Article

Did Biology Emerge from Biotite in Micaceous Clay?

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Abstract: This paper presents a hypothesis about the origins of life in a clay mineral, starting with the earliest molecules, continuing through the increasing complexity of the development, in neighboring clay niches, of "Metabolism First," "RNA World," and other necessary components of life, to the encapsulation by membranes of the components in the niches, to the interaction and fusion of these membrane-bound protocells, resulting finally in a living cell, capable of reproduction and evolution. Biotite (black mica) in micaceous clay is the proposed site for this origin of life. Mechanical energy of moving biotite sheets provides one endless source of energy. Potassium ions between biotite sheets would be the source of the high intracellular potassium ion concentrations in all living cells.

Keywords: clay, mica, biotite, muscovite, origin of life, abiogenesis, mechanical energy, work, wet-dry cycles

1. Introduction

Somewhere in the universe there was a habitat, hospitable for everything needed for the origins of life. This is an essential requirement for life's origins. The habitat may have been on Earth, ~4 billion years ago [1]. In this habitat, the components of life were evolving, resulting, eventually, in LUCA, the Last Universal Common Ancestor [2, 3]. Among these components, RNA or RNA-peptide 'worlds' [4-12] were evolving; proto-metabolic cycles were evolving into early metabolism [13, 14], ribosomes [15, 16] were evolving to synthesize proteins, and replication of information was emerging [17], perhaps in 'lipid worlds' [18-20], or in hydrothermal vents [21-24]. Vast numbers of interconnections were needed, for bringing the precursors to Earth or synthesizing them on Earth and carrying them to the sites of further evolution toward life and, eventually, to the hospitable habitat from which life emerged. The habitat was likely clay [25, 26], the stuff of life.

Why clay? "The genetic code drives all biological life. But even a mechanism this fundamental rests on still more ancient biochemical processes, as well as the intriguing chemical properties of a seemingly nondescript material—clay … While many biologists today delve into genome sequences to understand how organisms evolved, the history of life on Earth is not written solely in DNA. Clues to this history are also inscribed in something far more ancient: metabolism, the intricate networks of biochemical reactions that make our cells hum." [27]

Clay mineral surfaces catalyze or support polymerizations of amino acids and nucleotides, and the synthesis of amino acids from simple precursors, e.g., [28-33]. Nucleotides on clay polymerize preferentially in the 3'-5' orientation, as in life, and not in the non-biological 2'-5' direction [34]. A Molecular Dynamics study [35] of Montmorillonite clay indicates that polymerization in 3'-5' direction occurs fastest in clay sheets that are closer together, compared with the non-biological 2'-5'direction, which occurs fastest at greater clay sheet separations. Polymerizations occur preferentially in the clay interlayer, as opposed to the edges of the sheets. Homochiral polymerizations are favored over achiral polymerizations on clay. Clay minerals undergo wet-dry cycles in which entropic forces favor polymerization during the drying phase of wet-dry cycles [36].

Clays form in association with the water needed for life [37], which is another advantage of clay over other rocks and minerals.

Maybe the clay mineral contained black mica, biotite (Fig. 1). Maybe there were places between some biotite sheets where proto-metabolic cycles (e.g., [38-40]) were emerging and places between other biotite sheets where replication of genetic material was coming into being. These processes depended on precursors not synthesized within the clay or mica, including probably many of the monomers that would later react to form polymers. Membranes would be forming and encapsulating molecular complexes that were accumulating between the biotite sheets. Membrane-enclosed protocells would tend to aggregate, bringing together the molecular complexes for metabolism, self-replication, protein synthesis and other necessary components of life. This would be a slow, gradual, complex process, occurring at many locations in biotite mica and surrounding clays. After a long long time, occasionally a membrane would encapsulate *everything* needed for a self-reproducing living cell (Fig. 2). Some of these living cells would survive, while others would die after a few generations or more.

