

Essay

Mechanical Energy before Chemical Energy at the Origins of Life?

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Received: 4 June 2019; Accepted: 13 June 2019; Published: 9 January 2020

First Version Published: 16 August 2019 (doi:10.3390/sci1020050)

Second Version Published: 9 January 2020 (doi:10.3390/sci2010002)



Abstract: Mechanical forces and mechanical energy are prevalent in living cells. This may be because mechanical forces and mechanical energy preceded chemical energy at life's origins. Mechanical energy is more readily available in non-living systems than the various forms of chemical energy used by living systems. Two possible prebiotic environments that might have provided mechanical energy are hot pools that experience wet/dry cycles and mica sheets as they move, open and shut, as heat pumps or in response to water movements.

Keywords: origin of life; origins of life; mechanical energy; mechanochemistry; work; entropic forces; mica; biotite; Muscovite; wet/dry cycles; clay

1. Introduction

Mechanical forces and mechanical energy are prominent in living systems, at all size scales, from the molecular to the cellular and beyond [1–19]. Much of the cells' chemical energy, such as ATP, is used to generate these forces. Perhaps mechanical energy in living cells is a remnant of mechanical energy that brought life into being, before chemical energy was readily available.

Mechanical forces shift reaction pathways [20]. Mechanical force lowers the transition states for reactions by tilting the energy landscape. Mechanical forces can also give different reaction products than reactions without mechanical force [21].

Mechanical energy at life's origins would resemble synthetic mechanochemistry in the lab, because there were no enzymes to carry out the (bio)chemical reactions at life's origins. How feasible is synthetic mechanochemistry, in practice? Synthetic organic mechanochemistry has been used to produce many organic molecules, including pyrimidines [22], peptides, nucleosides, optically active products, oxidations, reductions, condensations, nucleophilic reactions, and cascade reactions [23]. The industrial appeal of synthetic organic mechanochemistry is that it reduces the use of solvents.

Many forces pushed molecules around before 'biochemical' energy was available. These forces include hydration, dehydration, and surface forces, as well as entropic forces. Entropic forces "can have the counterintuitive effect of apparently introducing 'order'" [24]. Entropic forces are also known as 'excluded-volume forces' or 'depletion interactions.' As water molecules become scarce during drying, the entropy increases when monomers polymerize. Monomer polymerization frees up a few water molecules that were constrained to linger near the ends of the monomers before they polymerized. The monomers experience an entropic force of attraction that brings them together.

Entropic forces would generate mechanical energy (the product of force and distance), without chemical energy, at life's origins. In living systems, the motions and forces of enzymes usually need energy transduction from an energy source such as ATP. ATP and most of the chemical energy sources now used by living systems were not available at life's origins. Mechanical forces, entropic forces, redox reactions—and of course, the sun!—were available for providing energy at life's origins.

The mechanical forces of mechanochemistry are a possible energy source for forming monomers as well as polymers. Some monomers, such as amino acids, may have been present on the early earth, but others, such as nucleotides, were not present and were synthesized in some way/s [25].

2. Materials and Methods

Muscovite mica was obtained from New York Mica Co., New York, NY, USA, and was scanned at 600 dpi with an HP Officejet 4635.

3. Results and Discussion

Research on Previous ‘Prebiotic’ Polymerizations. Proteins and nucleic acids are the main biopolymers involved in cell functions. Lipids are essential for cell functions but are not ‘beads-on-a-string’ polymers. Carbohydrates are also biopolymers but are used more for energy storage and cell structure. In most research investigating the prebiotic formation of proteins/peptides and nucleic acids/oligomers, the monomers are chemically activated, (e.g., [26–30]), which is not a realistic model for the origins of life.

More relevant research uses unactivated amino acids and nucleotides. Unactivated amino acids polymerized into peptides when dried but hydrolyzed when wet [31], which is also not ideal for the origins of life. A newer better ‘prebiotic’ way of forming peptides used hot/dry vs. cool/wet cycles [32]. Another improvement was the use of both amino acids and hydroxy acids to form depsipeptides, which have both amide (peptide) bonds and ester bonds. The ester bonds form and break more easily than the peptide bonds. Initially, mostly ester bonds formed. With cyclic wetting and drying, ester residues were replaced by amino acid residues, leading to a hetero-polymer that was increasingly rich in amino acids [32].

