Could Life Originate between Mica Sheets?: Mechanochemical Biomolecular Synthesis and the Origins of Life

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ABSTRACT

The materials properties of mica have surprising similarities to those of living systems. The mica hypothesis is that life could have originated between mica sheets, which provide stable compartments, mechanical energy for bond formation, and the isolation needed for Darwinian evolution. Mechanical energy is produced by the movement of mica sheets, in response to forces such as ocean currents or temperature changes. The energy of a carbon-carbon bond at room temperature is comparable to a mechanical force of 6 nanoNewtons (nN) moving a distance of 100 picometers. Mica's movements may have facilitated mechanochemistry, resulting in the synthesis of prebiotic organic molecules. Furthermore, mica's movements may have facilitated the earliest cell divisions, at a later stage of life's origins. Mica's movements, pressing on lipid vesicles containing proto-cellular macromolecules, might have facilitated the blebbing off of 'daughter' protocells. This blebbing-off process has been observed recently in wall-less L-form bacteria and is proposed to be a remnant of the earliest cell divisions (Leaver, et al. *Nature* **457**, 849 (2009).

INTRODUCTION

The hypothesis of this paper is that mica is in many ways an ideal environment for the origins of life. One potential advantage of mica is that it could provide an endless source of mechanical energy for synthesizing the many covalent bonds needed for even the simplest life.

The scenario might be something like this: Simple molecules bind to the edges and surfaces of the sheets in a mica book. The sheets move up and down in response to heating and cooling and water flow. These movements squeeze and stretch the molecules with enough force to make and break covalent bonds between them. Larger molecules are formed, including amino acids and other common monomers in the bio-polymers of life. Impurities in the mica lattice, such as iron, serve as reaction centers that bias the mechano-chemical reactions in favor of some molecular products over others. As molecular products accumulate, they diffuse between mica sheets and orient on the mica lattice. Their orientation is determined by the 0.5-nanometer periodicity of the mica lattice and its electronegativity. These constraints of the mica lattice bias the molecular binding, favoring isomers of the same handedness: either L- or D-isomers bind nicely next to each other on the mica lattice, while mixtures of L- and D-isomers do not bind as close to each other. Closely spaced molecules join, by losing a water molecule, and polymers form. These polymers are especially stable in dry spaces between mica sheets, where mass action favors polymerization over hydrolysis.

As time passes, polymers of different types accumulate between mica sheets. Different polymers form and accumulate between different mica sheets, due to stochastic processes. In some regions, RNA worlds may develop. In other regions, peptides may predominate, or lipids. Figure 1 is a sketch of the hypothesized system at this polymer-rich stage in prebiotic evolution.

Over time, complexity will increase. Self-replicating ribozymes from nearby regions will join to form larger ribozymes capable of storing and transmitting more genetic information. Ribopeptides may form from the interactions of RNA and peptides. Lipid bilayers self-assemble on and between mica sheets. These lipid bilayers periodically encapsulate collections of molecules on the mica sheets or their edges. Occasionally the lipid bilayers encapsulate a viable collection of molecules, capable of self-replication, metabolism, and some form of cell division. At least one of these collections of molecules survived and evolved into life as we know it today.

For delightful books on the origins of life, see Hazen,[1] for the research and the people who did it, and Dyson,[2] for a toy model of how prebiotic molecules might have evolved.
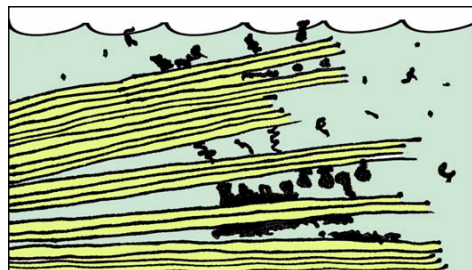
Figure 1. The mica hypothesis for the origins of life. A sketch of mica sheets under water, with 'molecules' of various sizes and conformations between the sheets. Mica sheets are 1-nm thick. The sketch shows the mica separated into layers as thin as 3-4 sheets (3-4 nm), but it is more realistic to propose that the thinnest layers are hundreds of sheets thick, to have larger spring constants and more robust compartments.