Mica is old enough to be a site for the origins of life [41]. Muscovite and biotite are among the major minerals found in zircon grains from the Hadean, along with quartz, plagioclase, K-feldspar, chlorite, and hornblende [42]. Most of the mica would not have been in clays as early as the Hadean, but, as Hazen says, even traces of a mineral could have been sufficient for the mineral to be involved in life's origins [43, 44]. Borates, for example, were not present in large quantities at life's origins [41]. Borates, however, are valuable for stabilizing ribose; and even traces of borate on the early earth might have served this function [45, 46].

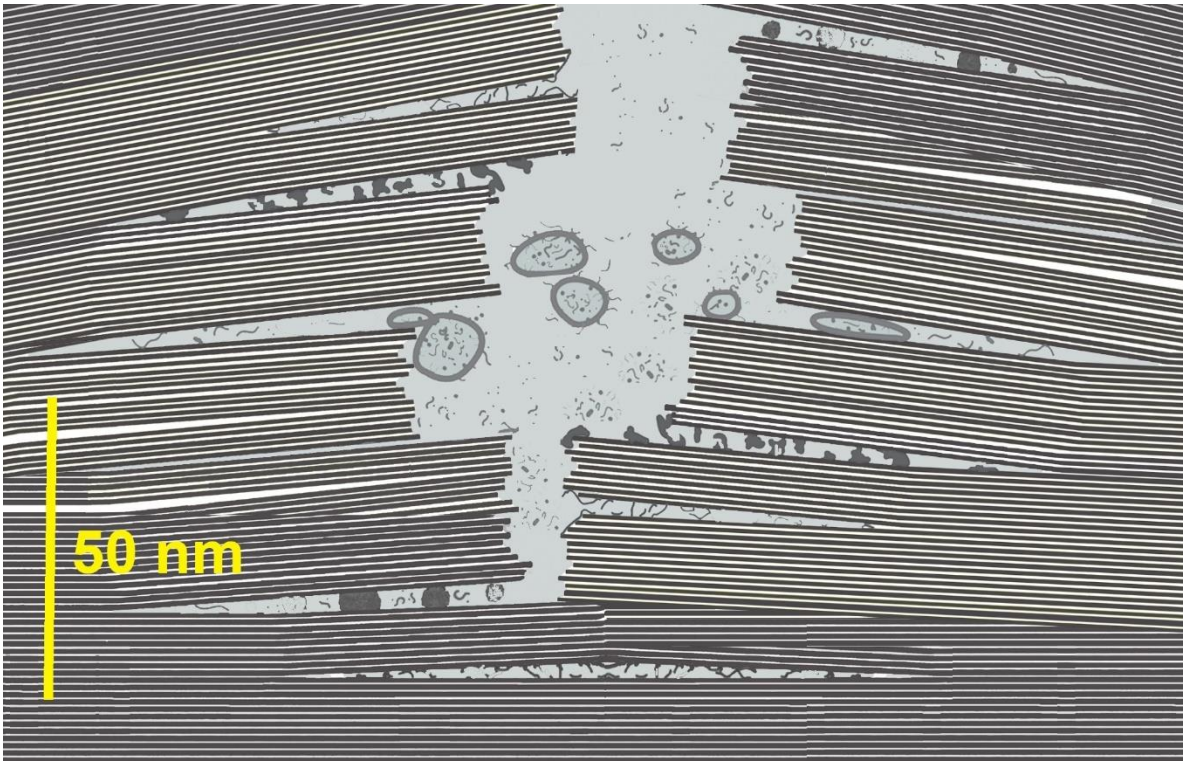

Figure 1. Nanometer-scale diagram of how the early stages of life might have originated between biotite mica sheets. Niches within the biotite sheets provide partially enclosed spaces for molecular evolution of different processes essential for life. Vesicles form, encapsulating molecules and molecular complexes from the niches.