Clays have been used for many ‘prebiotic’ polymerization experiments, catalyzing or supporting the formation of both peptides and oligonucleotides (e.g., [29,30]). Clays are layered silicate minerals that swell when wet and shrink when dry. Montmorillonite clays are best for these polymerizations. The anionic silicate layers of Montmorillonite clays are held together by hydrated sodium (Na) ions. The hydration of the Na ions causes the clay to shrink and swell in response to drying and wetting.

Two Embodiments of Mechanical Energy at Life’s Origins. Wet/dry cycles and moving mica sheets are two sources of mechanical energy available for powering the many types of chemical reactions that occurred as life was coming into being. Mechanical energy might be capable of forming monomers and polymers of prebiotic molecules. Polymer formation by mechanochemistry is diagrammed in Figure 1 for the reaction of alanine + di-alanine to form tri-alanine.

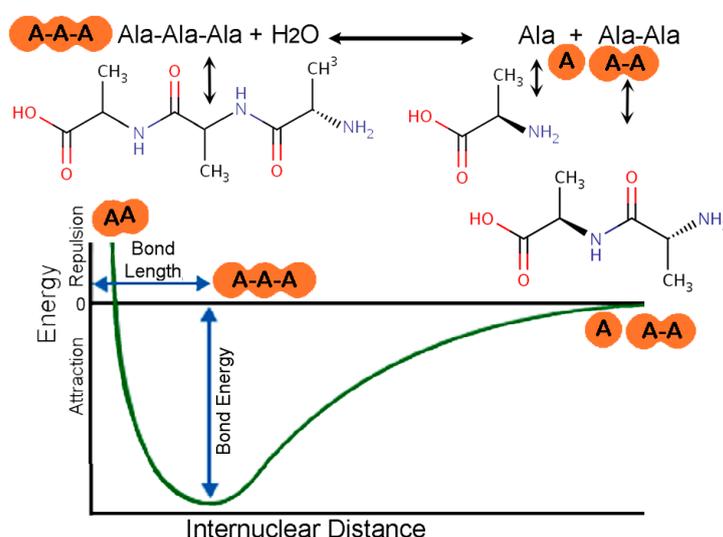


Figure 1. Energy diagram of the way that mechanochemistry might polymerize molecules, such as

Alanine (A), shown here. **(Top)** tri-alanine, A-A-A, forming, reversibly from, alanine and di-alanine (A-A), with the release of a water molecule. **(Bottom)** Mechanical force vs. distance curve showing Attractive and Repulsive regimes as molecules are pushed closer together, to the bonding distance. Modified from [33].

“Fresh water” origins are assumed here, because low ionic-strength solutions are needed to form lipid membranes [34,35]. (Deamer’s paper [34] has a wonderful analysis of lipids, membranes, and ‘informed guesses’ about their prebiotic assembly). There is also new evidence for origins in hot water on land [36–38] and evidence for origins in shallow ponds [39]. Whether life began in water on land or in water between mica sheets, the “fresh water” requirement holds for any origins scenario involving water–air interfaces. As Deamer points out, biochemists use dilute buffered aqueous solutions to do their biochemistry experiments, as opposed to ‘salt water’ [40].

3.1. Wet/Dry Cycles

Cyclic wetting and drying on land occur in hot puddles where volcanoes are forming, such as the Kamchatka peninsula in Russia [41] or in active geothermal fields such as The Geysers in California [42]. Cyclic wetting and drying occurs on mineral or rock surfaces and has the advantage of concentrating prebiotic molecules during the drying phase, which overcomes the problems of dilution in Darwin’s “warm little ponds”. Prebiotic chemistry was tested in the Kamchatka peninsula, by pouring a sample of white powder into a hot clay-lined pool. The powder contained four amino acids and four chemical bases that compose naturally occurring nucleic acids, plus sodium phosphate, glycerol, and a fatty acid. Foam and a white scum appeared quickly [36,41].

An amazing discovery from the Deamer lab is that unactivated mononucleotides will polymerize during wetting and drying in the presence of lipids [43,44]. Lipids protect the oligonucleotides from the hydrolysis that occurs during drying without lipids.

This lipid-assisted origin of life is proposed for the ancient Dresser Formation in the Pilbara region of Australia. These rocks contain evidence of the earliest life on land, more than half a billion years earlier than previously believed [36,45]. Once an active geothermal field, the Dresser Formation now has 3.48 billion-year-old stromatolite fossils, which appear to have formed on land and not in oceans, as was previously believed [40].

