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Mini-Review

Influence of Abiotic Factors in the Chemical Origin of Life: Biomorphs as a Study Model

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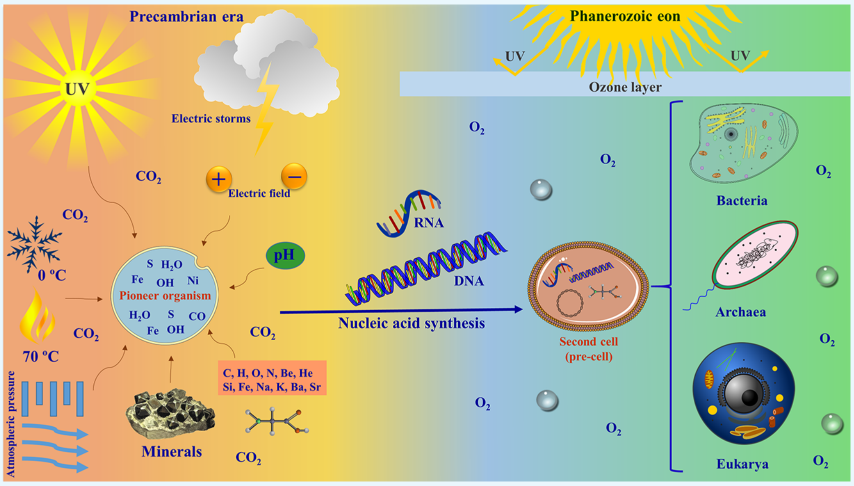

ABSTRACT: Since the formation of the Earth, minerals have been the key to understanding how life originated. It is suggested that life arose from minerals; they are considered to favor the formation and replication of biomolecules. In conjunction with minerals, the abiotic factors of the Precambrian era enabled the origin, development, and maintenance of life. To explain and understand the chemical origin of life, theories have been postulated for decades, and some of them have gone from mere postulates to evidence that have contributed to science in this direction. Several research groups have developed study models elucidating which could have been the first forms of life; in this sense, calcium, barium, or strontium silica carbonates have been synthesized in vitro to emulate morphologies of organisms. Aimed at understanding better the influence of abiotic factors in the formation of different chemical structures, the importance of the different types of physical and chemical abiotic factors in the origin of life are reviewed, as well as their influence on the morphology of biomorphs.

INTRODUCTION

Earth dates back to approximately 4,600 million years. Its chemical composition has been modified, giving rise to the atmosphere and to life as we know it. Different publications have described that minerals and rocks are the keys to understanding how life originated because it is inferred that life did not arise in an isolated manner but from the different chemical niches provided by minerals.[1] Other minerals that may have been formed, when the gases of the first stars became cold, are those formed by chemical elements such as silicon, oxygen, sodium, iron, potassium, titanium, magnesium, and nitrogen.[2] Thus, it is considered that life arose from minerals and clays based on the following characteristics: (i) they protect against UV radiation; (ii) they concentrate molecules, which are diluted in the ocean or in the atmosphere; (iii) they organize molecules (this issue is related to the homochirality); (iv) they catalyze polymerization of organic molecules; (v) they conserve and replicate structural defects, ionic substitutions, dislocations; and (vi) they act as genetic candidates.[3] Some of the minerals in which the formation and replication of biomolecules have been shown are montmorillonite and kaolinite.[3]

In the chemical origin of life, together with minerals, which are posited to be the basis for the generation of the first molecules, abiotic factors present in that era gave rise to the phenomenon called life. Abiotic factors are classified as physical and chemical and are considered preponderant in the chemical origin of life

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because, although they do not harbor life, without them, the development and survival of biotic factors would have been impossible. The physical abiotic factors are sunlight, temperature, atmospheric pressure, and climate. On the other hand, chemical factors include pH and the amount and type of chemical elements present in the soil, water, and air. In order to explain and understand the chemical origin of life, theories have been postulated for decades. Some of these theories have even become evidence with time, contributing therefore to this chemical origin. Several research groups have developed study models to elucidate the possible first forms of life. In this sense, calcium, strontium, or barium silica carbonates have been synthesized in vitro. They have been called biomorphs (this name was coined by García-Ruiz and Amorós, 1981) because they emulate morphologies of organisms like radiolarians, diatoms, leaves, flowers, worms, stems, shells, bones, among others.[4] Although biomorphs have been synthesized in vitro under different conditions, it is necessary to analyze how they influence the different abiotic factors in the adopted morphology. From these silica carbonate biomorphs, it is very common to see that the alkaline Earth metals like Ca, Ba, and Sr are the most widely studied. Particularly, calcium carbonate deserves special attention as it presents polymorphism with three anhydrous crystalline phases: calcite, aragonite, and vaterite. There are also two well-defined hydrated crystalline phases, monohydrocalcite ($CaCO_3 \cdot H_2O$) and ikaite ($CaCO_3 \cdot 6H_2O$). It is worth mentioning that amorphous calcium carbonate also exists.[5,6]

Aimed at a better understanding of the influence of abiotic factors in the formation of different chemical structures, the importance of the different types of physical and chemical abiotic factors in the origin of life is reviewed herein, as well as their influence on the morphology of biomorphs. On one side, the latter will help to understand the relation that existed between the physical and chemical factors in the first structures that originated the first cells in the primitive era. On the other side, biomorphs allow us to generate a hypothesis on the relation between the morphologies obtained in vitro in diverse conditions of synthesis and the morphologies of some of the organisms as we know them nowadays. Calcium, barium, or strontium silica carbonate biomorphs are self-assembled crystalline materials that usually display a variety of biomimetic morphologies. These biomorphs show characteristic curvatures, which are far away from the restrictions of the classic crystallographic symmetry. Additionally, these shapes are reminiscent of living organisms (this assumption was first suggested by García-Ruiz and Amorós, 1981).[4]