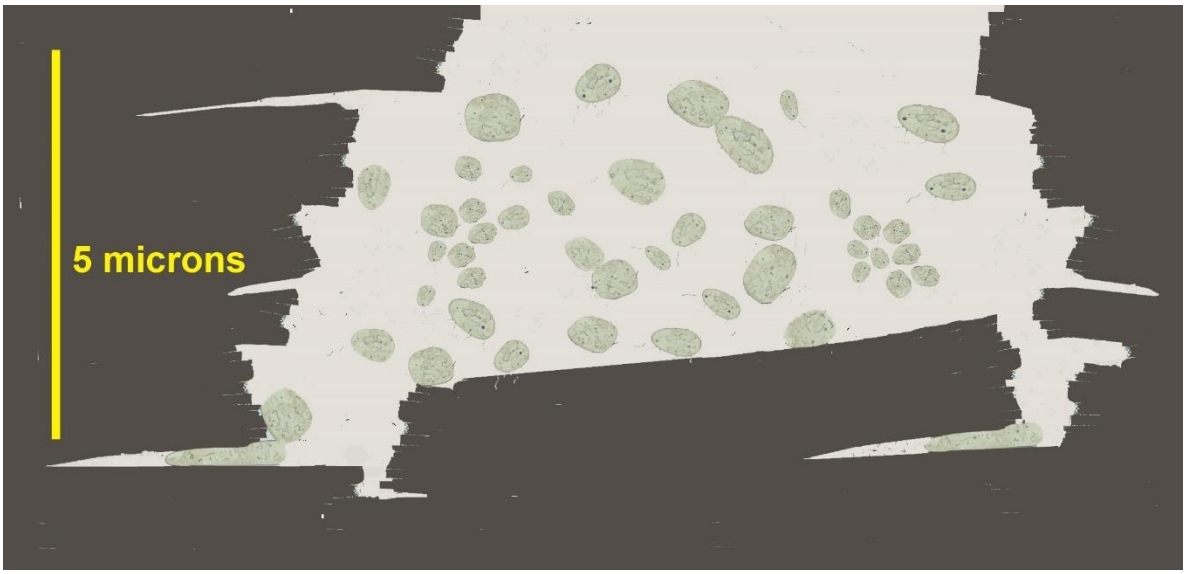

Figure 2. Micron-scale diagram of how life might have originated between biotite mica sheets. Protocells in the aqueous environment encapsulate prebiotic molecular aggregates in the niches between mica sheets. Mechanical energy from moving mica sheets can bleb off protocells, as seen in the lower left corner of the figure. Eventually, occasionally, a living cell will be produced, capable of self-reproduction.

2. Why micas?

Micas are non-swelling minerals, unlike smectite clays such as montmorillonite, which swells and shrinks during wet-dry cycles [47]. The swelling and shrinking of these clays is as if they were nanometer-sized sandwiches whose filling were growing thicker and thinner. In mica, water seeps slowly in and out, only at the edges of the mica sheets, leaving dry and nearly dry regions beyond the wet edges (Fig. 3). Experimentally, water seeped a few millimeters between the sheets of mica pieces that were cycled daily between 22ºC and 4ºC for 2 weeks [48].

Another advantage of micas is that their sheets are bridged by potassium ions (K^+), which are found at high concentrations in all living cells. This makes biotite and muscovite micas attractive minerals for life's origins, by providing the source of the K^+ for living systems. Mica particles are also much larger than clay particles, which are ~1-2 microns in size.

The origin of life has a 'water problem'. Polymers are needed and are often formed by dehydration, but polymers hydrolyze in the presence of water [32, 49-51]. The slow wet-dry cycles that can occur at the edges of mica sheets will generate longer polymers during the longer drying cycles, before hydrolysis occurs during the wet phase. These longer polymers will bind to mica better than short polymers and will, consequently, be more likely to remain bound to the surface. This is seen in Atomic Force Microscopy (AFM), where long DNA molecules bind to mica strongly enough for AFM imaging, but short DNA molecules do not bind to mica well enough to be imaged. In contrast, rapid wet-dry cycles in small clay particles will cause polymerization to be followed more quickly by depolymerization, resulting in shorter polymers that will more easily detach from the surface.