As Damer describes the wet/dry cycles, there was a 3rd stage in the cycles of vesicles forming and breaking—a moist gel stage [36,38,46]. Molecules reassorted and grew in complexity in the moist gel, climbing up an ‘evolutionary ladder’ and ‘booting up’ the functions of life, through ‘programs written in polymers.’ Doyle uses similar language in describing the emerging complexity of life and its processes: “All life and advanced technologies rely on protocol-based architectures” that are ‘robust yet fragile’ [47].

A fractionation of organic molecules would occur during drying in rocky puddles, with the most lipid-rich material forming ‘bathtub rings’ [40] with divalent salts at the earliest stages of drying. With continued drying and concentration of salts, prebiotic mixtures with less and less lipid would dry onto the rocky walls as the density of the salt solution increased, with a moist gel phase at the bottom that would be enriched in non-lipid molecules.

The situation is analogous to isolating lipoproteins from blood plasma, except that lipoproteins are isolated by increasing the salt concentration such that different lipoproteins float to the top. The most lipid-rich lipoproteins rise to the top of the initial solution, and successively more lipid-poor lipoproteins rise to the top as the solution density is adjusted with salt to densities of 1.02 g/mL for Low Density Lipoprotein (LDL) and 1.21 g/mL for High Density Lipoprotein [48]. A similar fractionation likely occurred in drying pools at life’s origins.

Theoretical analyses of the wet/dry cycles have provided additional insights: As polymers dry, polymerization rates increase, because diffusion distances are shorter. As polymers continue drying, polymerization rates decrease, because crowding decreases diffusion rates [49]. Polymerization can

be explained thermodynamically by excluded volume effects and molecular crowding [50], where entropic forces would generate mechanical energy.

3.2. Moving Mica Sheets

Mica is old—old enough to be the mineral from which life emerged [51]. Mica has a clay-like silicate structure with potassium (K) ions holding mica's anionic sheets together. K ions are larger than Na ions, so there is no space for water molecules between unsplit mica sheets. Therefore, mica does not shrink and swell with drying and wetting, providing a more stable environment than clay particles. However, water seeps in at the edges of mica sheets, with cycles of heating and cooling (Figure 2C) [20] and water can move farther in between the mica sheets, gradually, even to the point where the mica becomes 'matted', with large spaces between sheets.

Mica's mineral sheets move, open and shut, in response to water flow (Figure 2A) and heating and cooling of the mica sheets (Figure 2B). The movements of the mica sheets squeeze and stretch the molecules with enough mechanical force to make and break covalent bonds between them [52]. Spaces between mica sheets form cantilever-type springs, capable of generating a vast array of different mechanical forces, depending on the area and thickness of the mica cantilever.

Longer DNA molecules bind more strongly to mica sheets than shorter DNA molecules, which are more likely to be washed away, as observed by atomic force microscopy (AFM) [53,54]. This stronger binding favors the accumulation of longer nucleic-acid molecules on mica, thus accumulating nucleic acids long enough to carry 'enough' information.