Mica

Mica is a layered mineral with 1-nm-thick sheets bridged by potassium ions (K^+). These sheets are composed mostly of silicon (Si), oxygen (O) and aluminum (Al). Each 1-mn-thick sheet has 3 layers. The top and bottom layers of the sheets are a hexagonal net of mostly Si and O. The middle layer, sandwiched between the sheets' surfaces, is an octagonal layer of mostly Al and O. This Al-O layer has hydroxyl groups that are recessed slightly below the Si-O surface. These recessed hydroxyl groups are hexagonally spaced and 0.5 nm apart. Half of the recessed hydroxyls are ionized, giving a surface charge of 2 negative charges per square nanometer, in the absence of counterions. In unsplit mica, potassium ions bridge the recessed hydroxyls in adjacent sheets and hold the sheets together.[3]

Mica has an affinity for biomacromolecules of many types. Mica's affinity for DNA correlates with the ionic radius of the inorganic cation used to bind the DNA to the mica.[4]

Mica has a clay-like layered chemical structure on the scale of its crystal unit cell. Unlike clays, which have micron- or sub-micron-sized sheets, mica's crystalline sheets extend for millimeters, centimeters, and more.

HYPOTHESIS

Mica has the possibility of transducing solar or other heat energy and kinetic energy from water movements into mechanical energy for stretching and compressing molecules between mica sheets. A beautiful advantage of mechanical energy for life's origins is that it is endlessly available between mica sheets, due to water movements at mica's edges and temperature changes that may create heat pumps in mica's bubble defects.

Orientation and compression to inter-atomic distances should be able to form covalent bonds of prebiotic monomers and polymers. Polymerization of monomers is hypothesized to occur when monomers orient in adjacent sites on the mica lattice. The 0.5-nm periodicity of the anionic mica lattice is the same as the spacing between nucleotides in single-stranded nucleic acids and between amino acids in extended β-sheet structures. Inorganic cations are proposed to bridge the monomers and polymers to the mica.

These flows, expansions, and contractions of fluids exert mechanical energy in a cyclic fashion on whatever is present between the mica sheets. Forces and pressures would be expected to vary over many orders of magnitude, depending on the thickness and area of mica sheets, the temperature changes, the sizes of air bubbles, and other factors.

As shown in Figure 2 , two types of mechanical energy are envisioned for mica. In the first type, fluid flows in and out of the spaces between mica sheets, with the ebb and flow of water currents from prebiotic oceans or lakes. In the second type, fluid and air bubbles between mica sheets expand and contract during the earth's daily cycles of heating and cooling. This second type is a hot-air engine or heat pump.
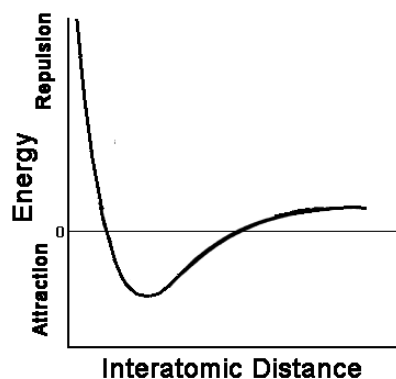
Mechanical Energy from Mica?
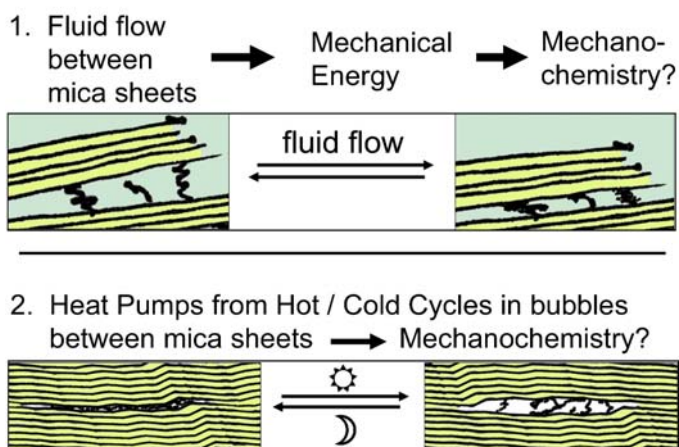
Figure 2. Sketches of two possible sources of mechanical energy from mica, for synthesis of prebiotic molecules. Top panel shows fluid flows at the edges of mica sheets that would stretch and compress molecules. Capillary forces would probably be the most likely forces between mica sheets with the smallest separations. Bottom panel shows how heat pumps or hot air engines might operate in the bubble defects in mica.

