mode of living against environmental stresses

Environmental Context	Environmental Stress Type	Free Living Risk	Biofilm Mode of Living Advantage	References
Modern Earth and Prebiotic Earth	Nutrient limitation	Starvation	Nutrients are trapped within the biofilm EPS and dead cells are recycled as nutrients, providing nutrients even in times of scarcity	[67,68]
Modern Earth and Prebiotic Earth	High Temperature extremes	RNA/DNA, membrane and protein damage	Stabilizes the temperature within the biofilm to be conducive for growth and reproduction; subpopulation of dormant persister cells are heat resistant; the accumulation of thermoprotectants; or able to form a thick and stable biofilm	[72-75]
Modern Earth and Prebiotic Earth	Desiccation	Rapid dehydration	EPS retains moisture, often by forming a dense film on its surface	[64,76,77]
Modern Earth and Prebiotic Earth	Prebiotic Earth		pH shifts	Inhibition of enzymes
Modern Earth and			species) in the EPS matrix; detoxifying	

		EPS maintains an internal pH conducive for microbial cells within the biofilm	[78-80]
Oxidative Stress	DNA/protein damage	Quenching and scavenging oxidizing agents (reactive oxygen species and reactive chlorine species) in the EPS matrix; detoxifying	[81,82]

			enzymes; biofilm heterogeneity	
Modern Earth	Antibiotics (either from the natural environment or man-made)	Direct and High exposure to antibiotics	Limited antibiotic penetration and reduced metabolism render antibiotics ineffective	[83,84]
Modern Earth and Prebiotic Earth	Ionizing radiation (UV, X-ray, Gamma radiation)	DNA and membrane damage	EPS acts as a shield and conducts radiation absorption, protecting cells within the biofilm	[85-89]
Modern Earth and Prebiotic Earth	Toxins/heavy metals	Membrane/enzymes and metabolic process disruption	EPS binds to heavy metals; metabolic detoxification; biosorption of metal ions to biofilm components	[90-92]
Modern Earth	Predation/immune attack	Vulnerable	Biofilms employ several strategies for immune evasion and defense. Modifications of exopolysaccharides (*e.g.*, deacetylation) can help avoid immune recognition. The complex polysaccharide matrix interferes with the ability of immune cell receptors to interact effectively, and immune cells can become physically trapped within the biofilm, preventing phagocytosis. In addition, biofilms may release toxins or enzymes that damage predators, while the exopolysaccharides cloak biofilms from detection.	[93-96]
Modern Earth and Prebiotic Earth	Salinity	Dehydration	EPS creates reduced exposure for internal microbes and alters its composition to provide added physical protection	[57, 59, 97, 98]
Modern Earth and Prebiotic Earth	Mechanical/shear stress	Easily displaced	Firm attachment to surfaces and adjacent microbes	[99,100]

behavior and structural support provided by the EPS matrix. If we shift this perspective to early Earth—during the

The comparisons in Table 2 briefly highlight how the biofilm-mode of living offers significant advantages over a free-living (planktonic) lifestyle. These features emerge not just from individual adaptations but from the collective

behavior and structural support provided by the EPS matrix. If we shift this perspective to early Earth—during the formation of membranous protocells or even to the time of LUCA's formation—the contrast becomes more apparent as a foundational consideration in conceptualizing the clear role of prebiotic gels in the OoL.

4. Environmental Pressures on Early Earth and the Need for Communal Support in Early Life

Early Earth was subjected to extreme environmental stresses, most notably intense ultraviolet (UV) radiation, including high levels of UV-C (wavelengths < 280 nm), due to the absence of an ozone layer. Surface UV radiation was up to 2–10 times higher than today, with UV-C and UV-B reaching the surface and penetrating shallow waters [101]. UV-C is especially destructive, causing rapid breakdown of nucleic acids and membrane vesicles, which would have been lethal to membranous protocells, and even LUCA[102–104].

In addition to UV stress, early Earth experienced significant thermal extremes. High temperatures posed further challenges, as primitive cells with limited complexity would have struggled to survive or adapt quickly enough. Modern analogs, such as thermophilic cyanobacteria, show that adaptation to heat can involve genomic reduction and metabolic streamlining, often resulting in less diverse communities [105]. The evolution of hyperthermostable proteins, while theoretically possible for primitive cells, would have required molecular sophistication and evolutionary time not available to the earliest life forms[106].

These environmental pressures highlight a critical point: surviving them (*e.g.*, intense UV-C, thermal stress, *etc*) would have demanded more than isolated, individual cell-level adaptations.

On a different note, though still grounded in the broader question of early life, recent genomic reconstructions suggest that LUCA was metabolically more complex, encoding thousands of proteins, than previously thought[107,108], and may have possessed the tools to navigate environmental stress. However, it is worth acknowledging that these reconstructions are based on conserved phylogenetic features of modern organisms and do not establish how prebiotic chemical processes unfolded before the emergence of genetics (that is used to reconstruct LUCA in these studies themselves). Notably in the same study[108], Moody et al. argued that LUCA was part of a broader "ecosystem", rather than an isolated organism, with metabolic interdependencies reminiscent of those observed in modern sedimentary microbial communities. This raises the possibility that some of LUCA inferred metabolic complexity may reflect communal capabilities rather than traits of a single cell.

5. Metabolic Limitations of Planktonic Protocells and a Case for Metabolic Cooperation

In addition to environmental pressures, membranous protocells would have also faced fundamental biochemical limitations. For example, it is likely that no single protocell could have initially carried out all the (bio)chemical transformations needed for a self-sustaining metabolism. Modern cells rely on hundreds of interdependent pathways (*e.g.*, amino acid synthesis, energy production), each requiring specialized enzymes and genes [109]. Even engineered minimal cells, like JCVI-syn3.0 with 473 genes, depend only on nutrient-rich environments and lack full metabolic autonomy[110–112].

If even highly precisely engineered synthetic cells are not truly autonomous and will likely not survive in the natural environments, then the much simpler (yet primitive) protocells would have faced even greater functional constraints on harsh early Earth environments. This makes it unlikely that a planktonic protocell could independently perform all biochemical reactions required for life, suggesting that a form of metabolic cooperation—where distinct entities exchange metabolites to enhance survival—may have been necessary. For example, modern anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria form biofilms in which ANME oxidizes methane while its bacterial partner reduces sulfate; neither organism can sustain this process alone[113].

Such interdependencies hint that early life systems may have relied on communal strategies to overcome metabolic limitations. Prebiotic gels or biofilm-like structures could have facilitated this cooperation, enabling division of labor and shared biochemical tasks long before genetic complexity emerged.

6. The Prebiotic Gel-First Framework for the OoL

The epistemological limitations of a modular, cell-centric frameworks coupled with the environmental and metabolic challenges outlined in Sections 4.0 and 5.0 highlight the need for alternative approaches to the OoL. Here, we present the *prebiotic gel-first framework,* which considers that early life may have emerged within surface-attached gel matrices.

Gels are generally defined as semi-solid materials formed by networks of cross-linked molecules (such as polymers, low-molecular-weight gelators, or colloidal particles like clays) dispersed in a liquid[114]. These networks can be stabilized by covalent, non-covalent, or physical interactions.

By “prebiotic gel,” we refer to any soft, structured material formed from plausible prebiotic compounds that creates a semi-solid matrix capable of supporting localized and integrated chemical interactions. This model changes the conventional sequence—*i.e.*, protocell → planktonic cell → biofilm—and instead posits a trajectory such as prebiotic gel → biofilm-like (or proto-film) system → planktonic cell, or alternatively, prebiotic gel → planktonic cell → biofilm.

The notion that gels could have played a role in the OoL was first proposed by Jack Trevors and Gerrard Pollack[115]. In their model, hydrogels, *i.e.*, water-saturated polymeric networks, were envisioned as pre-cellular environments that enabled molecular organization and retention. These gels could later have been enclosed by lipid bilayers to form primitive cells, shifting focus from membrane-first OoL models. Later work by Trevors hypothesized that the gel as an internal milieu that enabled cellular functions akin to a cytoplasm[116].