■ PHYSICAL ABIOTIC FACTORS

Sunlight. Solar radiation has played a fundamental role in the chemical origin of life because, to give rise to the first biomolecule, the sun was the first source of energy on Earth. Before life started, in the Precambrian era, high-energy solar ultraviolet (UV) radiation was found directly in the environment because the ozone layer had not been formed yet; the latter coincided with the lack of oxygen in that time.[7] The question that arises then is How was it possible that, in the presence of high UV radiation, the first biomolecules were synthesized as a whole to give origin to the first organism? The first cell could not be originated under these conditions because this is the type of radiation that usually damages the cells by forming reactive oxygen species. One of the pioneers to suggest that UV radiation and atmospheric electrical discharges could have favored chemical reactions to generate the first molecules was Oparin.[8] He specifically proposed that in a primitive reducing atmosphere some amino acids were synthesized, which fell on Earth, condensed, and bound through heat to form the first proteins. Thereafter, Urey and Miller followed with the Oparin theory, but to prove experimentally that it was possible to obtain essential chemical blocks from a primitive atmosphere, they prepared a mixture that emulated the primitive era.[9,10] When they analyzed the compounds formed in the primitive mixture, they identified amino acids and organic chemical compounds, showing, for the first time, that the origin of the first cells must have risen from the conditions prevailing in the Precambrian era. Starting with those experiments and until this date, a considerable number of experiments have been performed revealing that UV radiation affects directly the chemistry of small molecules, through photolysis, photoionization, and photoexcitation, mechanisms that have been suggested to affect the prebiotic chemistry.[11] For example, it has been shown that the photolysis due to UV radiation of sulfhydric acid (H_2S) generates H atoms that provide sufficient activation energy to dissociate other compounds like methane (CH_4).[11] In another experiment, solutions of 5-substituted hydantoins were exposed to UV radiation, and it was found that the main products of photolysis were 2,4-imidazolidinedione, glycine, and alanine.[11] In this way, it has been shown that UV light is implicated in the synthesis of amino acids[12] and pyrimidine ribonucleotides.[13] Another piece of information showing that UV light played a preponderant role in the chemical origin of life is that O_2 is obtained from the CO_2 photodissociation, showing that the high energy of UV light was able to produce O_2 in the reducing atmosphere existing in the Precambrian era.[14] These results and evidence as a whole show how UV light played a preponderant role in the origin of the first molecules, which together with the existing minerals, like montmorillonite, allowed for the polymerization of the first biomolecules, giving rise to the first cell. The effect of UV light in the formation of biomorphs has been evaluated in a work that used pyruvic acid as the source of CO_3^{2-} ions.[15] This work found that UV light performed photolysis of pyruvic acid, and depending on the initial concentration of the pyruvic acid, one or another biomorph's morphology was favored (Figure 1). This information shows that the photolysis caused by UV light in the morphology of biomorphs depends on the concentration of the CO_3^{2-} ions present in the synthesis medium.

Notwithstanding, it is important to assess whether, in certain conditions, UV light induces one or another morphology, independently from the concentration of CO_3^{2-} ions present in the medium. Our research group is currently researching in this sense to elucidate if UV light induces under certain specific conditions one or another morphology in the biomorphs.

Temperature. Temperature is another abiotic factor that influences the possible development of life. It has been estimated that, in the early era of life, temperatures ranged between 0 and 70 °C. This fact agrees with reports by other research groups, indicating that the origin of life points to temperatures below 100 °C because at this temperature biomolecules decompose rapidly. Additionally, some authors indicate that the hyperthermophilic organisms that inhabit at temperatures below 110 °C, as well as those inhabiting Earth currently at other temperatures, do not indicate an origin of life at these temperatures.[16] It has also been inferred that the silica isotopes found in cherts have been formed at seawater temperatures between 60 and 80 °C.[17] Based on this evidence, it is necessary

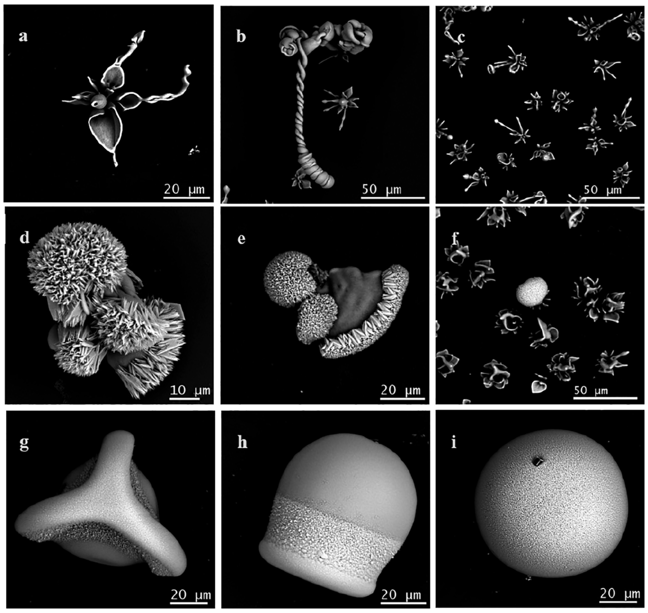

Figure 1. Barium silica carbonate biomorphs obtained during exposure to UV radiation for 24 h in the presence or absence of pyruvic acid: (a–c) without pyruvic acid; (d–f) morphologies obtained with pyruvic acid not in direct contact with the reaction solutions; (g–i) morphologies when the solutions are mixed with pyruvic acid. Reprinted with permission from ref 15 under an open access Creative Common CCBY license. Copyright 2019 MDPI.

