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Synthesis of Crystalline Silica–Carbonate Biomorphs of Ba(II) under the Presence of RNA and Positively and Negatively Charged ITO Electrodes: Obtainment of Graphite via Bioreduction of CO_2 and Its Implications to the Chemical Origin of Life on Primitive Earth

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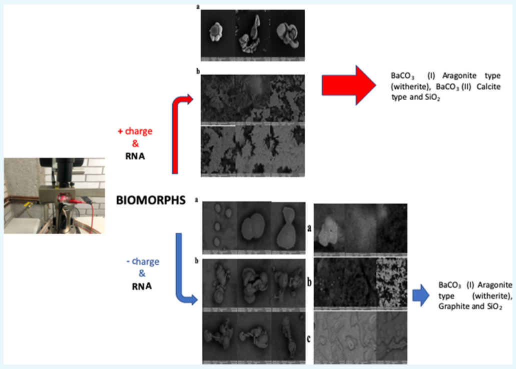
ABSTRACT: Since Earth was formed, in the Precambrian era up until our present days, electric current has participated in the morphology and chemical composition of organic and inorganic structures. Attempting to elucidate the mechanism by which electric current participated in the creation of the first cell in the Precambrian era is an intriguing and of a permanent subject of interest to be studied. One way of emulating the formation of structures similar to those that might have existed in the Precambrian era in the presence of a biomolecule and an electric current source is to use as a model, the silica–carbonate of alkaline earth metal compounds known as biomorphs. The objective of this work was to assess the influence exerted by an electric current (negatively or positively charged indium tin oxide electrodes) on the formation of biomorphs in the presence of RNA. The compounds obtained under both electric charges were visualized through scanning electron microscopy (SEM), and their chemical composition was analyzed through Raman spectroscopy. The biomorphs obtained under a positive electric current correspond to aragonite-type $BaCO_3$(I) and calcite-type $BaCO_3$(II). Whereas, under a negative current, carbon graphite and aragonite-type $BaCO_3$(I) were obtained. To the best of our knowledge, this is the first evidence showing that the presence of RNA and the electric current is fundamental in the rearrangement of atoms, suggesting that organic and inorganic compounds have coexisted since the primitive era.



1. INTRODUCTION

The Precambrian era is considered the first and longest geological era in the history of the Earth. This stage is critical in the genesis of the geological and natural history of the Earth because life and rocks were originated in this period.[1,2] The most important characteristics of this period are a reducing atmosphere, high temperatures, and constant thunderstorms with lots of electricity, revealing that since its formation, the Earth is under a constant exchange of electricity. The complex patterns followed by electric currents and magnetic fields surrounding the Earth respond to an adjustment of electric charges in our planet with respect to the potent electric field of the sun. Atmospheric electricity results from the ionization of the atmosphere by solar radiation and from the movement of ion clouds.[3] In this way, the Earth is electrically charged and acts as a huge spherical capacitor. The surface of the Earth is negatively charged,[4−7] whereas a positive charge of the same magnitude resides in the atmosphere, which gives origin to a flow of currents. It has been reported that the negative charge is carried over to the Earth during storms, and the descendent flow of positive current during good weather is counteracted by a returning flow of the positive current from zones of the Earth with storms.[5,7] These facts indicate that because the electric current exists since the Precambrian era, the electric charge is a part of the main components of the chemical reactions in the origin of life. This fact was considered by Miller (1953),[8] who, in his experiment synthesized amino acids emulating the conditions of the Precambrian era, also included an electric current generated by electrodes.[8,9] This is relevant because apparently life is associated to electric forces that direct all the processes inside the cell. Attempting to elucidate the mechanism by which the electric current participated in the formation of the first living cells in the Precambrian era is an exciting and intriguing subject that must be approached emulating, as best as possible, the conditions existing in the primitive era of the Earth.

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Table 1. Conditions of Biomorphs Synthesis in the Presence of an Electric Current[a]

number of conditions	combination/condition
1 (control without EC and RNA)	$Na_2SiO_3 + BaCl_2 + NaOH$, 37 °C
2 (control EC+)	$Na_2SiO_3 + BaCl_2 + NaOH + 2.0\ \mu A$ positive electric charge, 37 °C
3 (control with RNA and without EC)	$Na_2SiO_3 + BaCl_2 + RNA + NaOH$, 37 °C
4 (RNA and EC+)	$Na_2SiO_3 + BaCl_2 + RNA + NaOH + 2.0\ \mu A$ positive electric charge, 37 °C
5 (control EC−)	$Na_2SiO_3 + BaCl_2 + NaOH + 2.0\ \mu A$ negative electric charge, 37 °C
6 (RNA and EC−)	$Na_2SiO_3 + BaCl_2 + RNA + NaOH + 2.0\ \mu A$ negative electric charge, 37 °C

[a] EC: electric current. EC+: positive electric current. EC−: negative electric current.

This is the way by which our results will allow us to understand how the electric charge influences organisms nowadays. One way of emulating the formation of structures similar to those that could have existed in the Precambrian era in the presence of a biomolecule, such as RNA, and an electric current source is used as a model could be silica−carbonate of alkaline earth metals (Ba, Ca, and Sr) known as biomorphs. In the first place, they present morphologies that resemble fossil organisms that have been found in deep marine rocks, such as radiolarians, diatoms, foraminifera, and trilobites.[10] These organisms are considered to represent the past and present of our planet. In the second place, they are a good model of study to analyze the participation of the electric current, as they are silica−carbonate compounds whose chemical composition has been widely reported, as well as their crystalline structure in different conditions,[11−14] except under the influence of an electric current. Finally, in the third place, growing crystals of the polymorph in the presence of an electric current (dc/ac) is a novel method that can be used in any type of crystal growth. In this way, we attempt to understand how the electric current affects the formation of silica−carbonates both in the presence and in the absence of a biomolecule. The goal of the present contribution was to assess the influence exerted by an electric current (negative or positive charge) in the formation of crystalline silica−carbonate of Ba(II), in the presence of RNA, which is the first described biomolecule that was formed in the Precambrian era.[15,16] In this research, we have used RNA from *Candida* species (*Candida albicans*), which is a very ancient fungus that has colonized other kingdoms. The structures formed under both electric charges were visualized through scanning electron microscopy (SEM), and the chemical composition was analyzed through Raman spectroscopy. The synthesis of biomorphs obtained under positive electric current correspond to aragonite-type $BaCO_3$(I) and calcite-type $BaCO_3$(II), whereas under negative current, we obtained carbon graphite and aragonite-type $BaCO_3$(I). To the best of our knowledge, this is the first evidence that shows that the presence of RNA and electricity is fundamental in the rearrangement of atoms, suggesting that organic (formed by carbon) and inorganic compounds coexisted in the Precambrian era and could have some implications in the chemical origin of life on Earth.