In contrast, the prebiotic gel-first framework posit that these gels were not internal cytoplasmic precursors, waiting to be encapsulated by lipids to become a cell, but active, surface-bound entities—where the surface itself played a crucial role in enabling proto- metabolic and -replication processes. This emphasis on surface-associated prebiotic environments resonates with, yet can be distinguished from this framework, such as that recently presented by Ute Römling[117]. Römling argues compellingly that biofilm formation, defined as the close association of microbial cells with surfaces, is intrinsic to the prerequisites and molecular mechanisms that enabled the emergence of life itself. Their model underscores that the development of life, including metabolism, energy conservation, and cellular organization, required catalytic surfaces (*e.g.*, FeS, FeNiS [118]). On these surfaces, primitive prokaryotic life forms, such as acetogens and methanogens, would have existed as sessile ancestral forms of biofilms. Römling's view strongly emphasizes surface-dependence and the ancient origins of the biofilm lifestyle, however, it primarily describes the emergence and activity of (proto)cells already forming these early, surface-associated communities. Our framework, on the other hand, simply states that prebiotic gels *preceded* cellularization altogether.

We emphasize the role of prebiotic gels as structural and organizational platforms that enable key prebiotic processes (such as vesicle formation, proto-metabolism, and -replication) and potentially solving problems pertaining to OoL (such as the dilution or concentration problem[119,120]).

The following subsections review how physical properties of modern, and some prebiotic gels, can play an important part during the OoL in building a prebiotic-gel first framework.

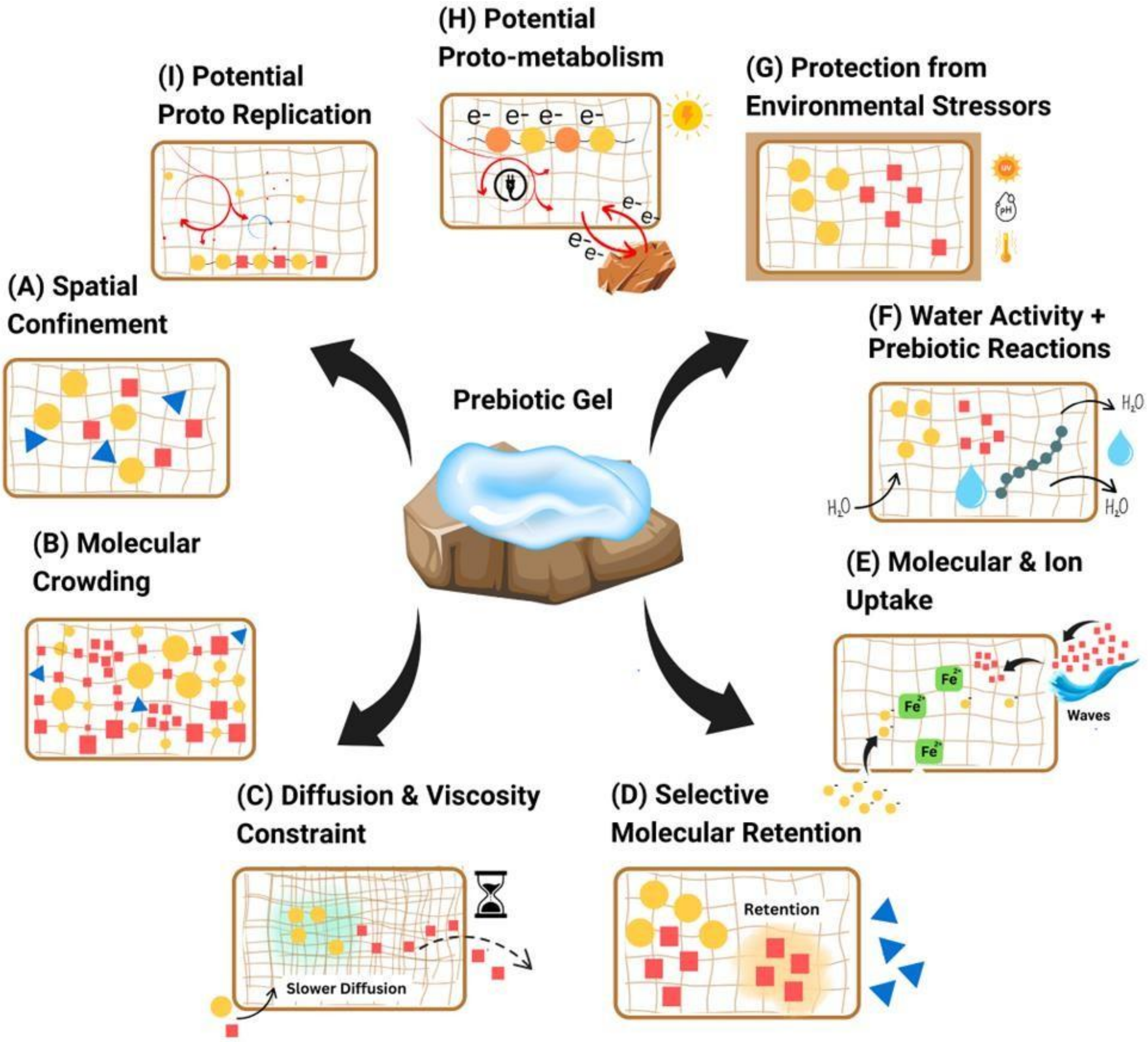

Figure 1. Summary of properties and characteristics of prebiotic gels that make them a suitable localized platform for supporting processes central to the formation of nascent biology

6.1 Spatial Confinement and Molecular Concentration Effects in Gels

First and foremost, a prebiotic gel would provide large spatial confinement and physical restriction of molecules within a limited volume[121] (Figure 1A). A defining feature of gels is their 3D network of cross-linked molecules[122], which physically constrains and organizes molecules in space[121].

Such confinement would increase the likelihood of molecular encounters and reaction efficiency through at least an extension of residency time for molecular entities within any given volume region of the gel. For example, using an example from material science, a hydrogel formed from imidazole-induced gelators, where imidazole is known for its ability to participate in acid-base catalysis and proton transfer. The gelators significantly enhanced the ester hydrolysis rate of *p*-nitrophenylacetate compared to its non-gelling analogue[123]. This enhancement was attributed to the high local concentration of catalytic imidazole groups within the gel network, the formation of hydrophobic pockets that bind substrates, and cooperative action between protonated and unprotonated imidazole species, effectively mimicking enzymatic catalysis. In this context, imidazole facilitates proton transfer and nucleophilic attack on *p*-nitrophenylacetate, *i.e.*, core functions in ester hydrolysis, thus allowing the hydrogel to emulate some of the behavior of natural enzymes through spatial organization alone.

In prebiotic chemistry, a clay hydrogel has shown to be able to concentrate and protect nucleic acids through electrostatic interactions, and significantly enhanced transcription and translation reactions in a cell-free system, producing up to 6.6 times more protein than control reactions in solution and preserving DNA function even under nuclease challenge, *i.e.*, enzymatic degradation[124].

Both these examples demonstrate how gels can provide confined environments that enhance reaction efficiency, concentrate molecules, and therefore show features that make them suitable platforms for prebiotic chemical processes to happen within a gel.

6.2. Molecular Crowding and Further Concentration Effects

Over time, accumulation of molecules within a prebiotic gel matrix induces molecular crowding, *i.e.*, a state where steric exclusion by adjacent molecules reduces solvent-accessible volume that could influence reaction dynamics (FIgure 1B)[125,126]. This phenomenon is ubiquitous within the modern cytoplasm[127,128] *and* in biofilms, where microbes are densely packed together, forming a complex matrix of EPS, DNA, and other materials[48,129].

Crowding effects have also been shown to stabilize molecules in gels relevant to prebiotic chemistry. For example, purine monomers such as adenosine monophosphate (AMP) and guanosine monophosphate (GMP) promote π-stacking interactions when embedded in polyethylene glycol (PEG) gels[130].

Being within a gel ensures that small ions, molecules, polymers, or catalysts remain in close proximity, thereby vastly increasing their effective concentrations compared to the bulk aqueous environments such as oceans, lakes, ponds and even smaller water bodies. Entrapment of prebiotic chemicals within a gel matrix allows prebiotic chemicals to accumulate overcoming the dilution (or the concentration) problem that has long challenged prebiotic chemistry[119,120].