to evaluate the different morphologies that the first cells could have been formed at different temperatures. It is also important to consider that glaciation events existed in the Precambrian era, in which the average temperature was −50 °C.[18] It is considered that during those glaciation events there was a reassignation of carbon among the different exchange reservoirs existing in that era. Aiming at understanding the different morphologies that could have been formed in the Precambrian era, our research group and others have synthesized biomorphs at different temperatures. There are reports on works that have synthesized biomorphs at high temperatures.[19] Morphologies of calcium carbonate biomorphs at high temperatures vary but, in general, correspond to typical structures; for example, biomorphs synthesized at 45 °C usually resemble flowers and twisted ribbons; those synthesized at 60 °C, however, normally resemble leaves and filamentous aggregates, and those synthesized at 70 °C resemble star-shaped aggregates (Figure 2).[19]

Interestingly, the morphologies obtained at low temperatures of 4, −20, and −70 °C for $CaCO_3$ biomorphs are druses at all temperatures. In contrast, the $BaCO_3$ and $SrCO_3$ biomorphs showed a different morphology depending on the temperature (Figure 3).[20]

These data show that the $CaCO_3$ silica biomorphs conserve their morphology at 25 °C, as well as at the three different low temperatures, probably because calcium carbonate is different compared with barium and strontium carbonates, as this is a polymorphic mineral composed of three anhydrous crystalline phases (calcite, vaterite, and aragonite) and two hydrated crystalline phases (monohydrocalcite and ikaite with six molecules of water) and amorphous calcium carbonate. This polymorphic difference conducts to a much more complex system of calcium carbonate, leading to a variety of chemical possibilities. However, from the physicochemical point of view, calcite is the most abundant and thermodynamically stable phase in ambient conditions, which is commonly observed in biological and geological calcium carbonate species.[5] The different morphologies of the biomorphs obtained in a temperature range from −70 to 70 °C allow one to consider the large variety of morphologies adopted by the first organisms in the Precambrian era.[20] Some of these morphologies were lost, others were modified, and only some were conserved along time and by the consequent modification of atmospheric conditions. These data allow inferring a correlation, but there are innumerable questions to be resolved about the origin of life, which will only be achieved with the joint effort of diverse groups and knowledge areas.

Atmospheric Pressure. For the chemical origin of life, the atmospheric pressure exerted on the different elements of an ecosystem is also considered a determining factor. However, to determine the atmospheric pressure that existed in the early era when the first biomolecules originated and, later on, the first cell, other factors must be considered, such as the chemical composition in that era. CO_2 concentration and its incorporation are considered evidence to infer the atmospheric pressure during the different eras of Earth.[21] Extrapolations have been made with other planets, like Venus, which has an atmospheric pressure of 90 bar with 96% CO_2, as compared to the current atmosphere of Earth with 0.03% CO_2, which corresponds to a 1 bar pressure of the current atmosphere. It has been suggested that, in time, the CO_2 of the atmosphere and the soil, when dissolved in water and infiltrating, carries the dissolved CO_2, which in turn becomes hydrated in the form of carbonic acid (H_2CO_3), which dissociated in a bicarbonate ion and a proton. This process allows for the dissolution of calcium carbonate of rocks. Through this set of reactions, the CO_2 present in the atmosphere and the soil in the early era of Earth diminished its concentration and, in this way, diminished the atmospheric pressure. This hypothesis is supported by biological, physical, and chemical arguments that propose that life originated in the depths of the Proto Ocean of the Hadean Earth and, thus, at a high pressure.[21] Experiments have been performed that show that life at determined high pressures is possible (Figure 4) because proteins, lipids, sugars, polysaccharides, and nucleic acids have been studied either isolated or in organisms at high pressures, revealing that, although they undergo changes in their structure, they do adapt to keep their function viable.[22]

Among the microorganisms living in the terrestrial subsoil or in the bottom of oceans are the extreme barophiles that live at 10,898 m, at hydrostatic pressures of 70–80 MPa of depth. These data show, as a whole, that the origin of life was possible in the early era of Earth, in which, despite the high concentration of CO_2 and, thus, a high atmospheric pressure, the first cell could have been originated. For the biomorphs, the influence of atmospheric pressure on their morphology has not been reported; our research group is working in this direction.

Electric Field. Earth's surface, the ionosphere, and atmosphere are called the global atmospheric electrical circuit. Hence, Earth is the universal conductor to which all the free electricity of other bodies tends to return. Since 1846, Karl Friedrich and Ebenezer West defined electricity as the force affecting our senses and which influences all bodies. According to its source, it is called friction electricity, contact electricity, thermoelectricity, and magnetoelectricity.[23] In this way, electric fields have been on Earth since its creation, which indicates that the electrical current in the Precambrian era was also implicated in the origin of life. The influence of the electrical current in the