2. EXPERIMENTAL SECTION

2.1. Fungal Strain Used. The strain *C. albicans* was used for RNA extraction. The yeast cells were cultured in a YPD medium (10 g/L yeast extract, 20 g/L peptone, and 20 g/L glucose) and incubated at 28 °C during 24 h.

2.2. RNA Extraction. The total RNA was extracted from *C. albicans* using the TRIzol (Invitrogen) method. To prepare each sample, 1.5 mL of the culture medium was centrifuged for 5 min at 5000*g*, and the supernatant was discarded; this was performed three or four times according to the size of the pellet. To homogenize the samples, cells were maintained, and the supernatant was discarded; then 0.75 mL of TRIzol was added per each 0.25 mL of the sample. Cellular lysis was performed through cell rupture with a vortex. Thereafter, the homogenized sample was incubated for 5 min at room temperature; this was done to attain a complete dissociation of the nucleus−protein complex. Once the complete dissociation had been achieved, 0.2 mL of chloroform was added per each 1 mL of TRIzol, and the assay tube was vigorously shaken for 15 s and then incubated for 2−3 min at room temperature. Thereafter, the sample was centrifuged at 12,000*g* for 15 min at 4 °C, and the aqueous phase was removed with a micropipette inclining the assay tube to 45°; the aqueous phase was placed into a new tube for RNA isolation; 0.5 mL of isopropanol was added, and the mixture was incubated at room temperature for 10 min; then, it was centrifuged at 12,000*g* for 10 min at 4 °C. To wash RNA, the supernatant was removed with a micropipette, leaving only the RNA pellet, and adding 1 mL of 75% ethanol (molecular biology grade) per each 1 mL of TRIzol; this was mixed softly and centrifuged at 7500*g* for 5 min at 4 °C. Then, the pellet was resuspended in 25 μL of water containing 1% diethyl pyrocarbonate (DEPC, Sigma-Aldrich, St. Louis, MO, USA). After obtaining the RNA, 1 μL of DNAseI (Invitrogen), 1.5 μL of DNAse buffer, and 2.5 μL of DEPC water were added to 10 μL of RNA. The concentration of total RNA was determined with a NanoDrop 2000/2000c spectrophotometer (Thermo Scientific) at 260 nm. The obtained RNA was used to form the biomorphs.

2.3. Biomorphs Formation. Biomorphs were synthesized in different mixtures and conditions (see Table 1). Biomorphs were synthesized through the gas diffusion method.[17] This synthesis was performed using an ad hoc growth cell made of indium tin oxide (ITO) (a glass-square electrode constituted by ITO) with an O-ring. It is important to remark that the ITO electrode is a semiconductor type n material pertaining to the group of transparent conductive oxides of 1 mm thickness; the size of the used ITO was of 10 mm height by 10 mm width. The conductive part of the ITO electrode with a plastic O-ring (this was fixed with vacuum grease) was the first part of the cell's design. Then the mixture (solution of synthesis) was poured inside the O-ring. Then, the solution was covered with an electrochemical fluid cell for atomic force microscopy (EC-AFM) containing a platinum wire electrode (working as counter electrode). This experimental set up was fixed using an electrochemical modulus of the atomic force microscope (AFM-Bruker NanoScope 8HR) with a temperature controller to keep the temperature constant along all the experiments. Finally, a constant electric current of 2 μA was applied using a galvanostat (VIMAR FC17, Mexico). The polarity of the ITO electrode with an O-ring was fixed changing the position of the alligators (clamps) creating a positively charged electrode (anode, red in color) or negatively charged electrode (cathode, black in color), as shown in Figure 1.

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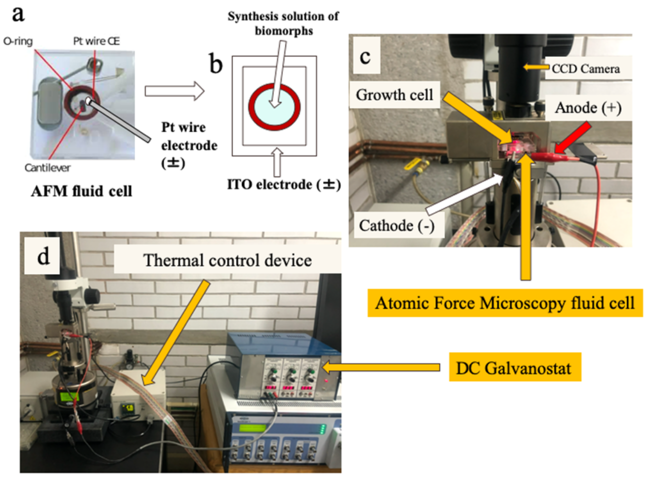

Figure 1. Experimental set up for the synthesis of biomorphs: (a) the fluid cell of the EC-AFM; (b) ITO electrode with an O-ring (containing the synthesis of biomorph solution); (c) connection of the electrodes (red color stands for the anode +) or negative (black color stands for the cathode −); (d) full overview of the experimental set-up.

The synthesis solution poured on the electrochemical cell contained 1000 ppm sodium metasilicate, barium chloride at a final concentration of 20 mM, and 0.1 ng RNA, at a pH 11.0 adjusted with sodium hydroxide. All reagents were from Sigma-Aldrich. Experiments were performed at 37 °C. Biomorph formation took place in 24 h; all experiments were repeated in triplicates.