6.3. Diffusion Constraints and Viscosity Effects

Beyond spatial confinement and crowding, gels also could impose a distinct diffusion regime due to their semi-solid, polymer-rich or metal-complex composition (Figure 1C). In contrast to bulk aqueous solutions, where solutes diffuse rapidly and stochastically, the interior of a gel presents a viscous medium in which molecular motion is significantly hindered. This hindrance arises from increased viscosity because of structural barriers within the gel matrix, which exert frictional drag on solutes and reduce their diffusivity[131]. For example, experimental and theoretical studies of hydrogels show that diffusion coefficients in hydrogels can be orders of magnitude lower than in bulk water (depending on solute size, gel mesh density, and polymer hydration)[132]. Even small solutes diffuse significantly slower in hydrogels. For instance, glucose was found to diffuse at only about one-third of its free-solution rate in a PEG hydrogel (diffusion coefficient: 0.17×10^{-5} cm²/s in the gel and $0.6–0.7 \times 10^{-5}$ cm²/s in water)[133]. Similarly, dissolved ions (K^{+}, Cl^{-}) in a polyacrylamide gel diffuse at ~30–40% of their normal diffusion coefficient in water[133,134]. These reductions in diffusion correspond to an effective increase in viscosity. Likewise, the cytosol, for instance, behaves as a fluid ~3–4 times more viscous than water for small macromolecules[135].

A compelling example of a prebiotic gel demonstrates how diffusion constraints and viscosity can influence chemical reactivity comes from the work of Gorrell *et al.*, 2017[136]. The group investigated prebiotic phosphorylation reactions within silica hydrogels, *i.e.*, a mineral-based matrix with geological plausibility for early Earth environments[137]. In their experimental setup, the researchers combined inorganic phosphorus sources (orthophosphate (Pi(V)) and phosphite (Pi(III)), along with ferrous ions (Fe^{2+}) (which served as a catalyst by facilitating redox chemistry essential for phosphorus coupling), into the silica hydrogel to investigate whether such an environment could promote the formation of pyrophosphate (PPi), *i.e.*, a prebiotic analog to adenosine triphosphate (ATP), an energy-rich molecule containing phosphoanhydride bonds central to metabolism[138,139]. They observed that the gel's structured and viscous nature significantly slowed diffusion and extended molecular residence times, effectively concentrating reactants and enhancing the formation of PPi. Compared to control reactions in bulk aqueous solution, the hydrogel matrix provided an environment that not only confined reactants physically but also modulated their interactions through diffusion limitation. Altogether, this study illustrates how metal-rich, gel environments could have promoted key prebiotic transformations by combining structural confinement, viscosity-induced diffusion retardation, and catalytic enhancement—making them plausible settings for early prebiotic chemical evolution.

6.4. Selective Retention of Molecules in Gels

Another complementary property of gels, in relation to concentration and crowding effects, is their ability to selectively retain certain molecules, while excluding others based on size, charge, or chemical affinity (Figure 1D). The selectivity for size arises from the gel's pore structure of cross-linked molecules. Similar to size-exclusion chromatography (SEC), porous polymer gels, such as cross-linked dextran or agarose beads have long been used to separate solutes by size: larger biomolecules, such as peptides or nucleic acids are retained within the gel matrix, while smaller or uncharged solutes diffuse out more readily [140]. Similar to SEC principles, biological systems offer a clear analogy to selective permeability seen in gels. The nuclear pore complex (NPC) in eukaryotic cells regulates traffic between the nucleus and cytoplasm through a hydrogel-like mesh formed by phenylalanine-glycine peptides-repeat nucleoporins. This mesh acts as a selective barrier, allowing only small molecules (~40 kDa) or those with specific transport signals to pass, while excluding others [141–143].

Other than size, charge-based selectivity is critical for molecular retention. Clay minerals such as montmorillonite (Mt), likely abundant on early Earth and Mars, possess unique surface charge and adsorption properties, enabling them to concentrate and organize biomolecules [144]. For example, they selectively retain positively charged amino acids/peptides and anionic RNA through cation-mediated electrostatic interactions [145,146]. Critically, Mt clays can catalyze RNA polymerization by adsorbing precursors and organizing them on their surfaces [147]. When Mt is incorporated with hydrogels (as shown in subsection 6.1), they combine the structural confinement of gels with selective binding and catalytic capabilities, synergistically promoting prebiotic reactions [124].

The third way for selective retention is chemical affinity. Engineered gels that are made with specific binding sites for certain molecules can do this. For example, hydrogels containing boronate groups have been shown to selectively bind ribose sugars [148,149]. While such specificity is readily achievable with modern tools, it raises the intriguing question of how similar chemical selectivity could have emerged during the OoL. One possibility is that, with increasing chemical complexity of a prebiotic system during the OoL, a degree of molecular specificity may have arisen naturally.

Overall, the ability of gels to retain molecules through various mechanisms suggests that similar properties could have been adopted by prebiotic gels, creating locally enriched chemical environments that may have facilitated further chemical evolution.

6.5. Uptake of Molecules and Ions by Gels

While earlier subsections showed that gels can concentrate molecules, become molecularly crowded, and be selective about which chemicals they retain and interact with, they still don’t explain how the gels initially attract or absorb those chemicals in the first place. This is especially important during the OoL, where we assume that prebiotic chemicals are available and are being produced in many different places (like the atmosphere, hot springs, or hydrothermal vents, *etc.*). So, the key question is: how do these gels actually draw those chemicals into themselves?

A defining feature of nearly all gels is the presence of pores, *i.e.*, networks of interconnected channels that are open to the exterior of the gel, allowing water and solutes (molecules and ions) from the surrounding environment to enter and move through the gel matrix (Figure 1E) [150–152]. Size, distribution, and connectivity of pores in any given gel vary dramatically depending on gel composition and formation conditions [153].

In a purely passive gel system, solute movement continues until an equilibrium concentration is reached between the gel matrix and the external solution, *i.e.*, assuming the matrix is in contact with an aqueous water body. The rate of this diffusion is governed by Fick's First Law and depends on several factors, including the concentration gradient, the size and chemical nature of the diffusing molecule, the temperature, and the properties of the matrix itself (such as its pore size, tortuosity (*i.e.*, how winding and obstructed a pathway is), and interactions with the solute) [154].

Likewise, passive diffusion is utilized by biofilms to take in nutrients from their environment primarily across their porous extracellular matrix, which contains water channels that allow solutes to penetrate and support microbial metabolism [155].

Note that passive uptake by biofilms can also occur with important distinctions from gels. For example, while Fick's Law is foundational, a biofilm's effective diffusion coefficient is often lower due to EPS density and tortuosity, meaning that the effective speed of diffusion can be lower than it would be in gels [156,157]. Biofilms also exhibit dynamic porosity (*i.e.*, their pore structure that changes over time) and are characterized by metabolically driven concentration gradients created by their microbial inhabitants, features generally absent in static man-made gels [158].

If prebiotic gels were porous, they could have facilitated passive diffusion; however, this process would still depend on concentration gradients, which assume a high availability of molecules, an assumption that may not hold, as prebiotic molecules were likely dilute [159].

Hence, beyond passive diffusion, dynamic mechanical loading (DML) presents another potential mechanism that can hasten molecular uptake in gels, one that can even move chemicals against their concentration gradient, an outcome reminiscent of cellular active transport [160,161]. DML of prebiotic gels could have been facilitated by environmental forces such as the repetitive compression from wave action in coastal or shallow waters, or the slower, cyclical dehydration-rehydration, *i.e.*, wet-dry cycles, in intertidal settings [162].

DML happens *via* a physical 'pumping' action: cyclical compression of the gel (*e.g.*, by waves or during the drying phase of a wet-dry cycle) expels solvent while hindering solute outflow (where the solute's molecules may be impeded by steric hindrance if large enough (compared to the pore's cavity size), or by interactions with the gel matrix, such as electrostatic attachment, *etc*), creating concentrated solute pockets near the periphery of the pore. Subsequent matrix recoil (*e.g.*, as a wave recedes or during rehydration in a wet-dry cycle) then advects these solute pockets deeper into the gel. This mechanically-induced active-like transport has been experimentally validated in simple gel systems like agarose with dextran under laboratory-simulated dynamic loading conditions [160,163]. Thus, we speculate that simple porous prebiotic gels subjected to cyclical environmental stresses, like wave action or repeated dehydration and rehydration could facilitate molecular uptake and concentrate them more effectively than by passive diffusion alone.