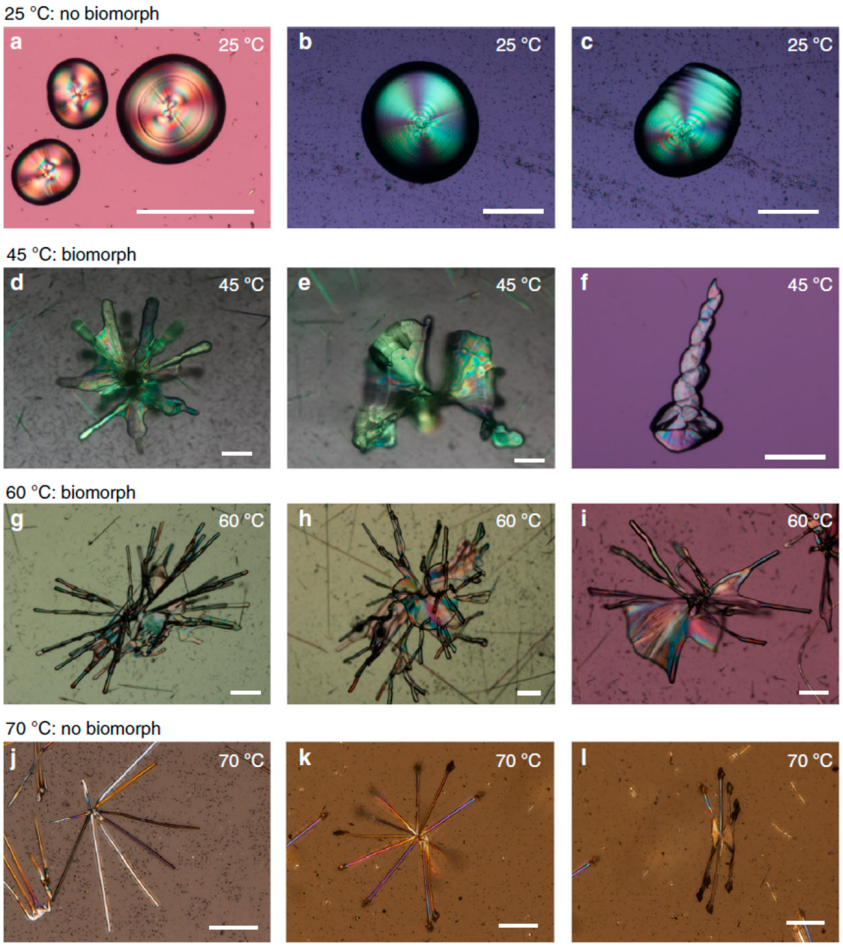

Figure 2. Monohydrocalcite silica biomorphs obtained at different temperatures. Optical micrographs of hemispherical (a,b) and caterpillar-like (c) aggregates at 25 °C; flower-like (d,e) and twisted ribbon-like (f) aggregates at 45 °C; curvilinear sheet and filamentary aggregates at 60 °C (g–i); star-like aggregates at 70 °C (j–l). Scale bar: 200 μm. Reprinted with permission from ref 19 under an open access Creative Common CCBY license. Copyright 2018 Springer Nature.

synthesis of the first molecule was evidenced by Urey and Miller, who synthesized amino acids and other organic substances from a mixture of gases, achieving this, among other factors, by the action of electrical discharges generated by electrodes.[10] Interestingly, in 1958, Miller performed other similar experiments in the presence of methane (CH_4), ammonium (NH_3), sulfhydric acid (H_2S), and carbon dioxide (CO_2), but the author did not analyze the samples, just labeled and kept them. Until after his death, one of his disciples analyzed them and found 23 amino acids and 4 amines, including 7 organosulfate compounds. These experiments showed, for the first time, the synthesis of sulfured amino acids, in which the electrical discharges played a preponderant role in the abiotic synthesis of these organic compounds.[23] Moreoever, the abundance of the synthesized amino acids in the presence of H_2S is similar to that found in some meteorites.[23] Our research team emulated the formation of structures, similar to those that could have existed in the Precambrian era (biomorphs), in the presence of a biological macromolecule (RNA) and an electrical current source using biomorph synthesis as model. We synthesized biomorphs into an electrochemical growth cell (electrolysis cell); for this, we used an indium tin oxide glass plate as the working electrode and platinum wire as the counter electrode introduced into the solution for the synthesis of biomorphs. The polarity of the electrodes (cathode or anode) was selected from the potentiostat/galvanostat to fix the positive or negative electrode always having the surface of the ITO electrode. The biomorphs were synthesized on the surface of the ITO electrode.[24] The biomorphs obtained under positive electrical current corresponded to $BaCO_3$ (I) aragonite type and $BaCO_3$ (II) calcite type, whereas under negative current, graphite carbon and $BaCO_3$ (I) aragonite type were obtained. Being able to reduce CO_2 to a carbon by the action of RNA and negative electrical current is relevant, as it is the first report in which this reduction is obtained. To our understanding, this is the first evidence showing that the electrical current is fundamental in the rearrangement of atoms, a fact that suggests that organic compounds (formed by carbon) have coexisted with inorganic compounds since the primitive era.[24]

■ CHEMICAL ABIOTIC FACTORS

pH. The pH is fundamental in organisms because the adequate performance of biomolecules is maintained by regulating systems that help to keep a constant pH inside the cell. Minimal variation in the internal pH upsets the functioning of a living system. The pH has changed along time due to the variation in CO_2 concentration existing in the different eras of Earth; in this way, the pH of oceans has gone from 6.6 (+0.6−0.4) to 7.0 (+0.7−0.5) and up to 8.2 in the current times. These data suggest that the pH of primitive Earth was another