2.4. Characterization of Biomorphs. The biomorphs synthesized in different conditions (Table 1) were observed through SEM with a VEGA3 model microscope (TESCAN, Brno, Czech Republic). Afterward, the biomorphs were characterized through Raman spectroscopy. This method was chosen because it has been reported as a powerful method to investigate polymorphs because of their crystalline structure.[18] In addition, in our another study, we determined the chemical composition and the crystalline phases through both Raman and X-ray diffraction, and the results were similar.[13,19] Raman measurements were made with a confocal Raman microscope WITec alpha300 R system at room temperature. The Raman laser excitation wavelength is 532 nm, and the spectral resolution of the spectrometer is 1.0 cm^{-1}. Raman spectra were recorded with a WITec alpha300 Series Raman atomic force microscope (WITec GmbH, Ulm, Germany) using a 672 lines/mm grating with a 100× Zeiss objective (0.9 NA). Nb:YVO_4 green laser with a wavelength of 532 nm was used as an excitation source with 14.4 mW of laser power. Punctual Raman spectra with 0.5 s of integration time and 10 accumulations and Raman map with 0.03 s of integration time.

3. RESULTS AND DISCUSSION

3.1. Biomorphs in the Presence of RNA and a Positive Electric Current influencing Their Crystal Structure. To assess the influence exerted by the electric current in silica−carbonate compounds, we used biomorphs as a model because they are silica−carbonate compounds whose chemical composition has been widely reported as well as their crystalline structure under different conditions,[13,14] except for the influence of an electric current. The obtained results will somehow emulate the electric current existing on Earth and will, therefore, allow us to know whether the electric current influences the morphology of inorganic and organic compounds, including living beings. To assess the participation of electric current, the experiments shown in Table 1 were performed. In these experiments we evaluated both a positive and a negative current on the formation of biomorphs. We also evaluated whether a biomolecule such as RNA, in the presence of an electric current, influences the morphology of the formed biomorph. The way in which the electric current, either positive or negative, interacts with the chemical elements present in the combination as well as in the synthesis of biomorphs is as follows: when an electric current passes through an atom, the theory of bands is followed, in which electrons of one atom valence are the ones located in the most external energetic levels allowing, therefore, the bonds between/within atoms in the compounds or between/within atoms of the same type in a molecule or a crystal (valence band). In turn, the conduction electrons are those that have been promoted to empty energy levels, giving rise to their greater mobility and eventually originating the electric currents (conduction bands). To evaluate what happens within an atom, we take silicon as one of the main components of silica (SiO_2). Silica is present in our synthesis mixture, as shown in Table 1. In this chemical element (Si), without electric current, when an electron of the valence band is transferred to the conduction band, a hole is created that acts as a carrier of positive charges because one electron is displaced leaving an empty space that is equivalent to having a positive hole, which is immediately occupied by the adjacent electron and the events proceed successively. However, in the presence of a constant electric current, the electric properties change. Hence, in the presence of a negative charge, the proportion of electrons will be higher than that of the holes, and the element will behave as a carrier of negative charges. Likewise, in the presence of a positive electric current, the element will be a carrier of positive charges (holes) with a lower proportion of negative charges.

Aimed at evaluating only the effect of an electric current on the formation of biomorphs, the first evaluated combination consisted of Ba^{2+}, without RNA, in the presence of a positive constant electric current of 2.0 μA (Table 1). Formation of biomorphs was performed on an ITO plate, as indicated under the Experimental Section. As a control of this combination, the biomorph was synthesized without electric current. Observation of the morphology of biomorphs formed without electric current revealed that they form a nonuniform sphere with slight protuberances (Figure 2a). Whereas biomorphs synthesized under a positive electric current present hat-like structures, similar to mushrooms (Figure 2b). Some of these hat-like structures present an apparently smooth structure, however, most of these structures show a rugose or fibrillose texture because of the presence of crystals (Figure 2b). In addition, the fibrillose structures are joined by braided threads (Figure 2b). These results show that the positive current does influence the morphology of the formed biomorphs (Figure 2), which agrees with that previously reported in this section. However, although a change was observed in the morphology of the biomorphs obtained under a positive current as compared to biomorphs obtained without electric current, it was necessary to identify their chemical composition and crystalline phase. These determinations were performed through Raman spectroscopy, as this technique allowed us to determine the polymorphs of crystalline compounds.[18]

The analysis of the biomorphs formed without electric current revealed bands at 96, 154, 225, 693, and 1060 cm^{-1} (Figure 3a). These vibrations correspond to $BaCO_3$(I) in its aragonite-type

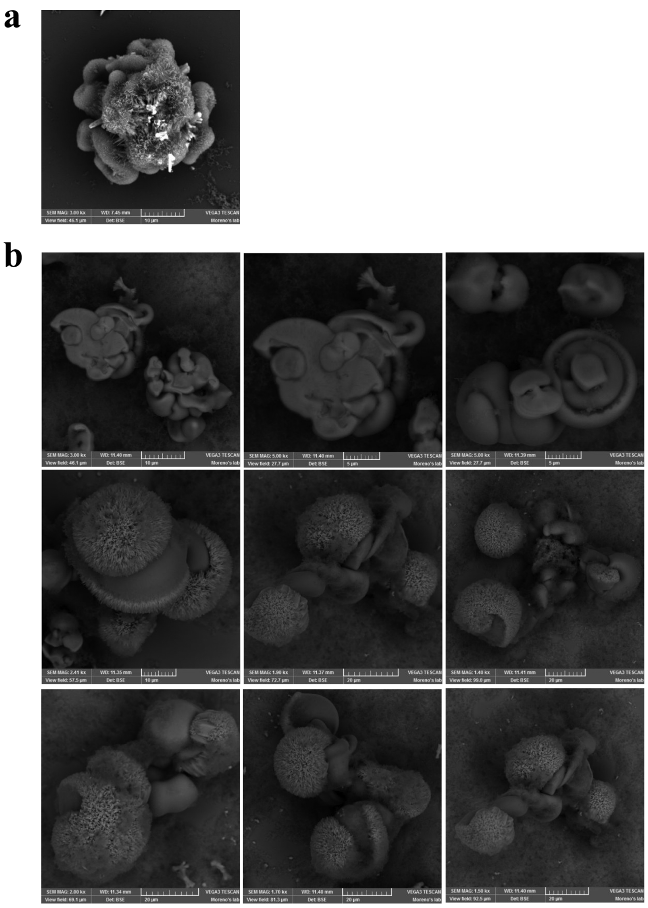

Figure 2. SEM microphotographs of biomorphs obtained (a) without electric current and (b) with positive electric current. All biomorphs were synthesized without RNA.