In addition to the uptake of organic molecules, it is important to note that prebiotic gels can in principle also effectively sequester a variety of dissolved ions crucial for prebiotic chemistry. This includes not only transition metal ions such as Fe^{2+} and Fe^{3+}, but also monovalent ions like sodium (Na^{+}) and potassium (K^{+}), as well as divalent ions like calcium (Ca^{2+}) and magnesium (Mg^{2+}). These ions can be incorporated into the gel matrix through direct chemical interactions, such as electrostatic attraction to charged polymer backbones, coordination with specific functional groups within the gel (*e.g.*, carboxylates, phosphates) [164], or by acting as cross-linking agents that contribute to the gel's structure and stability (*e.g.*, [165,166]. Such sequestration would lead to the concentration of these inorganic components within the gel, making them readily available for structural roles or as components essential for subsequent prebiotic chemical reactions (see later subsections).

6.6. Modulation of Water Activity and Prebiotic Reactions

Gels (especially hydrogels) can absorb substantial volumes of a solvent (commonly water) [167] along with any dissolved (prebiotic) chemicals or monomers. As the gel absorbs the solvent, it expands or swells [168,169], altering its internal structure and physicochemical environment. These changes may directly impact prebiotic chemical evolution, particularly by affecting water activity and molecular reactivity within a (prebiotic) gel (Figure 1F).

In gel systems that involves polymer-based hydrogels, metal complexes, or mineral-based gels (like silica or clay hydrogels), which are by nature highly hydrated, much of the water they hold is “bound” within their respective networks (*e.g.*, *via* hydrogen bonds or electrostatic interactions) or confined to narrow pores (*e.g.*, hydrogels [152] and silica hydrogels under specific conditions [170]). As a result, the effective availability of free water (and thus it water activity) for chemical reactions is lower than in bulk solution [171]. This reduction in free water activity shifts the thermodynamic balance in favor of condensation reactions—such as the formation of prebiotic peptide, phosphodiester, and ester bonds, as well as energy-rich molecules like thioacids, thioesters (prebiotic analogues of acetyl-CoA), and phosphoanhydrides—which are typically disfavored and prone to hydrolysis in fully aqueous environments [139,172–175].

On the other hand, while reducing free water activity in prebiotic gels is important, the overall water in the gels is still prone to extreme dehydration, especially on early Earth. A simple way that prebiotic gels can mitigate dehydration can be similar to how biofilm does is by the formation of a dense “skin” on the surface preserving residual water content on the inside [65]. As the outer layer of a prebiotic gel dries, it helps protect the interior from further water loss. In addition to this, other mechanisms may have contributed to water retention, within a gel, such as the inclusion of deliquescent salt (*e.g.*, calcium chloride ($CaCl_2$), ammonium chloride (NH_4Cl), *etc*.), and also the presence of hygroscopic macromolecules (that could have been formed by the reactions (*e.g.*, polymerization) mentioned earlier).

First, incorporating deliquescent salts into the gel matrix could enable direct moisture absorption from the atmosphere—an especially advantageous feature when a prebiotic gel is no longer near a liquid water source. For instance, modern hydrogels embedded with salts like $CaCl_2$ or LiCl demonstrate substantial water uptake capacities (*e.g*., up to 1.75 g of water per gram of dry hydrogel at 80% relative humidity (RH), and 0.74 g/g at 35% RH) by exploiting the salts’ ability to hydrate and deliquesce, with the hydrogel matrix trapping the resulting brine and preventing leakage [176].

The principle above has direct prebiotic relevance where deliquescent salt (such as KCl and NaCl) within a wet-dry cycling environment have been shown to autonomously regulate hydration [177]. The systems absorb just enough atmospheric moisture through deliquescence to dissolve reactants during 'wet' phases, while the 'dry' phases promote condensation reaction of glycine. This self-regulating hydration significantly enhanced the yield of glycine oligomers (tenfold higher, reaching up to 21% yield with peptide lengths up to 13 residues) compared to non-deliquescent systems.

Second, the presence of hygroscopic macromolecules (*e.g.*, potentially early prebiotic polymers that may have formed within the gels) can enhance water retention. These macromolecules can reduce pore size and interact with water *via* hydrogen bonding, slowing evaporation. For example, hygroscopic macromolecules (*e.g*., sucrose) in agarose or polyacrylamide hydrogels reduce pore size and slow evaporation, retaining 45% water after 4 hours at 60°C [178].

Taken together, this dynamic regulation of internal hydration, whether through deliquescent salts or hygroscopic macromolecules, continuously maintains internal water activity at levels potentially favorable for prebiotic chemical evolution. As hydration fluctuates cyclically, gels may repeatedly create environments that tip chemical equilibria toward condensation rather than hydrolysis. This feedback between hydration control and reaction promotion suggests that prebiotic gels are not just passive entities, but can be active participants in polymer evolution, accumulating, protecting, and facilitating functional macromolecules essential for the emergence of life.

6.7. Protection from Environmental Stresses

In the previous subsection, we briefly discussed how prebiotic gels could protect their interior from dehydration and safeguard polymers and energy-rich molecules from hydrolysis. However, hydrolytic and dehydration stress are not the only challenges that could hinder the OoL process. Other environmental stresses are listed in Table 2 and Section 3.0 could also exert adverse effects on early prebiotic systems. Without adequate protection, both the prebiotic gel structure and the chemical systems within it can be easily destroyed, ultimately halting the continuity required for prebiotic systems to persist and evolve.

Prebiotic gels may have helped buffer or mitigate against a spectrum of environmental stresses (Figure 1G).

For instance, the attenuation of harmful and widespread UV radiation by prebiotic gels, especially those made with minerals, could represent a critical survival strategy for early OoL systems especially on an ozone-free early Earth. Mt clay exemplifies this protective capability. Studies on modern gel analogues, such as montmorillonit-alginate-Ca^{2+} (Mt-Alg-Ca^{2+}) hydrogel, demonstrate that they can block over 90% of UV-C radiation (200–280 nm) at gel thicknesses exceeding 1 mm [179]. While the alginate (a long linear organic polymer found in seaweed and some EPS) [180] in this modern hydrogel would not have been present prebiotically, it's plausible that other simpler prebiotic polymers, such as peptides, polyesters, or polynucleotides could have interacted with the Mt to form hydrogels. The primary UV-attenuating properties, however, stem from Mt's intrinsic layered aluminosilicate structure especially when it is mixed with other elements (such as iron and calcium) [181] and/or organic molecules, all of each likely existed on early Earth.

Even in the absence of minerals, the incorporation of polycyclic aromatic hydrocarbon (PAH)-rich macromolecules can form protective layers or contributing to prebiotic gel structures, that provide significant protection against UV and ionizing radiation [182]. The aromatic moieties in PAHs are capable of absorbing UV light through $\pi \rightarrow \pi^*$ transitions (bonding orbitals to antibonding ones), with the wavelength and intensity dictated by conjugation length, substituents, and environmental factors [183,184]. In other words, the aromatic rings parts of PAH molecules can soak up UV light; they do this because UV light makes electrons in these rings jump to a higher energy level. Exactly what kind of UV light they absorb (like short-wave or long-wave UV) and how much they absorb depends on how many rings are joined together, what other atoms are attached to the rings, and what material the PAHs are in. This UV blocking feature of PAHs is also utilized in biology. Melanin, a biological macromolecule that also contains aromatic ring structures as fundamental building blocks similar to PAHs is a ubiquitous group of pigments found across all three domains of life [185]. They provide photoprotection by efficiently absorbing UV radiation and dissipating energy, thereby shielding cellular components like DNA from damage, among other benefits to the organism that produces them [182,186,187].

The relevance of such PAH-rich macromolecules to prebiotic scenarios is underscored by their widespread presence in astrochemical environments, including the interstellar medium and in the insoluble organic matter (IOM) of carbonaceous chondrites [188,189]. Consequently, the delivery of this IOM *via* meteorites could have led to its accumulation in early Earth environments. Here, it might have become incorporated into gel matrices, thereby potentially acting as shielding for other less stable organic compounds within these gels. Contemporary material science provides compelling examples where both melanin and PAH-based structures are intentionally incorporated into hydrogels to harness these very properties for advanced applications (*e.g.*, [190–192]).