Heat pumps have been proposed as a possible energy source for the origins of life[5] and are hypothesized to form in mica defects. Even the highest grade of mica has visible defects that appear to be flattened air bubbles between mica sheets. These bubble defects appear as roughly circular areas, typically several millimeters in diameter. These bubbles between mica sheets may expand and contract by a few picometers or more in response to solar heating and night-time cooling. Thus mica may function as a heat pump. This source of mechanical energy from mica is more problematic than the first source in Figure 2, arising from fluid flows between mica sheets. Heat pumps raise questions such as how small precursor molecules got between the mica sheets. The first panel in Figure 2 shows a mechanism that seems highly probable.

In the earliest stages of prebiotic molecular synthesis, the up-and-down motions of mica sheets might bring small molecules close enough together to enter the attractive regime of the energy-vs.-distance profile (Figure 3). At the earliest stages, monomeric molecules would be forming from whatever chemical precursors were present in the prebiotic 'soup'. At intermediate stages of prebiotic molecular synthesis, polymer synthesis is expected.

DISCUSSION

Motions of mica sheets are a possible source of energy for forming covalent bonds in prebiotic molecules, for changing the conformations of macromolecules, and for extruding lipid-enclosed protocells, as proposed recently, based on observations of L-form bacteria.[6] The spaces between mica sheets provide other advantages for the origins of life. When chemical reactions occur in confined spaces, there are fewer reaction products.[7] This would be an advantage, for example, for the formose reaction, which produces sugars by an autocatalytic process. Ribose is the only sugar currently found in RNA, but a great variety of sugars and branched sugars are produced by the formose reaction.[8] Perhaps the confinement between mica sheets, and the 0.5-nm-periodicity of the mica lattice, produce fewer sugars with the formose reaction.

Figure 3. Mechanochemical synthesis of prebiotic covalent bonds is hypothesized to result from the close approach of molecules, into the attractive regime of the energy profile. Unlike thermal or chemical energy sources, mechanical energy can be uni-directional, thus favoring specific bond angles and reaction products. Orientation on the 0.5-nm mica lattice is also hypothesized to favor the polymerization of 0.5-nm-sized monomers such as the common amino acids and nucleotides.

Mica's chemical structure is similar to the chemical structures of many clays. Some of the advantages hypothesized here for mica apply also to clays. Others apply only to mica. The specific advantages of mica include the possibility of mechanochemistry with orders-of-magnitude variations in forces and distances, and the large closely spaced isolated compartments formed by the spaces between mica sheets. These advantages both stem from mica's property of having extremely large mineral sheets relative to clays.

Mechanochemistry and Nanomechanics

'Mechanochemistry' is the formation of covalent bonds by the use of mechanical energy.[9] In the origins of prebiotic life, covalent bond formation produced the monomers needed for biopolymers and the polymers resulting from polymerization of the monomers. These two synthetic processes would involve mechanochemistry on the picometer scale for synthesizing monomers and on the nanometer scale for synthesizing polymers.