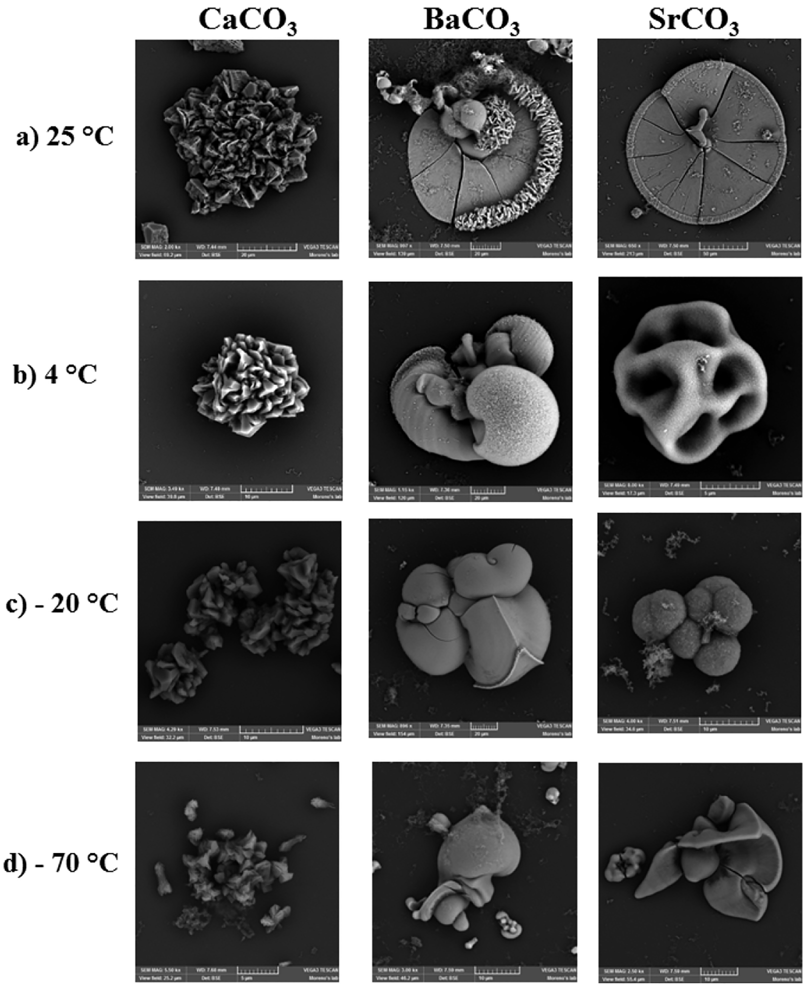

Figure 3. $CaCO_3$, $BaCO_3$, and $SrCO_3$ biomorphs obtained at different temperatures. Control: (a) 25 °C. Low: (b) 4 °C, (c) −20 °C, and (d) −70 °C. Adapted in part from ref 20. Copyright 2020 American Chemical Society.

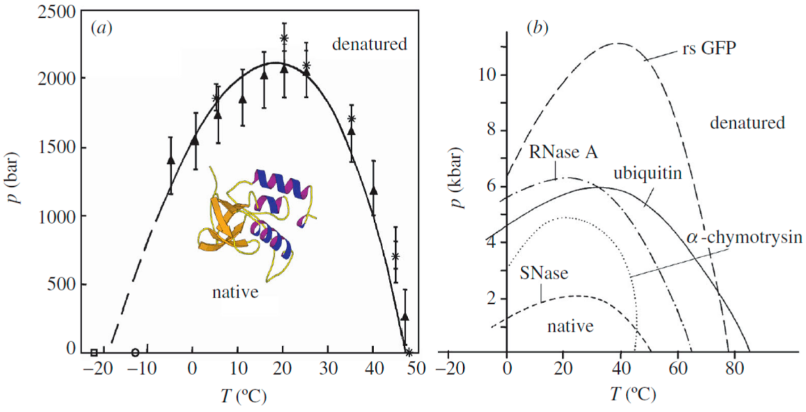

Figure 4. Pressure (p)−temperature (T) stability diagram of (a) SNase at pH obtained by *SAXS, ▲FT-IR, and ○,□ differential scanning calorimetry measurements and (b) of several other monomeric proteins. Reprinted with permission from ref 22. Copyright 2005 The Royal Society of Chemistry.

important factor in the origin of the first cell. To elucidate how the pH influenced the formation of the first organisms, samples of microfossils (a microfossil is the carbonate shell of organisms that converts them into fossils and has been kept until the current times) have been collected, and the conditions were emulated under which these different shells were formed, including the pH. This has led to infer the prevailing conditions in that era. For biomorphs, the role of the pH in their morphology has been widely studied in an interval of 9.0 to 12.8.[25] The morphologies obtained in this pH range are wide, and many different types have been observed, for example, globular aggregates, leaves, discoid leaves, worms, double helices, stars, curved rods, striped structures, among others.[25] At a pH range of 9.0 to 11.5, at different concentrations of barium ions, biomorphs with fractal growth and curvilinear growth can be obtained (Figure 5).[25] The pH determines the