In addition to intense UV radiation, the early Earth environment likely presented significant thermal challenges. For prebiotic gels to persist and facilitate chemical evolution under such hot conditions, they would have required properties to resist thermal degradation. This protection could have been conferred in several ways. For instance, silica minerals (composed by SiO_2), which were abundant on early Earth exhibit notable thermal stability [193,194] and dry silica gels have shown to be thermally stable up to 950^{O}C [193]. However, it is worth noting that dry silica "gel" (as commonly encountered, for example, in desiccant packets) is not a soft material [195]. It exhibits true gel-like properties only when hydrated, forming a silica hydrogel in which the porous silica matrix is saturated with water [136,196,197]. Indeed, modern silica hydrogels demonstrate their advantages for practical applications because of their high transparency (allowing light to penetrate) and thermal stability when compared to biopolymer gels [198,199]. Nevertheless, the inherent thermal stability of silica hydrogels would have been particularly crucial for the persistence of prebiotic gels in thermally challenging prebiotic environments.

Other mineral gels, *e.g.*, Mt, when forming Mt-hydrogels, can also exhibit thermal stability, particularly when interacting with other molecules or ions that reinforce their structure [200]. This is likely because of interlayer cations (like Na^+ , Ca^{2+} , Mg^{2+}) in montmorillonite coordinate with water molecules, forming hydration shells [201,202]. The stability of these hydration shells contributes to the thermal behavior of the clay and may have played a similar role in relation to Mt-prebiotic gels.

While some early Earth environments were hot, not all areas would have been uniformly so. Prebiotic gels might have formed in locations with more moderate temperatures or within thermal gradients [203]. Even if prebiotic gels were transient and susceptible to thermal disruption, fluctuating conditions, such as wet-dry cycles (by cooler nights and hotter daytime temperatures), are frequently invoked for prebiotic synthesis (*e.g.*, [204–207]. In such scenarios, prebiotic gels might degrade and re-form, with temporal periods of stability allowing for crucial chemical steps.

Beyond all these, the thickness of a prebiotic gel may be useful against heat by insulating internal regions and buffering thermal changes regardless of a specific type of gel that can provide protection against heat.

In essence, the thermal resilience of prebiotic gels likely depended on the inherent properties of their constituent minerals (such as the high heat resistance of silica and Mt), the protective influence of dissolved ions, their thickness, their specific location within early Earth's diverse thermal landscapes, and the dynamic interplay of surrounding environmental conditions [208].

Another early Earth environmental stress is pH fluctuation. This fluctuation could have happened on early Earth because of constant or periodic release of acidic volcanic gases and the weathering of continental and seafloor crust, early water bodies likely experienced significant pH shifts. Notably, a geological transition in ocean chemistry from acidic conditions during the Hadean (~pH 5) to near-neutral conditions by the early Archean (~pH 6.5-7.0) is thought to have occurred over approximately 500 million years [203,209]. While these global conditions provide a crucial backdrop of average early Earth's conditions, they don't capture the full spectrum of pH variability that could have existed in specific, localized prebiotic environments.

For instance, proximity to active volcanoes or hydrothermal systems could have led to significant local inputs of acidic gases (*e.g.*, SO_2 , HCl, CO_2) resulting in pH values changing rapidly compared to global average [210,211]. Small, isolated water bodies, such as ponds and small crack space between rocks (*e.g.*, [205,212], undergoing wet-dry cycles can be particularly susceptible to rapid pH shifts due to the concentration of dissolved substances or specific interactions with local mineralogies. The nature of these mineral interactions was also critical; the dissolution of particular minerals in a localized area could create unique pH conditions, with regions rich in mafic rocks, for example, potentially weathering to produce more alkaline conditions locally compared to areas dominated by more silicic rocks [213]. Furthermore, shallow ponds or lakes, with their greater surface area-to-volume ratios, would have experienced more rapid equilibration with atmospheric gases like CO_2 , significantly influencing local pH [214].

One simple way gels might respond to and potentially manage pH variations is through basic pH-responsive swelling mechanisms, building on their general ability to absorb water (mentioned in subsection 6.6). For example, a prebiotic gel that has polymers containing ionizable groups such as -COOH, carboxylates side groups (*e.g.*, polymers of aspartic acid, glutamic acid, or citric acid), which can exist in both their protonated (-COOH) and deprotonated ($-COO^-$) forms depending on the pH, can act as a buffer system. They resist large changes in pH by reacting with added acids or bases. This same chemical transition (ionization) between -COOH and $-COO^-$ also causes the gel to swell or shrink due to changes in electrostatic repulsion within the polymer network.

Inorganic buffering systems could also be helpful in mitigating pH fluctuation of a gel. For example, buffering agents like phosphate [215], which can stabilize pH within ±0.5 units of neutrality, or borate [216], which buffers effectively in the pH range of 8.2 to 10.2, could, in principle, be incorporated into prebiotic gels.

We have shown that prebiotic gels may confer protection against environmental pressures and stresses. While it is likely that such gels, despite their resilience, could still degrade or perish, this could reflect an early form of selection in which only the most robust systems persisted during the OoL. However, while persistence is important, it is not sufficient. To be relevant for life's emergence, prebiotic gels must also perform functional roles. A chemically inert system that survives unchanged over time does not transform or evolve, does not support complexity, and does not contribute to the transition from chemistry to biology. It is therefore critical to consider their potential in facilitating energy transduction and information storage—functions that may have been analogous to proto-metabolism and proto-genetics.

6.8. The Potential for Proto Metabolism in Prebiotic Gels

Life depends on maintaining far from equilibrium thermodynamics [217]. Prebiotic gels, on their own, would rapidly equilibrate without any mechanisms to harvest and direct energy. For example, under equilibrium conditions, spontaneous reactions (*e.g.*, hydrolysis) dominate, degrading complex (and useful) molecules [218]. Furthermore, the synthesis of prebiotic macromolecular structures and energy-rich molecules is energetically unfavorable and requires coupling to exergonic energy sources [219].

Addressing this challenge, early energy transduction could have played a crucial role by enabling the conversion of external energy sources into usable chemical or mechanical work by coupling endergonic reactions with energy-releasing processes such as redox reactions or photon absorption (Figure 1H). Such energy transduction mechanisms likely preceded the emergence of more organized, self-sustaining systems of linked reactions such as autocatalytic networks, *i.e.*, proto-metabolism [220], and subsequently proto-replication (discussed in the next subsection).

In particular, redox-based chemistries can influence prebiotic processes within a prebiotic gel in multiple ways. When adhered to a mineral surface, such as pyrite (FeS_2), magnetite (Fe_3O_4), or hematite (Fe_2O_3), which are known to donate electrons under specific conditions [221–224], a prebiotic gel could potentially facilitate electron extraction from the substrate. This extraction process necessitates close physical contact, fostering interaction between the mineral's electron-donating sites and the gel. For a prebiotic gel to effectively extract electrons, it must also be at least partially conductive, which can be achieved by incorporating free metal components (see subsection 6.5), prebiotic redox-active molecules (*e.g.*, quinones, flavins, *etc.*) [225], or a structure capable of accepting and holding electrons, such as metal-organic complexes [226]. Thus, a prebiotic gel could function as a hybrid organic-inorganic system which mediates redox reactions.

This flow of captured electrons provides the means to overcome energetic barriers in prebiotic synthesis. For instance, it would be ideal for a primitive chemical system to directly enable specific prebiotic endergonic reactions within a gel, such as the reductive amination of pyruvate to alanine using mixed-valence iron oxyhydroxides [227], abiotic ATP formation from ADP catalyzed by Fe^{3+} and acetyl phosphate [228], and the prebiotic formation of thioacids and thioester [172]. This can be achieved because the energy released from the exergonic electron transfer process can be coupled to these endergonic reactions. Electrons transferred to a molecule can reduce it, making the molecule more reactive, or the electron flow can activate intermediates (*via* prebiotic molecules doing the functions similar to NADH [229]), effectively lowering activation energy barriers for prebiotic synthesis, especially for the reactions mentioned above.

More fundamentally, beyond direct coupling, redox activity also drives the overall thermodynamic landscape within a gel. This latter effect, in principle, favors the formation and accumulation of certain types of prebiotic molecules that are more stable (lower Gibbs energy) under these specific redox conditions. This may include key (yet unknown) prebiotic building blocks, precursors to biomolecules, energy-rich molecules, or even biomolecules themselves, such as those that can form autocatalytic networks, *i.e.*, catalytic networks where proto-enzymes/catalyst catalyze their own synthesis creating a self-sustaining cycle [230–232].