crystalline structure commonly named witherite that pertains to the orthorhombic space group.[20,21]

From the biomorphs formed under electric current, we chose several biomorphs formed under positive electric current to be analyzed through Raman, in which bands at 94, 139, 223–225, 694, 1060, and 1503 cm^{-1} were identified as shown in the analysis of a representative biomorph (Figure 3b). These data are interesting because they show that the positive electric current influences the morphology of biomorphs, but not their chemical composition nor the crystalline polymorphs obtained. The second evaluated combination was Ba^{2+}, RNA, and a positive constant current at 2.0 μA. Tables 2 and 3 show a summary of these experiments performed under the presence of positive electric charge in the absence and presence of RNA. The control of this combination was performed with the same components but without electric current.

These results show that the positive electric current influences the morphology adopted by the silica–carbonate compounds formed. In addition, the presence of RNA participates in the structural morphology of the synthesized biomorphs because the morphology is different in the presence (Figure 4) or absence (Figure 2) of RNA. Chemical identification as well as the crystalline structure of the silica–carbonates formed with RNA in the absence or presence of a positive electric current were analyzed through Raman. The bands found in the control sample (RNA, without positive electric current) correspond to the witherite polymorph (data not shown). For the compounds formed with RNA and a positive electric current, several

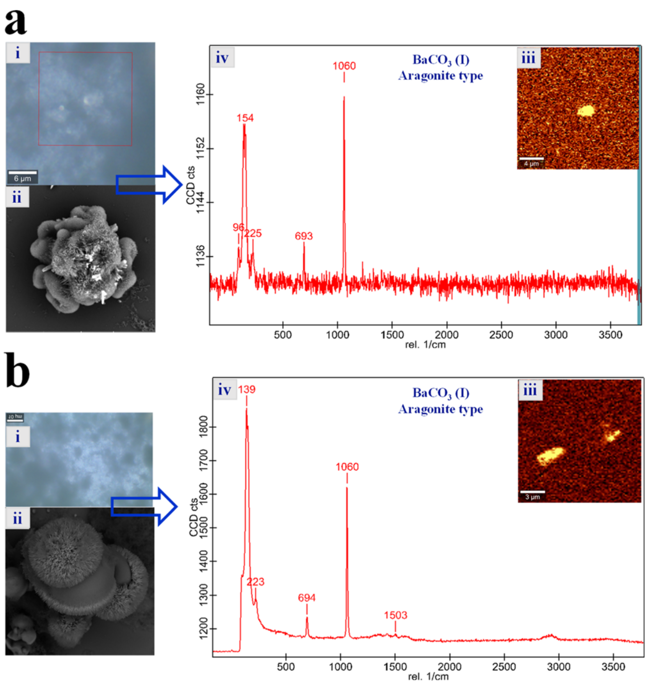

Figure 3. Raman spectra of biomorphs synthesized in combinations: (a) without electric current and (b) with positive electric current. All biomorphs were synthesized without RNA. (i) Optical image; (ii) SEM microphotograph; (iii) mapping of biomorphs; and (iv) Raman spectra of biomorphs.

biomorphs were analyzed and, interestingly, different chemical compositions were found as well as different $BaCO_3$ polymorphs (Figure 5). In the first group of silica–carbonate compounds analyzed, peaks at 99, 145, 229, 695, 1063, and 2670 cm^{-1} were found, which correspond to the aragonite-type polymorph of $BaCO_3$, commonly called witherite (Figure 5a). The second group of analyzed polymorphs showed peaks at 110, 191, 465, 625, 991, 1063, 2912, and 2971 cm^{-1}, which correspond to the calcite-type polymorph of $BaCO_3$ (Figure 5b). This result is really interesting and important because this type of polymorph is not commonly found, and it has only been identified when $BaCO_3$ (witherite) was transformed into the $BaCO_3$(II) $R\bar{3}m$ calcite type through high pressures and/or temperatures.[20,22,23] This result is relevant because producing the $BaCO_3$(II) $R\bar{3}m$ calcite type polymorph in a constant positive electric current would be equivalent to generate this crystalline polymorph at a high pressure and/or temperature. In addition, the use of a positive electric current could be an alternative technique for the growth of other polymorphs obtained under extreme conditions such as high pressures and temperatures. The presence of RNA and a positive electric current seemed to have a function equivalent to pressure and temperature, as can occur in an element, metal, or compound as a function of pressure and temperature, depicting different crystalline forms, which is a feature named allotropy or polymorphism.[24]

The third analyzed zone was that where bright needles were observed that when evaluated through Raman, revealed peaks at 11 and 491 cm^{-1}, which correspond to SiO_2 (Figure 5c). This formed material does not correspond to a biomorph, although a crystalline system, it does not have at all the inherent properties of the silica–carbonates of Ba compounds. As a whole, these data reveal that the presence of RNA with a positive electric current can lead to obtain different aragonite- or calcite-type

Table 2. Summary of Results When Applying a Positive Electric Current on the Synthesis of Biomorphs for the First Group

number of conditions	combination/condition	type of crystalline aggregate
1. synthesis of biomorphs without RNA and without positive electric charge applied	Na_2SiO_3 + $BaCl_2$ + NaOH, 37 °C	$BaCO_3$(I) aragonite type (witherite) (Figure 3a,b). These biomorphs show changes in morphology, but not in composition (Figures 2 and 3)
2. synthesis of biomorphs without RNA and with positive electric charge applied	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA positive electric charge, 37 °C	