'Nanomechanics' is used here to describe noncovalent rearrangements of biopolymers. These changes include molecular-level processes such as the aggregation/denaturation vs. renaturation of proteins, and cellular-level processes such as the blebbing off of lipid vesicles and their internal contents.

Mechanochemistry brings a directional component to reaction processes, unlike thermochemistry, in which the heat-induced forces are in random directions. The observations for mechanochemistry are that tensile stress makes reactions faster if the reactive site is elongated during the reaction and slower if the reactive site is shortened during the reaction.[9]

The energy of a carbon-carbon bond at room temperature is comparable to a mechanical force of 6 nN moving a distance of 100 picometers. Force can lower the energy barrier for

chemical reactions, as shown by atomic force microscopy (AFM) and other single-molecule force-exerting techniques. Rupture forces, from AFM pulling measurements, are 1-2 nN for covalent bonds[10] and ~ 0.1-0.3 nN for the unfolding of protein domains.[11] Often, protein domains unfold and refold repeatedly as a protein with tandem domains is repeatedly stretched and relaxed.

Mechanical forces play a large role in living systems even at the molecular level. This is becoming increasingly obvious as the motions of single biomacromolecules are being explored. Fluid-filled spaces between mica sheets, moving on the nanoscale, have a resemblance to the nanoscale motions in subcellular structures such as enzymes and ribosomes. Hinge-like up-and-down motions are one of the most common movements in enzymes. These up-and-down motions might have arisen as an artifact of the up-and-down motions of mica sheets as shown in Figure 2. Other intra-macromolecular motions such as twisting, rotating (e.g., F1 ATPase), and walking (e.g., molecular motors such as kinesins and dyneins) are hard to relate to mica sheets' motions; and, of course, they probably evolved long after the Last Common Ancestor (LCA).

Intermolecular and surface forces of many types would have been involved in the hypothetical prebiotic mechanochemistries and nanomechanics. Molecules and surfaces interact within and between themselves through a multitude of forces, including electrostatic, hydrophilic, hydrophobic, van der Waals, solvation/hydration, protrusion, steric, and fluctuation forces.[12] Some of these interactions are sketched in Figure 1: One water-filled compartment shows tethered string-like molecules stretched between two mica surfaces. The next water-filled compartment shows bulbous molecules that will experience protrusion forces, and the bottom compartment shows molecules with good adhesion to mica. Intermolecular and surface forces act over distances ranging from less than 1 nm to over 100 nm.

Although research on mechanochemistry usually seems to result in bonds being broken, there are a few instances of synthetic mechanochemistry. For example, mechanically induced intramolecular rearrangements produced molecular products not formed with thermal or light-induced reactions.[13] Pressure is reported to induce the polymerization of glycine and to inhibit the degradation of poly-glycine.[14] Pressure affects the rate and equilibrium constants of chemical reactions.[15] In a destructive process, Molecular Dynamics calculations of thiols on copper showed that carbon-sulfur bonds cleaved when heat was the energy source, while copper-copper bonds cleaved when the energy source was an upward-moving mechanical force. Therefore the relative bond strengths were significantly different when the energy source was thermal as opposed to mechanical.[16]

Nanomechanics research, like mechanochemistry research, seems to show both breaking down and building up of molecular aggregates. For example: Pressure induces the aggregation of an amyloidogenic protein[17] and increases the aggregation of a IFN-gamma protein by exposing more of the protein surface area to solvent[18] On the other hand, pressure can renature and disaggregate some proteins. For example: Pressure causes aggregated human growth hormone to refold.[19] Pressure induces the non-covalent polymerization of G-actin monomers to F-actin fibrils in blood vessels.[20] Pressure can even induce the growth of blood capillaries.[21]

CONCLUSIONS

The origin of life is one of the major unanswered questions in science. Hypotheses for the origins of life, however, are hard to falsify convincingly and impossible to prove absolutely.

Nonetheless, the mica hypothesis raises useful questions about the extent to which mechanochemistry can be used for molecular syntheses.

ACKNOWLEDGMENTS

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