The potential for prebiotic gels to foster autocatalytic networks and host self-sustaining dynamics can also be associated with oscillating chemical systems. A prominent example is the Belousov-Zhabotinsky (BZ) reaction [233]. The reaction has been analogously compared to the Krebs cycle as a chemical model to study the cycle since the reaction discovery [234]. The BZ reaction spontaneously exhibits temporal rhythms and spatial patterns (which can be viewed by the naked eye) without external control, as long as reactants are supplied [235,236]. This autonomous oscillation is a hallmark of a system operating far from equilibrium, much like metabolism, which requires a continuous input of energy and/or matter to maintain its organized state.

When the BZ reaction occurs within a gel, *e.g.*, a poly(N-isopropylacrylamide (PNIPAAm) gel with a covalently bonded catalyst like tris(2,2'-bipyridine)ruthenium ($Ru(bpy)_3$) that drives redox reactions, $Ru(bpy)_3^{2+} \rightleftharpoons Ru(bpy)_3^{3+} + e^-$), the gel itself can exhibit autonomous swelling and de-swelling oscillations under constant conditions, *i.e.*, a form of chemical oscillations that are converted into mechanical actuation (chemomechanics)[237,238]. Simply put: when the BZ reaction happens in a gel with a Ru catalyst, the gel rhythmically swells and shrinks on its own, needing no external controls. This direct chemomechanical coupling between the redox state of the catalyst and the gel's mechanical properties establishes a crucial feedback loop, where in the oxidized state the gel becomes hydrophilic, swells, and softens, whereas in the reduced state: the gel becomes hydrophobic, shrinks, and stiffens [237]. These physical changes, in turn, could have significant functional consequences for the gel, such as enhancing the uptake of necessary reactants (solute) by drawing in fresh solution during periods of gel swelling. Conversely, non-swelling phases could facilitate the removal of metabolic byproducts or waste from the gel [239].

Therefore, the phenomenon of chemomechanical coupling in a prebiotic gel system offers a valuable way for understanding how an early 'metabolic' process may work. If such a system possesses an autocatalytic capacity like the BZ reaction, it could exert direct influence over the physical state and behavior of its confining matrix or 'container,' thereby actively managing internal environment and resource exchange with the external environment. Unlike DML (introduced in subsection 6.5), where the environment does the work on the gel, prebiotic gels with autocatalytic activity can do work on *itself* and its surroundings through internal chemical dynamics. Such systems depend less on external fluctuations and represent a step toward the autonomous, energy-driven behavior characteristic of living systems.

While redox chemistry provides a robust pathway for prebiotic gels for energy transduction, early Earth was also bathed in solar radiation. Particularly, UV radiation and the harnessing of plasmonic effects, which occur when visible light and near-infrared (NIR) interact with embedded metallic components in the gel, could lead to enhanced energy capture and reactivity [240].

In previous sections, we detailed how UV radiation posed a significant threat on early Earth (Section 4.0) and how prebiotic gels could offer protection (Subsection 6.7). However, it is also important to consider that some undetermined amount of UV light penetrating into the gel, or interacting with specific components therein, could have been harnessed as a useful energy source for prebiotic chemical reactions and energy transduction.

For example, we have previously discussed the capability of gels to concentrate molecules (Subsection 6.1 and 6.2) and retain these molecules within a crowded internal environment. This concentrating effect is highly relevant for UV-driven prebiotic reactions, such as the photoreduction of hydrogen cyanide (HCN) with bisulfite (HSO_3^-), a reaction known to generate precursors to nucleobases like adenine and guanine when exposed to UV light [101,241]. If a prebiotic gel can facilitate UV-driven reaction within it while simultaneously protecting reactants and products from harmful UV-C radiation yet allowing beneficial UV-A/B wavelengths to penetrate [242], the gel can achieve a balance between necessary energy input for the reaction and protection of the newly formed, potentially UV-sensitive products.

Another less discussed mode of energy transduction in prebiotic chemistry, but well studied in materials science, is the plasmonic effect. These effects arise when light, often in the visible (400 to 700 nm) and NIR (700 nm to 2,500 nm) spectrum, interacts with embedded metallic nanoparticles or components within a material. This interaction excites collective oscillations of the metal's free electrons (*i.e.*, plasmons), which can generate localized electromagnetic fields and heat, among other things [243–245]. We take special interest in this because prebiotic gels could potentially incorporate such metallic components (mentioned in Subsection 6.5) and may confer on new plasmonic prebiotic utility. Nevertheless, many plasmonic studies focus on gold (Au) and silver (Ag) due to their stability and strong optical responses, other metals like copper (Cu), aluminum (Al), and magnesium (Mg) can also display significant plasmonic properties, though to varying degrees and with different characteristics [246].

For example, Mg-nanoparticles have shown a unique capacity for dynamic plasmonic tuning through reversible hydrogenation. This involves a phase transition between metallic Mg, active in the UV-visible spectrum, and magnesium hydride (MgH_2), which interacts with NIR [246,247]. While this reversible process is often facilitated by metals like palladium (Pd) in modern studies due to its hydrogenation catalyst, geochemically more abundant metals during the OoL like nickel (Ni) could have served a similar catalytic function in prebiotic scenarios [248,249]. The underlying principle of a material shifting its light absorption properties in response to changes in its chemical environment (*e.g.*, presence or absence of reducing agents like H_2 can be relevant for some prebiotic scenarios.

Imagine Mg-nanoparticles embedded within a prebiotic gel and exposed to fluctuating environmental conditions—a scenario that is theoretically plausible, since gold Au-based plasmonic materials have been successfully incorporated into gels [250]. In locations with available reducing agents (perhaps from certain mineral-water interactions [251] or atmospheric chemistry leading to H_2 [252], the Mg could transition towards MgH_2 , enabling the gel system to harness energy from the NIR portion of sunlight. This absorbed NIR energy could manifest as localized heating, potentially creating thermal gradients within the gel that drive prebiotic reactions by locally increasing the temperature, an especially significant advantage in cooler early Earth environments, particularly in regions closer to the poles [253]. While not enzymatic themselves, localized warm spots within a gel could have played a crucial role in helping essential prebiotic reactions overcome activation barriers. While not enzymatic themselves, localized warm spots within a gel could have played a crucial role in helping essential prebiotic reactions overcome activation barriers. Higher temperatures can dramatically accelerate extremely slow prebiotic chemical reactions, sometimes by millions of times, greatly hastening the kinetics of prebiotic chemistry and making the emergence of life more feasible within Earth's available time frame [254,255].

Conversely, in more oxidizing conditions or when H_2 is scarce, the material would remain as metallic Mg (or revert to it), making the gel system responsive to UV for different photochemical processes. This adaptability in energy capture, switching between different parts of the solar spectrum based on local chemical conditions, represents a rather sophisticated form of environmental interaction.

*(**Note**: Nanoparticles have rarely been discussed in OoL studies, largely because the metals that make up nanoparticles tend to oxidize under aqueous conditions, or because the availability of exotic metals (that are used in material science studies) are likely not prebiotically accessible and was extremely limited on early Earth. However, nanoparticles' potential role in prebiotic chemistry has begun to receive attention in prebiotic chemistry—see [256,257] for details.)*

6.9. The Potential for Proto-replication in Prebiotic Gels

In the earlier subsection, we mentioned the potential of autocatalysis for proto-metabolic processes and contextualized these concepts (commonly explored in OoL studies [231]) within the framework of prebiotic gels. We now extend this line of reasoning by applying autocatalytic principles to a framework for proto-replication (Figure 1I). Within this context, the Graded Autocatalysis Replication Domain (GARD) model offers a compelling theoretical framework for understanding how mutually catalytic networks of molecules can form self-reproducing compositional assemblies, known as composomes, which replicate their compositional information [258,259]. This idea represents a form of proto-replication, where the focus is on the replication of molecular composition (composomes) rather than exact sequence (or template) replication, providing a plausible pathway for the emergence of early self-sustaining chemical systems.