Table 3. Summary of Results When Applying a Positive Electric Current on the Synthesis of Biomorphs for the Second and Third Groups

number of conditions	combination/condition	type of crystalline aggregate
3. synthesis of biomorphs with RNA and without positive electric charge applied	Na_2SiO_3 + $BaCl_2$ + NaOH + RNA, 37 °C	control with RNA and without positive electric current produces spherical biomorphs with rugose crystals (Figure 4a). The synthesis of biomorphs with RNA and positive electric current produced $BaCO_3$ witherite (Figure 5a)
4. synthesis of biomorphs with RNA and with positive electric charge applied	Na_2SiO_3 + $BaCl_2$ + NaOH + RNA + 2.0 μA positive electric charge, 37 °C	on the other hand, synthesis of biomorphs with RNA and positive electric current produced cluster-like crystalline structures intertwined in the form of plates (Figure 4b). These biomorphs were $BaCO_3$(II) calcite type (Figure 5b). The third group was SiO_2 (silica) (Figure 5c)

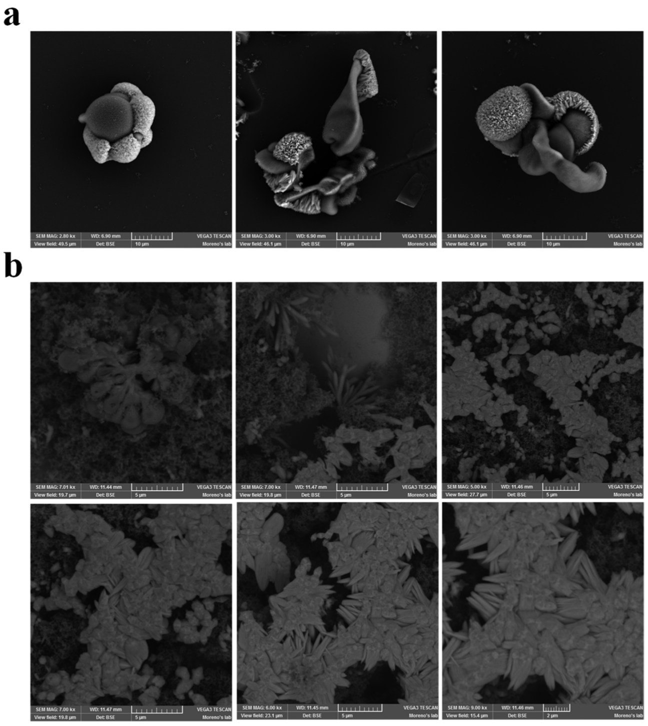

Figure 4. SEM microphotographs of biomorphs obtained in the following combinations: (a) without positive electric current and with RNA; and (b) with positive electric current and RNA.

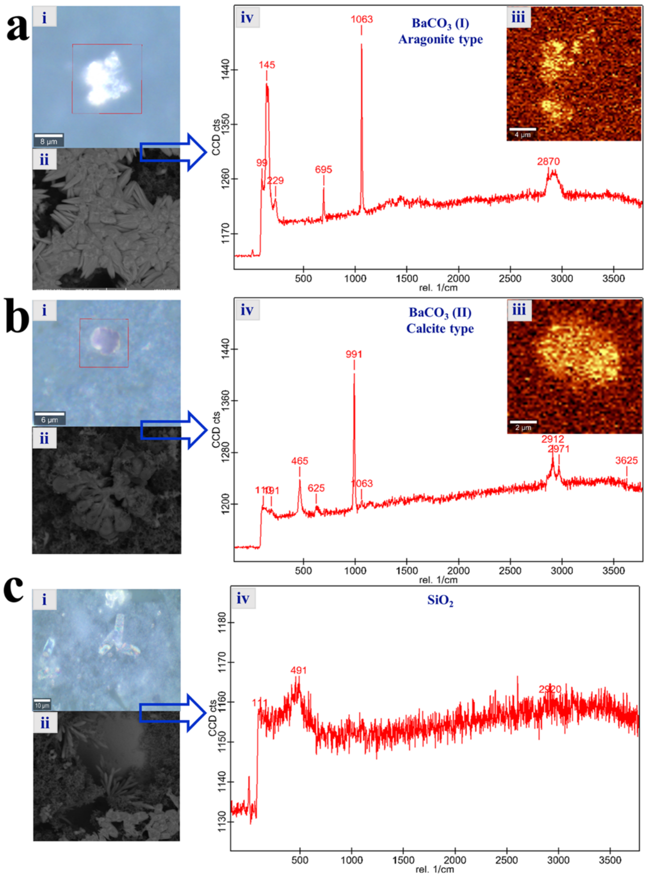

Figure 5. Raman spectra of biomorphs synthesized in combinations: (a) without positive electric current and with RNA and (b) with positive current and RNA. (i) Optical image; (ii) SEM microphotograph; (iii) mapping of biomorphs; and (iv) Raman spectra of biomorphs. (c) The third zone analyzed revealed peaks at 11 and 491 cm^{-1}, which correspond to SiO_2.

$BaCO_3$ polymorphs. In previous studies, it has been shown that biomolecules, being nucleic acids, are the ones that direct the structural form of biomorphs.[13] In this part of the research, we have shown that with RNA and a positive electric current, we can additionally modify the structural morphology of barium silica–carbonates and change their crystal structure. The synthesis of two types of polymorphs of witherite by the presence of a specific current and RNA obtaining also silica (SiO_2) is particularly interesting.

3.2. RNA under a Negative Electric Current Bioreduces the CO_2 to Graphite.

In addition to assessing the negative electric current in the synthesis of biomorphs, we analyzed the influence of this current in the production of silica–carbonate compounds. For this, the evaluated combination was constituted by Ba^{2+} and a constant negative current at 2.0 μA. The control of this combination was performed with the same components but in the absence of the electric current. The control sample was the same for both the positive and negative electric current as shown in Figure 2a. Biomorphs obtained under a negative current were visualized under SEM. Microphotographs showed biomorphs with different morphologies, such as semi-spheres divided by a septum (Figure 6a) that emulated dividing cells. The relevant and interesting aspect here is that we have found this type of morphology under a negative current (we must not forget that the Earth has a negative charge since the Precambrian era, and it was precisely in that era where