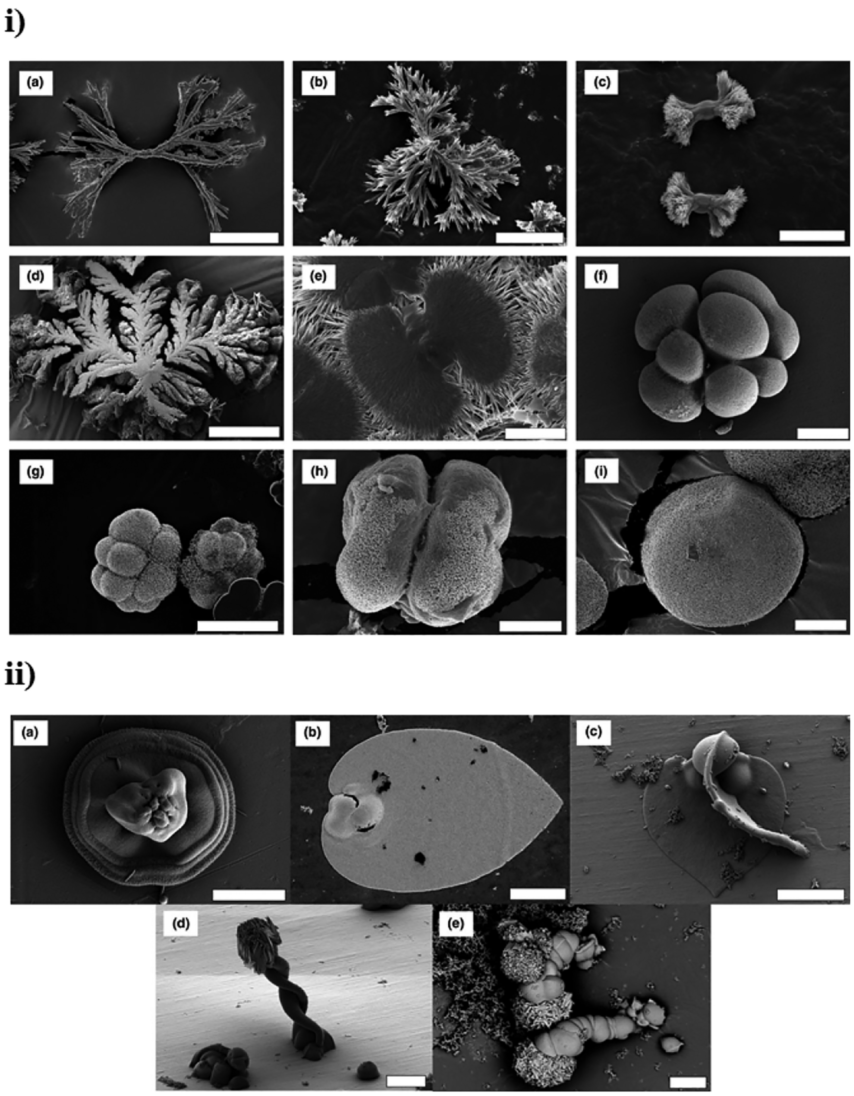

Figure 5. Morphologies of barium silica carbonate biomorphs obtained. (i) (a−c) Dendrites; (d) fern-like biomorph; (e−h) Framboidal-type biomorphs; (i) spheroidal biomorph. (ii) (a) Discoidal sheet; (b,c) leaf-like biomorphs; (d) helical braid; (e) wormlike braids. Reprinted with permission from ref 25 under an Creative Commons License Deed-Attribution 4.0 International (CC BY 4.0). Copyright 2018 John Wiley & Sons Ltd.

morphology that biomorphs acquire; complete studies have been performed in which it is known what type of growth will be favored at different pH and the same concentration of the barium ion.[26]

Another study revealed that, when increasing the pH, fibrillation is favored. This mechanism promotes the increase in carbonate ions and, hence, of barium carbonate, which leads to a monocrystalline growth, generating a polycrystalline front of nanocrystals co-oriented with the single crystal.[26] Another study revealed that the pH changes in the local microenvironment of the biomorph, which, in the structure of the biomorph, is found like intrinsic bands with the same periodicity. It has been found that the biomorph morphologies favored at a pH between 8.5 and 9.5 correspond to fractal globular dendritic spiculated structures and/or branched structures,[27] whereas at a pH from 10.46 to 10.80, globular aggregates are observed. From a pH of 10.85 to 11.42, structures emulating a worm are found. Structures like helices, double helices, and worms have been found at a pH from 11.11 to 11.51.[27]

Synthesis of the different morphologies of biomorphs at different pH is finely a regulated process because one pH unit can change the morphology completely. For example, it has been found that at different values of pH and time, during the precipitation of witherite biomorphs, the synthesis is most efficient at lower pH, regardless of time (Figure 6).[27]

This process of favoring one or another morphology of biomorphs could be reminiscent of those organisms formed at early eras of Earth.[28] In addition to the diverse morphologies of biomorphs showing how to obtain a unique structure in shape and characteristics, the synthesis is directed by the different abiotic factors, like the pH. Another important information is that biomorphs, although being inorganic compounds, show how their synthesis is finely regulated by the pH, a characteristic that is shared with unicellular and pluricellular organisms. For example, the physiological processes occurring in our organisms, such as the adequate performance of enzymes and, in general, cellular metabolism are influenced by the pH of our internal medium because, if there is even a minimal variation of the pH, our organisms can undergo severe consequences that can even lead to death. As a whole, it can be concluded that all that exists on Earth is regulated by the pH.[27]

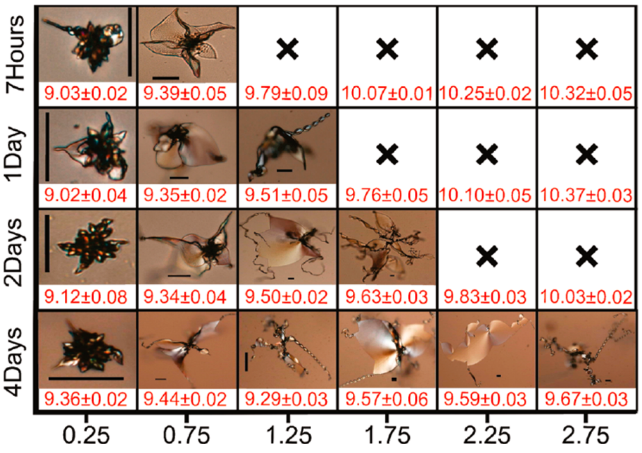

Figure 6. Barium carbonate biomorphs: Spatial and temporal morphogram made with photographs of representative aggregates. Black bar is 50 μm long. Beneath each photograph, it is indicated the correlated value of the pH. Black crosses indicate the absence of aggregates. Reprinted from ref 27. Copyright 2009 American Chemical Society.