While the GARD model traditionally employs micelles and membrane vesicles as (static) containers [260,261], prebiotic gels offer distinct advantages that may make them superior environments for such dynamics. Gels exhibit stability and protection against environmental stressors. Unlike micelles and membrane vesicles prone to rupture under shifts in pH, gels maintain structural integrity, thereby preserving composomes. This robustness is complemented by the possibility of a gel having a dynamic feedback mechanisms; chemomechanical coupling (*e.g.*, BZ reactions) in gels enables active resource management, such as swelling and deswelling to expel waste or mix reactants an intrinsic responsiveness micelles and membranous vesicles lack. Finally, gels can potentially form large, interconnected networks, facilitating molecular exchange and cooperative interactions between composomes over larger spatial scales (subsection 6.1), compared to to discrete micelles or vesicles, enabling more frequent and diverse molecular interactions across a greater space and volume, which may support chemical evolution

However, while autocatalytic sets and the GARD model, particularly when adapted to such a conductive gel environment, offer valuable insights into the establishment of self-sustaining chemical networks and the replication of compositional information, they are inherently limited. Because it does not readily lend itself to a more precise, high-fidelity inheritance of detailed structural information or the open-ended evolution of complex functions that characterize life [231,262,263]. For this, a transition towards sequence-based information storage and replication becomes necessary.

This is where template-directed synthesis emerges as a critical advancement, potentially arising within these already organized and energized gel systems. By enabling the sequence-specific replication of informational polymers, (*e.g.*, such as RNA or other unknown information polymer), template-directed processes introduce the capacity for higher fidelity information transfer and, consequently, the potential for a more sophisticated form of Darwinian evolution. Within the prebiotic gel, the conditions can be uniquely favorable for this transition. The inherent ability of gels to concentrate monomers (*e.g.*, activated nucleotides or amino acids) and align them with existing template molecules would significantly enhance the efficiency of non-enzymatic copying. The reduced water activity characteristic of gel environments further aids this process by favoring polymerization reactions over hydrolysis, crucial for the formation and stability of these early informational polymers. Moreover, the protective nature of the gel shields these delicate templates and newly synthesized strands from environmental degradation.

Therefore, while compositional proto-replication within gels marks a significant milestone in establishing self-sustaining and selectively responsive chemical systems, the emergence of template-directed synthesis within these same environments represents a pivotal (and desirable) transition. However, it is important to caution that the leap from compositional networks to sequence-based replication under prebiotic conditions remains unresolved, highlighting a significant epistemological and theoretical gap between them [264]. Nevertheless, this leap, if envisioned, would pave the way for proto-replication systems capable of supporting heredity based on specific sequence information, setting the stage for the open-ended evolution that is a hallmark of living systems.

6.10. A speculative narrative of continuity from Prebiotic Gels to Planktonic Protocell

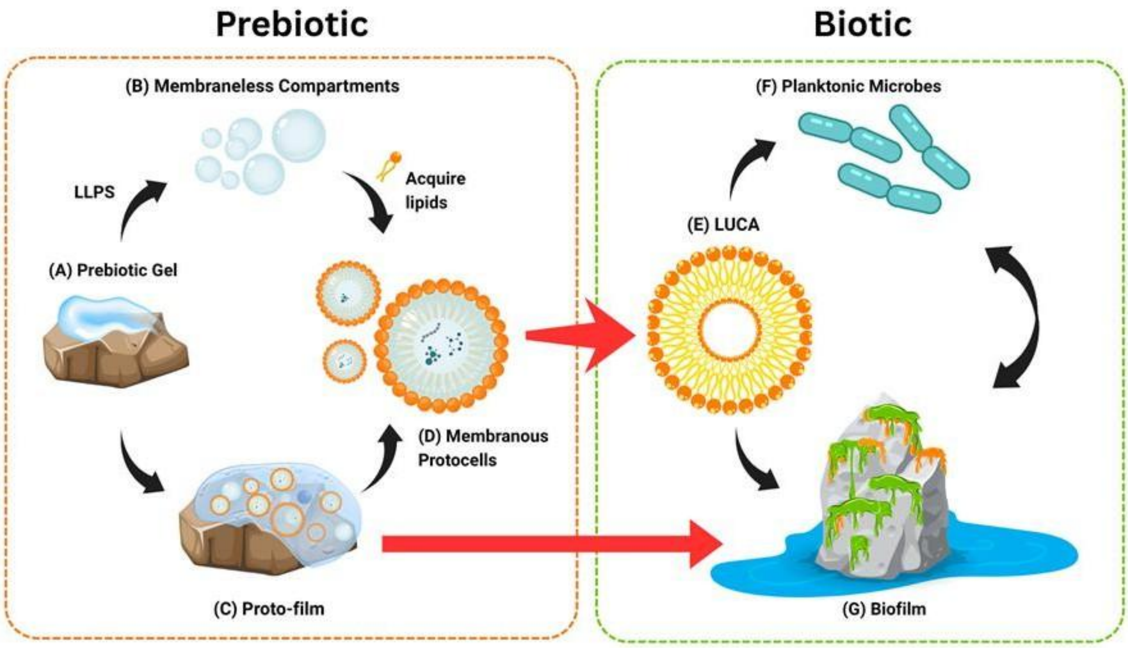

Figure 2: Schematic representation of potential prebiotic gel-based pathways leading to the emergence of life.

(A) A prebiotic gel;

(B) Formation of membraneless compartments *via* liquid-liquid phase separation (LLPS);

(C) An alternative scenario where membranous protocells form within the gel, giving rise to a proto-film;

(D) Membraneless compartments acquire lipids and become planktonic protocells, or alternatively, protocells are released from proto-films;

(E) Protocells develop into LUCA as a single cellular entity;

(F) LUCA diversifies into free-living, planktonic single cells that evolve into the primary domains of life;

(G) LUCA may have adopted a biofilm lifestyle early on to endure harsh conditions. Another alternative is that a communal LUCA could also have emerged from the protocells within the proto-film **(C)**, transitioning directly into a biofilm state.

Double-headed arrows, in the right panel, indicate that microbial biofilms periodically release free-living cells to colonize new environments—driving evolution—or that planktonic cells transition into biofilms, a dynamic seen in modern microbial ecology. This cycle of biofilm formation and dispersal likely began early and persists to this day.

While we have established how prebiotic gels can be advantageous during the OoL, we have yet to surmise the potential pathways for gels to become individual protocells, leading to LUCA.

We posit that planktonic cells (microbes) are *the* quintessential explorers of the biological realm because they possess the capacity for motility [265], enabling them to traverse distances, escape unfavorable conditions, discover and colonize new resource-rich environments, and thus 'start something new.' This engagement with their surroundings, the ability to sense, respond, and even shape their niches, anoints cells as a kind of 'meaning-making machine,' actively interpreting and interacting with the world [266–268].

In stark contrast, biofilms—and their prebiotic analogs, prebiotic gels—are “sessile.” Hence, prebiotic gels are vulnerable to prolonged local resource depletion, irreversible environmental change, as well as the accumulation of waste products. Therefore, adopting a planktonic way of life may have enabled early life forms to escape the limitations of a sessile existence.

There are two ways we envision prebiotic gels becoming protocells and eventually LUCA (Figure 2): (1) *via* liquid-liquid phase separation (LLPS), and (2) through amphiphilic compartmentalization occurring within the gel itself.

LLPS, in particular, occurs in modern biology as an energetically cheap, effective, adaptable, reversible, and rapid mechanism that allows cells to organize and compartmentalize various kinds of biochemical reactions (*e.g.*, RNA/DNA processing and storage, signal transduction, stress response, *etc.* [269]) without the specific need for membranes and potentially in a transient manner depending on the biological need at the time. LLPS on early Earth could have also occurred, potentially resulting in the assembly of precursors of protocells, such as in the form of polyester microdroplets [270], aqueous two-phase systems [271], or coacervates [272]. Prebiotic gels could phase-separate to form these entities where a dense, macromolecule-rich liquid phase separates from the surrounding aqueous solution, forming distinct membraneless compartments [273,274]. Over time, these droplets could have acquired lipids (*e.g.*, [275]), forming protocells.