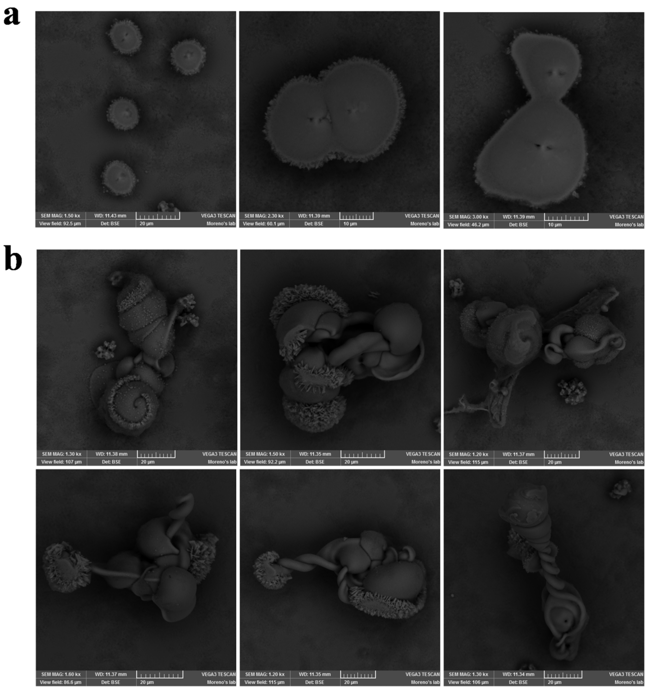

Figure 6. SEM microphotographs of biomorphs obtained under negative electric current with different morphologies (a,b). All biomorphs were synthesized without RNA.

the first cell was formed on Earth from the first biomolecules).[15] This report is totally concordant with our data. The generation of similar morphologies to cells (Figure 6a) suggests that possibly the morphology adopted by the first primitive cell since the Precambrian era was influenced by the negative electric current present on the Earth in that era. This cell morphology has been conserved until our present days. Other types of morphologies found were spherical structures with rugose covers and joined by spiral-shaped loops (which emulate the alpha helices in proteins) (Figure 6b). These data indicate that a negative electric current does influence the morphology adopted by silica−carbonates (Figure 6a,b). Besides the structural morphology found under the negative electric current (Figure 6) is different from the morphology observed under the positive electric current (Figure 2). Table 4 shows a summary of these experiments performed under the presence of negative electric charge in both absence and presence of RNA.

To identify the chemical composition and the crystalline phase of the obtained biomorphs, several of them were chosen to be analyzed through Raman spectroscopy. As shown in Figure 7, the spectra of the different chosen biomorphs showed bands at 97, 101−106, 138, 146, 155, 164, 225, 236−237, 673, 693−695, 1060−1064, 1361, and 2941 cm^{-1} (Figure 7). These peaks correspond to the aragonite-type $BaCO_3$ polymorph, indicating that the negative electric current influences the morphology of the produced biomorphs but not their chemical composition nor their crystal structure.

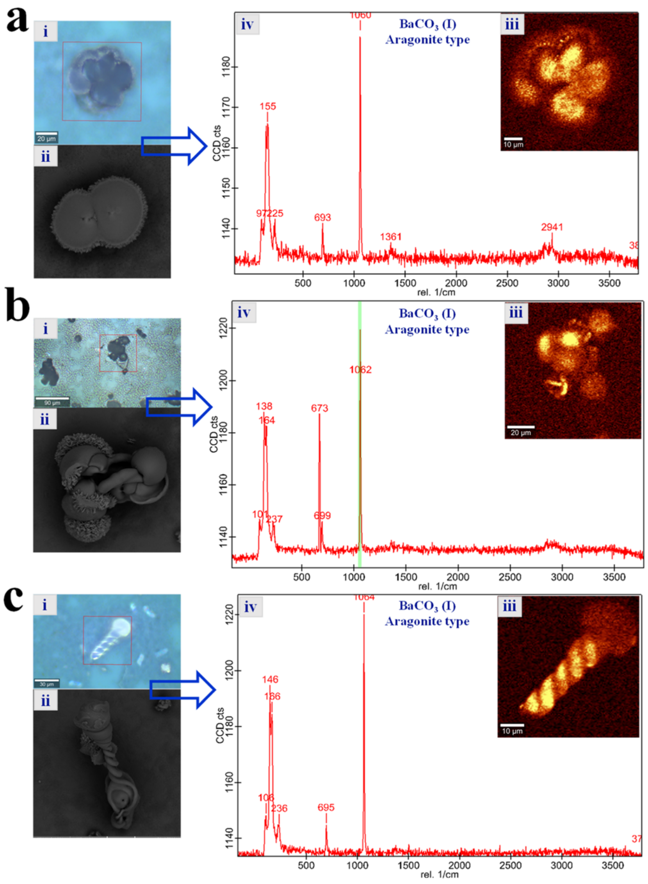

Figure 7. Raman spectra of biomorphs under negative electric current with different morphologies (a−c). All biomorphs were synthesized without RNA. (i) Optical image; (ii) SEM microphotograph; (iii) mapping of biomorphs; and (iv) Raman spectra of biomorphs.

The next combination that was assessed consisted of Ba^{2+}, RNA, and a constant negative electric current of 2.0 μA (Table 1). Interestingly, these samples, observed under SEM, did not reveal typical structures of biomorphs, as in the previous combinations. This combination revealed leaf-type and layer-type structures (Figure 8a), clusters of brilliant dots or cubes that emulate small squares (Figure 8b) and laminae in which circles and lines with apparent crystals were observed (Figure 8c).

These structures formed in these conditions are completely different from those found in the previously analyzed combinations, which is an intriguing finding. To know their chemical composition and the crystalline phase of the formed compounds, they were analyzed through Raman (Figure 9). The compounds that emulate layers showed peaks at 122, 1362, and 1566 cm^{-1} (Figure 9a). These bands correspond to graphite.[25−27]

Table 4. Summary of Results When Applying a Negative Electric Current and RNA on the Synthesis of Biomorphs

number of conditions	combination/condition	type of crystalline aggregate
5. synthesis of biomorphs without RNA and with negative electric charge applied	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA negative electric charge, 37 °C	$BaCO_3$(I) aragonite type (witherite). See Figure 6a,b, these show changes in morphology, but not in composition demonstrated by Raman spectroscopy (Figure 7)
6. synthesis of biomorphs with RNA and with negative electric charge (first group)	Na_2SiO_3 + $BaCl_2$ + NaOH + RNA + 2.0 μA negative electric charge, 37 °C	these biomorphs leaf-like structures (Figure 8a), brilliant dots (Figure 8b) and laminae and lines (Figure 8c). All of them were characterized as graphite