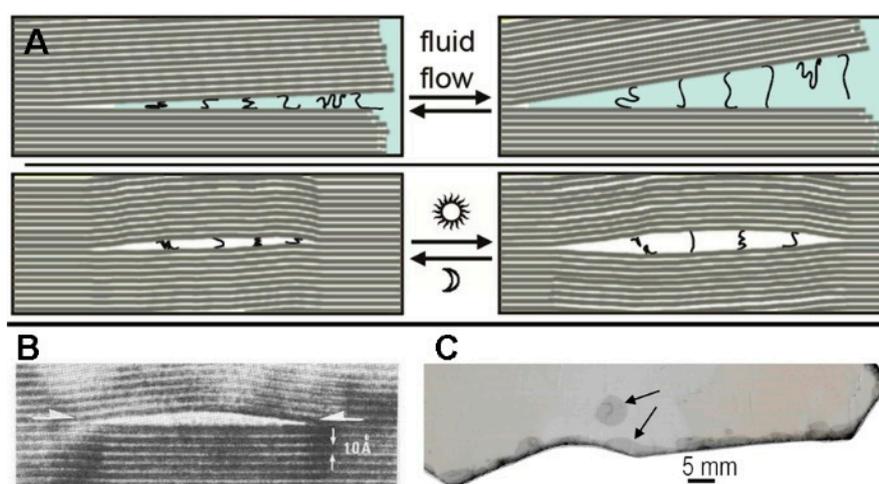


Figure 2. (A) Diagram of mechanical forces between biotite mica sheets, stretching and compressing polymers, due to: (Upper panels) water flow at the edges of the biotite sheets, and (Lower panels) heat pumps in a biotite bubble. (B) Biotite bubble imaged by HRTEM (high-resolution transmission electron microscopy). The thickness of a single biotite sheet is 1 nm (10 Angstroms) [55]. (C) Top view of a bubble in Muscovite mica (upper arrow) and of sheet separation at the edges of the mica sheet (bottom arrow). Bubbles are common even in 'high grade' micas. Biotite is now the preferred mica, for life's origins between mica sheets [56,57].

Mica's anionic crystal lattice has a periodicity of 0.5 nm (Figure 3), which is also the periodicity of phosphates on extended nucleic acids and the periodicity of sugar residues of carbohydrates. This shared periodicity makes mica a possible template for polymerizing nucleotides into nucleic acids or sugars into polysaccharides.

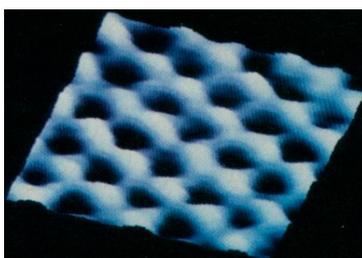


Figure 3. Crystal lattice of Muscovite mica imaged by atomic force microscopy (AFM), showing locations of recessed hydroxyl (OH) and ionized hydroxyl (O^-) groups, as depressions (dark spots) on the mica surface. Image size is 2.6 nm \times 2.6 nm. Modified from [58].

DNA and mica are both also anionic, and cations bridge the anionic charges in both DNA and mica. In mica, the 0.5 nm periodicity of anionic negative charges corresponds to the recessed hydroxyl groups in the mica surface, each of which carries $\frac{1}{2}$ negative charge (i.e., either OH or O^- groups). In DNA, the phosphate groups are anionic and interact with cations in living cells. Perhaps DNA, and life, emerged on anionic mica sheets [54]. Amino acids in peptides have a smaller periodicity, such that a tripeptide has a length of ~ 1 nm.

Mica sheets might shelter emerging life without the need for membranes. Membranes are fragile. They leak, acquire and lose molecules, swell, and rupture. Mica is a robust mineral with nearly endless spaces between its sheets.

In living cells, membraneless organelles such as nucleoli contain RNA and protein. Although ribosomes are smaller than membraneless organelles in living cells, ribosomes have some of the most ancient RNAs and proteins. Ribosomes were present in the Last Universal Common Ancestor of life (LUCA) [59]. When life was coming into being, in the pre-LUCA stages, ribosomes and their precursors may have been the first ‘membraneless organelles’ [60]. Membraneless organelles form by liquid-liquid phase separation [61]. Phase-separated membraneless organelles at life’s origins are now proposed by various groups [62–66]. A delightful news article for [14] is titled “In the Beginning was the Phase Separation” [67].

Life might have started in mica without membranes, but membranes and lipids are compatible with mica surfaces, as seen through atomic force microscopy (AFM) of lipids and membranes on mica [68–70]. Therefore, mica could be the site for life’s origins, whether lipids were needed at the earliest stages of proto-life, or only at later stages in life’s emergence.

4. Conclusions

Mechanical energy in living systems provides energy in a form that is common in non-living systems. Why do living systems convert chemical energy to mechanical energy, instead of using chemical energy directly? Perhaps this is because mechanical energy was an original energy source at the origins of life. Entropic forces provide mechanical energy during drying or molecular crowding.

Mechanical work can be done without chemical energy, ion gradients, or proton gradients, which now provide energy for most of the processes in living systems. Ion gradients and proton gradients need an energy source to create the gradients, and they need a continuous supply of energy to maintain the gradients. Mechanical energy is a readily available energy source that may have brought life into being, and it is now found throughout living systems.

Funding: This research received no external funding.

Acknowledgments: Thank you to Bruce Damer and the other participants at the Origins of Life Gordon Research Conference in January 2018 for helpful discussions. Thank you to Katherine Lieban for writing advice and to Fyl Pincus for the stimulating presentations he facilitated at UCSB about entropic forces. Thank you to the reviewers for their suggestions and recommended references.

Conflicts of Interest: The author declares no conflict of interest.

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