Another possible pathway from prebiotic gels to LUCA involves the direct formation of membranous protocells *within* the gel matrix. This could occur if amphiphilic molecules already present in the gel reorganized into discrete vesicular compartments embedded within the matrix, resulting in what we refer to as proto-films. (Figure 2 (C)). This scenario presents a conceptual reversal to the ‘Hot Spring Hypothesis’ [276], where protocells (in their hypothesis) are described as key pre-existing entities that subsequently aggregate to form gels. On the contrary, the literature described herein suggests that the prebiotic gel would be present *first*, with membranous protocells forming within it. This aligns with aspects of the ‘Scum Hypothesis' [208], that suggest a multi-compartmentalized 'scum’ layers could form from the re-organization of amphiphilic surface films or foams into vesicles, although this model primarily assumes these scum layers are floating at the air-water interface (which is a plausible scenario in its own context).

The primary benefit of proto-films is the creation of protocells that can host proto-metabolism and -replication, akin to microbes in a biofilm (*e.g.*, the mutualistic metabolic relationship between ANME methanotrophic archaea and sulfate-reducing bacteria, first mentioned in Section 5.0). Protected by the surrounding gel, these embedded protocells could have carried out individual proto-metabolic processes, potentially contributing to the broader prebiotic gel maintenance and survival. Furthermore, any informational material within them (when it existed) might have engaged in horizontal gene transfer-like activities or participated in emerging autocatalytic cycles. The protocells within the gels are subsequently released into the surrounding environment.

Both proposed pathways (protocells deriving from membraneless compartments and proto-films) leading towards emergence of life likely possess a communal stage, *i.e.*, a progenote stage (not shown in Figure 2) [277]. This stage refers to a "community" of aggregated and interacting protocells within a gel or as membraneless compartments, which, through a gradual 'bootstrapping' of complexity, was likely a necessity for the eventual emergence of more robust cellular life, until one lineage ultimately transition into LUCA on early Earth (Figure 2 (E)). Two scenarios can be envisioned from this point onward. On one hand, LUCA emerged from the protocellular community as a free-living cell (Figure 2F), which later gave rise to the familiar domains of life as we know them, with biofilm formation (Figure 2G) evolving later as an adaptation for protection, resource sharing, and metabolic efficiency. On the other hand, LUCA may have transitioned directly into a biofilm state (Figure 2G), from which the familiar domains of life eventually emerged as free-living descendants (Figure 2F).

Though not shown explicitly in Figure 2, a third alternative scenario is also plausible: LUCA was likely communal [278–280], rather than a single-cell entity (as described in the earlier paragraphs), and may have arisen within a proto-film, transitioning into biological cells while still embedded in the gel matrix. These cells' activity may have included the innovation of producing EPS-like materials, contributing to the structure and function of the surrounding environment and making the overall gel increasingly biofilm-like. This proto-film-to-biofilm phase could have supported early biological processes before eventually releasing planktonic forms of life as we know them (Figure 2F), initiating dispersal and broader ecological expansion.

Nevertheless, it is worth mentioning that the exact mechanisms underlying all of the OoL stages mentioned above remain largely undefined and speculative at this stage and require further detailed investigation. Recognizing these uncertainties helps to frame this discussion as a conceptual contribution, at least in the field of OoL, while highlighting areas for future experimental exploration through prebiotically plausible means (as most of the studies up until now do not focus on OoL).

7.0 Caveats with the Prebiotic Gels First Model

With the exception of a few examples (to our knowledge) such as prebiotic clay hydrogels, polyester gel-like phases, and silica hydrogels [124,136,275], only a limited range of potential prebiotic gels has been explored, despite gels themselves being the target of a large number of studies from an applicational point of view (*e.g.*, [281,282]). Hence, a notable caveat to this model is that both the diversity of gel types and the specific prebiotic mechanisms by which they could have formed remain largely undefined. The prebiotic chemical space is vast and diverse [283], hence, while we have demonstrated the potential benefits of prebiotic gels as an OoL framework, our understanding would be greatly enhanced if more and different kinds of gels were shown to form under plausible prebiotic conditions on early Earth.

Expanding on this view, it is also worth noting that 'gel-like' matrices may have formed prebiotically on early Earth. These materials share many properties with modern gels but may have lacked a permanent polymeric network, and thus fall outside the conventional definition of a gel (section 6.0). Modern analogs of gel-like materials include highly viscous liquids like honey, concentrated glycerol or PEG solutions, and lipid cubic phases, all of which slow molecular diffusion and entrap solutes [284–287]. Hence, for the OoL, we can adopt a broad, functional definition of "gel" that includes conventional gels and gel-like matrices where we can include transient or loosely structured systems that can still create localized environments and, importantly, could ideally have formed under prebiotic conditions from available prebiotic compounds.

Another point to consider is that the potential diversity and prevalence of prebiotic gels in early Earth environments would have depended critically on the composition of the local prebiotic reservoir. Over time, the introduction of exogenous organic molecules, such as those delivered by carbonaceous chondrite meteorites (*e.g*., amino acids, hydroxy acids, carboxylic acid, ribose, *etc*.), could have enriched this reservoir, enabling the formation of novel gel types with distinct physicochemical properties. At the same time, shifts in global planetary geochemistry such as pH gradients, or redox states, atmospheric composition, *etc*., could have modulated gel stability and their progress towards early life. In other words, unless early life emerged and rapidly stabilized, such global changes might have directed prebiotic gel pathways toward outcomes that were either conducive to life, only marginally beneficial, or ultimately irrelevant to the OoL [288].

Finally, practically speaking, without the benefit of a time machine, it remains unclear how to construct an unambiguous narrative for the OoL. Our best option so far is the recreation of prebiotically plausible reactions and life-like components in laboratory settings—a significant, and perhaps still distant, goal. Another potential path lies in the discovery of extraterrestrial life, which could provide valuable comparative insight. Only with such empirical evidence can we begin to distinguish which of the many theoretical pathways—whether involving surface-attached prebiotic gels or other OoL models, regardless of their initial perceived plausibility—were truly critical to the emergence of life (in the universe), and which were merely coincidental or ultimately unproductive dead ends [22,289].

8.0 Xeno-films and their Astrobiological Implication

Biofilms have been suggested as potential biosignatures due to their structured nature, association with minerals (biomineralization), and the persistence of their EPS [63]. However, this perspective, and the biosignature frameworks derived from it, remain largely based on earth-bound understanding and terrestrial examples. While such approaches are valid for 'life as we know it', and particularly pertinent if one assumes a highly deterministic pathway for abiogenesis limited to specific building blocks and the processes these building blocks do, these approaches pose a significant limitation when extrapolated to extraterrestrial contexts.

Specifically, these approaches may overlook the possibility that extraterrestrial life (if and when they exist) may not be composed of terrestrial biochemistry and could be based on an entirely or partially different suite of molecular building blocks and operate using unfamiliar biochemical machinery [22]. Consequently, biosignature detection strategies focused exclusively on earth-like EPS components or specific biomineralization patterns risk 'false negatives,' potentially overlooking life forms simply because they do not conform to terrestrial biochemistry or morphology. This earth-bound focus inherently limits our ability to detect truly alien biofilm-like structures, or 'xeno-films,' should they exist. Such xeno-films could possess fundamentally (or even partially) different building blocks, *i.e*., employing alternative polymers for their matrix, or engaging in mineral interactions shaped by unique planetary chemistries and evolutionary histories [22,290].

Therefore, while studies of terrestrial biofilms provide essential insights, the plausible existence of xeno-films elsewhere in the universe necessitates a dual approach: one that both leverages our understanding of familiar life and actively incorporates agnostic biosignature detection strategies capable of recognizing of what life—both as we know it and as we don't *yet* recognize—might look like.

9. Summary

We reviewed the structure and functions of biofilms, modern gels, and some examples of prebiotic gels, and presented a conceptual framework for the OoL to illustrate the potential advantages of a hypothetical prebiotic gel system, including the formation of proto-films. This framework highlights how such gels could have supported prebiotic organization, molecular concentration, protection from environmental stressors, and the emergence of proto-metabolic and proto-replicative processes. This prebiotic gel system also suggests that protocells may not have been the first step in the OoL, but rather represent a later stage in other words, an outcome of an earlier chemical organization.

We further extend the model by introducing the speculative yet plausible concept of "Xeno-films" that may also originate from proto-gel systems, but be composed of entirely (or partially) different chemistries, highlighting the importance of agnostic life-detection strategies in astrobiology.

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The figure illustrates a prebiotic gel on the early Earth's surface, serving as a platform where chemical evolution toward life is presumed to occur.