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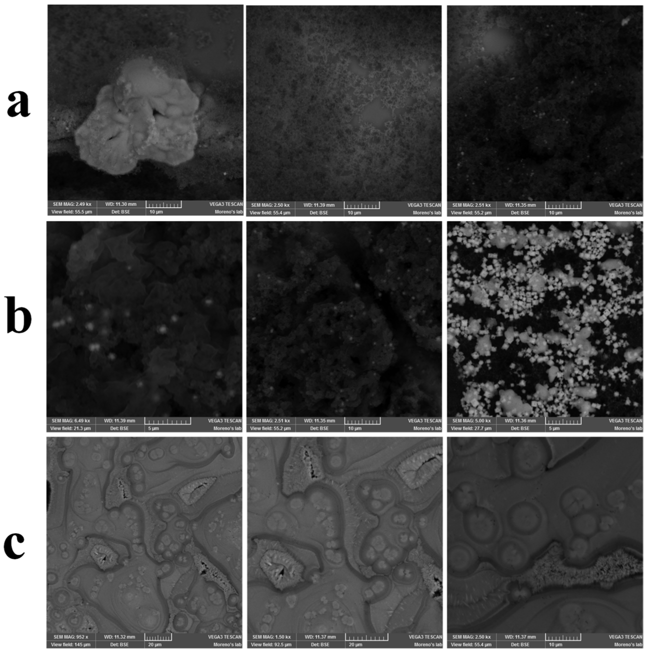

Figure 8. SEM microphotographs of biomorphs obtained under negative electric current with RNA with different morphologies (a−c).

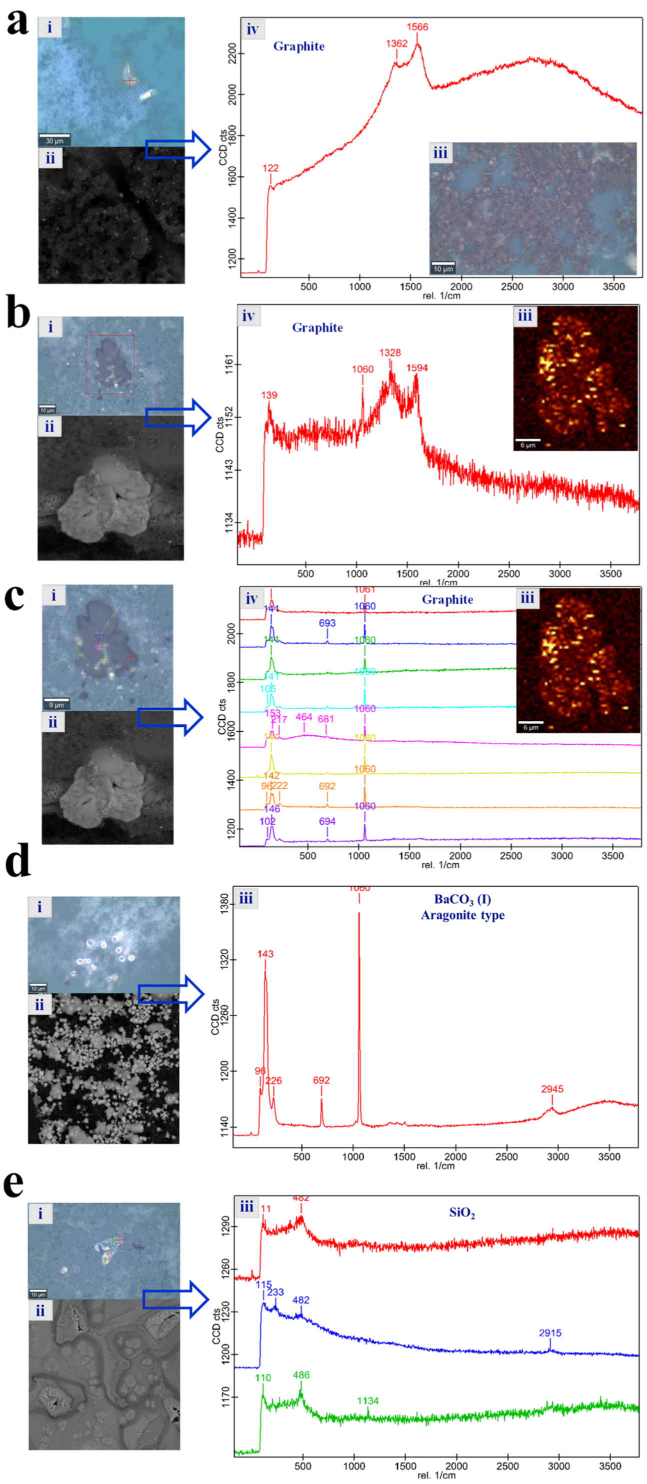

Figure 9. Raman spectra of biomorphs synthesized under negative electric current with RNA with different morphologies (a−e). (i) Optical image; (ii) SEM microphotograph; (iii) mapping of biomorphs; and (iv) Raman spectra of biomorphs.

This result is very interesting and surprising because graphite was the mainly obtained polymorph as opposed to the previous combinations, where only the $BaCO_3$ polymorph was mainly obtained. For the leaf-shaped structures (Figure 8a), their chemical composition and crystalline phase were also analyzed through Raman. The Raman analysis in both the global and punctual spectra identified peaks at 139, 1060, 1328, and 1594 cm^{-1} (Figure 8b,c), which correspond to graphite. These results were confirmed by analyzing several biomorphs; besides, Raman spectroscopy is a powerful technique for the identification and characterization of all carbon members.[27−29] For example, through the Raman spectrum it is possible to distinguish within graphite and without ambiguity, monolayer graphene, bilayer graphene, graphene with few layers and amorphous graphene.[30] Based on reports and comparing with our results in the analyzed conditions, it is clear that the identified structures are formed by carbon, specifically graphite (Figure 9a−c). The identification of structures with different morphologies but with the same chemical composition and the same crystalline phase in the presence of RNA and under a negative electric current is relevant and intriguing because due to that several questions arise that evoke the chemical origin of life. Let us take for instance the existence of a negative electric charge on Earth since the primitive era, aside from favoring the RNA synthesis; did it favor the formation of carbon structures? If this is the case, why is it then that the morphology of the different structures of organisms, from one cell to a higher organism, has been conserved? Is it linked to the fact that biomolecules such as RNA and the negative electric current have also been conserved? In order to understand the mechanism by which the synthesis of carbon structures is favored under a negative electric current and RNA, it is necessary to understand first how carbon is formed from chemical reactions. These chemical reactions within the atoms of the chemical elements present in the primitive era would have been the first reaction to occur to give rise to the first carbon structure and, subsequently, to the first cell. In this sense, the first hypothesis on the origin of life from a chemical point of view was posed by Oparin in 1938 who proposed that the conditions of the primitive era favored the gradual chemical evolution of molecules based on carbon, from which more complex organic substances were formed. The formation of these complex organic substances gave rise to the first molecules to finally originate life.[31] Carbon is a widely distributed element in nature, although it only constitutes 0.025% of the terrestrial