Chemical Elements. Understanding the chemical origin of life entails asking how the chemical elements were chosen in the Precambrian era that would give rise to the first cell, or rather were the chemical elements present in that era the ones that formed part of the first cell. These and other intriguing questions on the chemical composition existing in the Precambrian have been attempted to respond for decades because there are scarce fossil recordings and the rocks formed in that era must have change along millions of transformation years. According to reports, the first chemical elements that must have existed on Earth are those generated during stellar nucleosynthesis, called the Big Bang nucleosynthesis that gave origin to the universe, where the generation of hydrogen and helium are proposed in the form of isotopes, mainly, and as lithium and beryllium traces. It is estimated that for millions of years after the Great Explosion, no new nuclei were created until hydrogen started to be depleted in the center of the star; the nuclear fusion ceased, and expansion was inhibited, which led to an increase in temperature, heating the external layers and expanding them, a phenomenon known as the Red Giant. Fusion of hydrogen produces more helium, and once the helium nuclei have enough kinetic energy to overcome the electrostatic repulsion among them, they fuse to form a single carbon (^{12}C). Specifically, it has been reported that a proton is adsorbed from the ^{12}C, emitting energy in the form of γ radiation. This process is repeated, and at the end, four nuclei of ^{1}H are consumed, and one ^{4}He is generated. From this nuclear synthesis, the ^{13}C, ^{14}N, ^{15}N, and ^{17}C nuclei were formed in the universe, which is considered the origin of isotopes. In these conditions, ^{16}O nuclei could have also been produced when fusing a ^{12}C with another of ^{4}H. From this on, ^{20}Ne, ^{24} Mg, ^{28}S, ^{32}S, and other elements until ^{56}Fe are generated.[9,14] Afterward, the planet cooled, and the hydrogen and helium bound to heavier elements, but it is considered that a large part of the helium was lost because it is poorly reactive with other compounds. However, hydrogen formed compounds with methane (CH_4), ammonia (NH_3), sulfhydric acid (H_2S), and water (H_2O). Moreoever, in the recently formed Earth, there were important CO_2 concentrations. However, many authors are sure that there was no free oxygen (O_2) nor was there ozone in the Precambrian era, thus it is considered that the solar UV rays by reaching Earth's surface directly favored, on one side, the photodissociation of CO_2 and, on the other side, the formation of primitive chemical compounds.[14] This hypothesis has been confirmed with time and apparently seems to have been confirmed by experiments that show that amino acids, nucleotides, and peptides have been synthesized from elemental chemical compounds.[9,10,12,13] Although many experiments have been performed to elucidate the chemical compounds that existed in the Precambrian era, which gave origin to the cell, there are still unresolved questions: Was the first cell formed by the chemical elements that currently form the cells of organisms? Were other chemical elements eliminated or incorporated with the passing of time? Now it is known that all cells are formed by H, C, N, O, and S, besides other essential elements like K, Mg, Na, Ca, Fe, Mn, Co, Zn, Mo, Se, and Cl. Additionally, some organisms require other chemical elements, like Sr, Ba, B, Si, As, Br, I, V, Cr, Ni, Cu, Cd, and/or W. These data, as a whole, indicate that the diverse organisms that currently inhabit Earth's surface, although sharing most of the chemical elements, at some point, certain organisms required one or another additional element, or it could also be possible that some discarded some chemical elements from the composition. Aiming at starting to elucidate whether the use of certain chemical elements by the organisms is due to an element dominating over another, our research team performed different mixtures of biomorph synthesis and evaluated which was the predominating chemical element. Mixtures were formed by Ca^{2+}, Ba^{2+}, and Sr^{2+} in the presence of nucleic acids, RNA, and genomic DNA (gDNA).[29] We found that the chemical element that dominated the different biomorph structures in the presence of nucleic acids was calcium, followed by strontium. The result allows one to infer that these chemical elements have been part of the different organisms, possibly since the origin of the first cell in the Precambrian era. Notwithstanding, these results are the start of a large number of experiments that still have to be performed, in which we are currently working on.

■ EFFECTS OF BIOMOLECULES ON BIOMORPHS: MORPHOLOGY AND CHEMICAL COMPOSITION BEFORE AND AFTER RNA

Once it was determined that the structure of biomorphs is regulated by the different abiotic factors, we asked ourselves whether the structure could be modified by biomolecules like nucleic acids or proteins. Being able to know whether structures are conserved or modified in the presence of biomolecules is of special relevance, as it would help to support or refute the hypothesis that the first primitive cell could have existed in the Precambrian era with a determined morphology and chemical composition. However, after molecules became polymerized and the RNA was obtained, later on, other biomolecules appeared originating the cells as we know them nowadays.[29] We consider that indeed a cell existed before the synthesis of biomolecules. This is proposed in the theory of Wächtershäuser, who posited the existence of a pioneering organism that would be formed by an inorganic substructure and an organic superstructure. This pioneer organism would be formed in the inorganic substructure by iron, cobalt, nickel cores, and other transition metals with sulfide, carbonyl, cyano, and other ligands that promote the organic superstructure through carbon fixation, triggered by the reduction potential of volcanic exhalations (Figure 7).[30] From this primary cell on arises a secondary evolution process by the genetic machinery. In this way, the pioneering organism hypothesis of Wächtershäuser is

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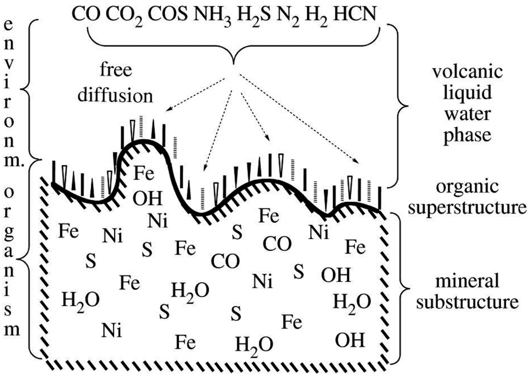

Figure 7. Cross-sectional representation of the minimal organization of the pioneer organism. Reprinted with permission from ref 30. Copyright 2006 The Royal Society of Chemistry.

presented as a precursor of the hypothesis from RNA. Based on this theory, other authors indicate that from a precell diverged the Bacteria, Archaea, and Eukarya domains.[30]

In the theory proposed by Wächtershäuser, it is proposed that the origin of the pioneering organisms could have been favored in hydrothermal conditions, as those found in the natural vents of volcanic gases in the bottom of oceans. This leads to the evidence of the first living organisms that have been found in the sedimentary plates of marine origin.[30] The first primitive cells were originated millions of years ago, in the Precambrian era, probably with a lower degree of evolution than that of current cells, which evolved until reaching the degree of development and complexity of organisms that inhabit the Earth as we now know it. What we need to do now is to explain the mechanism by which the pioneering cell evolved to form the cell as known nowadays. Aiming at resolving whether nucleic acids modify the morphology of inorganic structures, taking as basis the biomorphs, we synthesized biomorphs in the presence of genomic DNA, plasmidic DNA, or RNA.[29] Interestingly, we found that biomorphs, in the presence of nucleic acids, present a unique and specific morphology, in contrast to control samples in which different morphologies are observed (Figure 8).[29]