Table 5. Summary of Results When Applying a Negative Electric Current and RNA on the Synthesis of Biomorphs

number of conditions	combination/condition	type of crystalline aggregate
6. synthesis of biomorphs with RNA and with negative electric charge (second group)	Na_2SiO_3 + $BaCl_2$ + NaOH + RNA + 2.0 μA negative electric charge, 37 °C	these biomorphs shown on Figure 9d, brilliant dots were $BaCO_3$(I) aragonite type (witherite) and Figure 9e was characterized as SiO_2 (silica)

Table 6. Prevalent Polymorphs Obtained in the Different Electric Current Conditions[a]

number of condition (number)/biomorph analyzed (letter)	combination/condition	prevalent polymorphs
1 (control without EC and RNA)	Na_2SiO_3 + $BaCl_2$ + NaOH, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
2 (control EC+)	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA positive electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
3 (control with RNA and without EC)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
4A (RNA and EC+)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA positive electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
4B (RNA and EC+)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA positive electric current, 37 °C	$BaCO_3$(II) $R\bar{3}m$ calcite type
4C (RNA and EC+)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA positive electric current, 37 °C	SiO_2
5A (control EC−)	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA negative electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
5B (control EC−)	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA negative electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
5C (control EC−)	Na_2SiO_3 + $BaCl_2$ + NaOH + 2.0 μA negative electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
6A (RNA and EC−)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA negative electric current, 37 °C	graphite
6B (RNA and EC−)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA negative electric current, 37 °C	graphite
6C (RNA and EC−)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA negative electric current, 37 °C	graphite
6D (RNA and EC−)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA negative electric current, 37 °C	$BaCO_3$(I) *Pmcn* aragonite type
6E (RNA and EC−)	Na_2SiO_3 + $BaCl_2$ + RNA + NaOH + 2.0 μA negative electric current, 37 °C	SiO_2

[a] EC: electric current. EC+: positive electric current. EC−: negative electric current.

crust, mainly in the form of carbonates. Carbon dioxide is an important constituent of the atmosphere and the main source of carbon becomes incorporated into the living matter. But which are the chemical reactions by which carbon is formed in its graphite form? The graphite in our reaction mixture could have been obtained from the reduction of CO_2 by means of an enzymatic-type mechanism (catalyzed by the RNA) because CO_2 reduction through redox reactions requires high overpotentials,[32] as well as having catalysts of both homogeneous and heterogeneous types.[33,34] Our reaction mixture was not performed with high overpotentials but with the presence of RNA, which is a nucleic acid thw behaves as an enzyme with catalytic properties.[16] This is very interesting, as this result indicates that RNA, in a negative electric current, is capable of reducing CO_2 to carbon in its more stable form: the graphite (Figure 9). All these results are summarized in Table 5.

This evidence could help us understand the chemical origin of life on Earth since the first biomolecule formed in the Precambrian era was RNA.[15,16] RNA, by acting as an enzyme, could catalyze CO_2, which was present at high concentrations, in that reducing environment, together with a negative electric current, to originate carbon. From the latter, more complex biomolecules were formed that finally allowed the formation of the first cell. The fact that RNA in the Precambrian era could have acted as an enzyme and that our results show that in the conditions given under a negative electric current (which emulate the net electric current of the Earth), this biomolecule reduces CO_2 to carbon in its more stable form, agreeing with studies that have used enzymes capable of reducing CO_2.[35−39] Additionally, in this combination of RNA and constant negative electric current, a second group of silica−carbonate compounds was obtained, which through Raman showed peaks at 96, 143, 226, 692, 1060, and 2495 cm^{-1}, corresponding to the aragonite-type $BaCO_3$ polymorph (Figure 9d). This barium polymorph is commonly found in barium biomorphs.[13,14] The third analyzed zone was that showing brilliant needles, which analyzed through Raman showed peaks at 11, 110−115, 233, and 482−486 cm^{-1}, corresponding to SiO_2 (Figure 9e). This material does not correspond to a biomorph, although it is a crystalline system, it does not have all the properties inherent to the barium silica−carbonate compounds. Having found that the barium polymorph is commonly found in other conditions, as well as SiO_2 in the presence of RNA and a negative electric current, this indicates that organic (carbon base) and inorganic compounds have coexisted since the primitive era. The Table 6 summarizes all the experiments performed and the polymorphs obtained for each experiment.

As a whole, these results indicate that the chemical origin of life comprises a set of factors that include the chemical elements, as well as the environmental conditions, together with the negative electric charge in the primitive era, which gave origin to the phenomenon called life. Our research group is working in this direction, however, complete elucidation of the chemical origin of life does not have an end insight.

4. CONCLUSIONS

The electric current is fundamental in the re-arrangement of atoms because under a positive electric current, a certain type of barium polymorph is generated; whereas in the case of a negative electric current, a carbon graphite is obtained through the enzymatic activity of RNA. To our knowledge, this is the first report showing that RNA can catalyze the reduction of CO_2 into carbon under the presence of a negatively charged ITO electrode. However, our results are barely a contribution in this pathway, in which several other areas of knowledge need to be studied in depth before we can even attempt to unravel in a forthcoming future the great mystery surrounding the phenomenon called life.

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Notes

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