Moreoever, it was found that biomorphs synthesized at 37 °C in the presence of $CaCO_3$ and DNA or RNA correspond to vaterite and aragonite biomorphs, in contrast to the biomorphs obtained without nucleic acids, in which the crystalline structure is calcite. However, at 50 °C, the opposite occurs. This is interesting because it could explain why calcite and aragonite polymorphisms are the most abundant crystalline structures in organisms like corals, shells of different marine, and Earth animals to less abundant in humans, where carbonates are only in inner ear (otoliths) and in some calcifications. The characteristic that a unique morphology of biomorphs is synthesized only in the presence of nucleic acids is relevant. Additionally, other biological macromolecules, like proteins, could be used to obtain different morphologies of biomorphs in the same mixture.[29]

As a whole, these are relevant results because they are the first evidence indicating that pioneer cells evolved from the moment that nucleic acids were synthesized, and that the morphology adopted by secondary cells has been conserved along time, reproducing always the same morphology. This is an essential attribute of living organisms because the capacity to self-replicate accurately and to self-assemble is a property that has no similarity to any inanimate object. In this way, starting with the synthesis of nucleic acids in the Precambrian era, it was possible that inanimate molecules constituting organisms remained organized and were able to maintain and perpetuate life.

■ CONCLUSIONS AND FUTURE PERSPECTIVES

Some minerals and abiotic factors have played a relevant role in evolving diverse structures and morphologies of many organisms. These are indispensable to originate, maintain, and perpetuate life. In the origin of life, there are some physical and chemical properties of these abiotic factors that participate together with the existing minerals in the synthesis, polymerization, and assembly of complex biomolecules. This synergistic

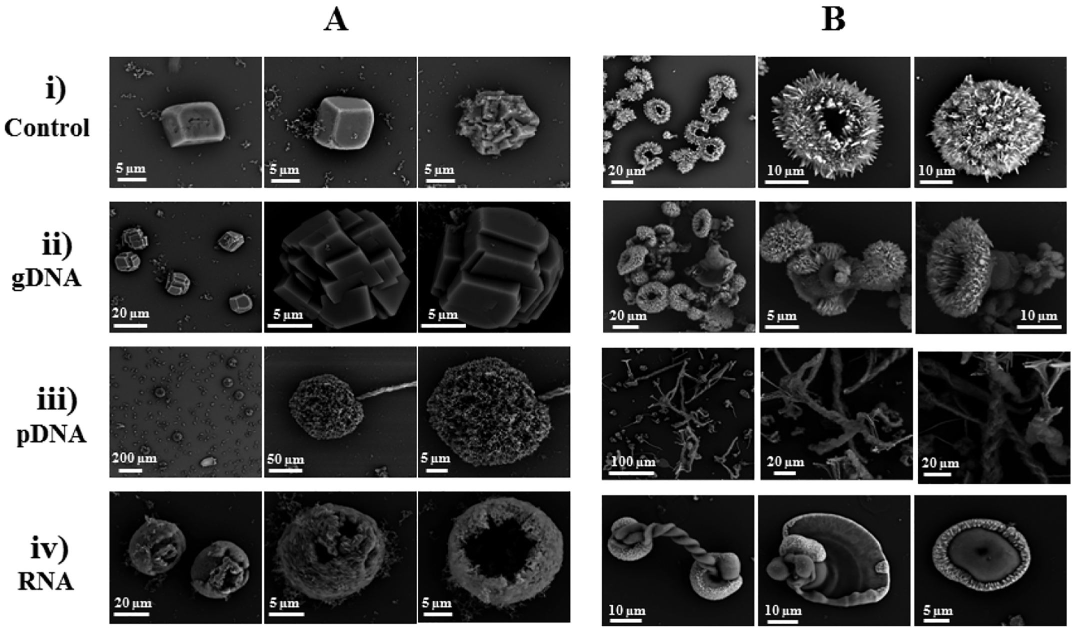

Figure 8. Influence of nucleic acids on the formation of silica biomorphs of (A) $CaCO_3$ or (B) $BaCO_3$. Adapted in part from ref 29. Copyright 2019 American Chemical Society.

process gave origin to the biological membranes to form the first cells and then complex systems. From this first cell, pluricellular organisms were formed; some of which have been conserved, whereas others have been extinguished. Biomorphs are structures that are reminiscent of the shape that perhaps is the hallmark of ancient organisms formed in the Precambrian era that are still present nowadays. Undoubtedly, this is barely the start of a long journey to elucidate the chemical origin of life. This is a multifactorial process that has evolved for a long time; we cannot go back in time to take samples or to see in situ the original processes. However, based on chemical and physical approaches nowadays, some geochemical processes that happened millions of years ago can be plausibly reproduced in the laboratory. The next step will be to understand not only the origin of life per se but also human origin and the evolution of the mind. These are the most challenging issues to deal with in the future.

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Notes

The author declares no competing financial interest.

Biography

Prof. Mayra Cuéllar-Cruz is a graduate in Chemistry from the Autonomous University of the State of Hidalgo. M.Sc. is in Sciences, specialized in Biochemistry by the CINVESTAV (the Center for Research and Advanced Studies of the National Polytechnic Institute). PhD with specialty in Molecular Biology was from the IPICyT (Potosi Institute of Scientific and Technological, México) since 2009. She is currently a faculty and Researcher at the University of Guanajuato, México. Currently, she is *Topic Editor* for the Crystals Journal of the MDPI (Switzerland) and scientific reviewer for various important indexed journals. Her scientific interests are mainly focused on the biomineralization, biophysics, biochemistry, molecular biology, and the chemical origin of life. Prof. Cuéllar-Cruz is an expert in the development of vaccines and in the identification of dual function and location of proteins and in the formation of nanocrystals of various species of *Candida*. She is a pioneer in the synthesis and identification of biomorphs (silicacarbonates of alkaline-earth metals) with nucleic acids. Prof. Cuéllar-Cruz is the founder and current President of the Mexican Society of Synchrotron Light, A.C. She is also member of the advisory board of the Latin America Asia Africa and Middle East Program (LAAAMP) of the IUCr−UNESCO−IUPAP.

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