The spaces between the sheets in mica 'books' could have been the ancient pre-cellular spaces that confined and concentrated the earliest biomolecules, before membrane-bound cells emerged (Fig. 1) [48, 52-56]. Mica sheets move, open and shut, at their edges, as fluids flow and temperature changes; they are thus in a constant state of thermodynamic non-equilibrium necessary for life. These pre-cellular spaces have an anionic crystal lattice, with 'ceilings' and 'floors' in which solid-state synthesis [53] could have occurred. The mineral

sheets of biotite and muscovite micas have a layered silicate structure, like montmorillonite and illite clays, which have been used successfully to catalyze reactions non-enzymatically, such as the synthesis of biopolymers. [28-30, 57].

2.1 Mechanical energy from moving mica sheets

Moving mica sheets can produce endless energy for the origins of life (Fig. 3) [56]. This is mechanical energy, which can be used for mechanochemistry, to make and break chemical bonds. Mechanochemistry is a growing research field, in which biomolecules are synthesized with mechanical forces [58]. Mechanochemistry has been used in possible prebiotic syntheses [59, 60] and nucleobase pairing [61].

Mechanochemical polymerizations will create oligomers and longer polymers that will bind to the mica surface more strongly than monomers and short oligomers. Monomers and short oligomers will be preferentially washed off the mica sheets, favoring polymerization by mechanochemistry over polymer breakdown by mechanochemistry.

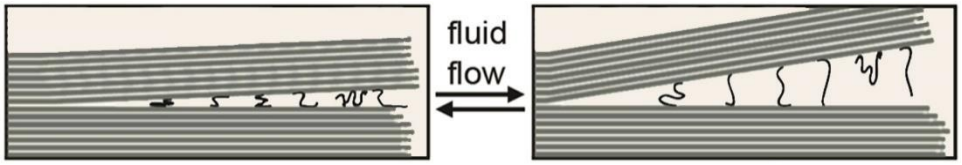

Figure 3. Diagram of fluid flow between moving mica sheets, capable of generating mechanical energy This mechanical energy can be used to synthesize prebiotic molecules, stretch and compress polymers (as shown in the diagram), or bleb off protocells [48]. Seven mica sheets, as shown in this diagram, provides enough force to form a covalent bond in air, when moved a distance of 0.1 nm.

How much energy can moving mica sheets provide? If the mica sheets move even 0.1 nanometer (nm) closer together, in air, they can push together 2 molecules to form a covalent bond, if the mica has a spring constant stiff enough to provide 170 piconewtons (pN) of force [48]. The equation for a spring constant, $F=kx$, with $x = 0.1$ nm, shows that a spring constant (k) of 1.7 N/m (Newtons/meter) is stiff enough. The spring constant of the mica depends on the number of mica sheets in the layer that is moving open and shut. Each mica sheet is ~1 nm thick. Only about 7 mica sheets are needed to provide this spring constant, in air [62]. In practice, the layers of moving mica sheets will often have thickness of microns, not nanometers, due to the fragility and consequent damage to nanometer-thick layers of mica sheets.

2.2 How big do the mica sheets need to be?

One needs only tiny pieces of mica for mechanochemistry. The mica fragments in micaceous clays are large enough. The ‘mica world’ diagrams in Fig. 2 are lengthened, in Fig. 4, to show that even sub-millimeter-sized mica fragments are big enough to generate mechanical energy for life’s emergence with nanometer-sized movements. Therefore, life may have emerged in micaceous clay, as opposed to larger pieces of mica. The swelling clay particles surrounding the mica fragments would also be advantageous for life’s emergence. For example, polymer syntheses might occur during the drying phase of wet-dry cycles in clay, and solutes in the surrounding fluid would be concentrated during drying. Some of these molecules and other solutes would move between the mica sheets.

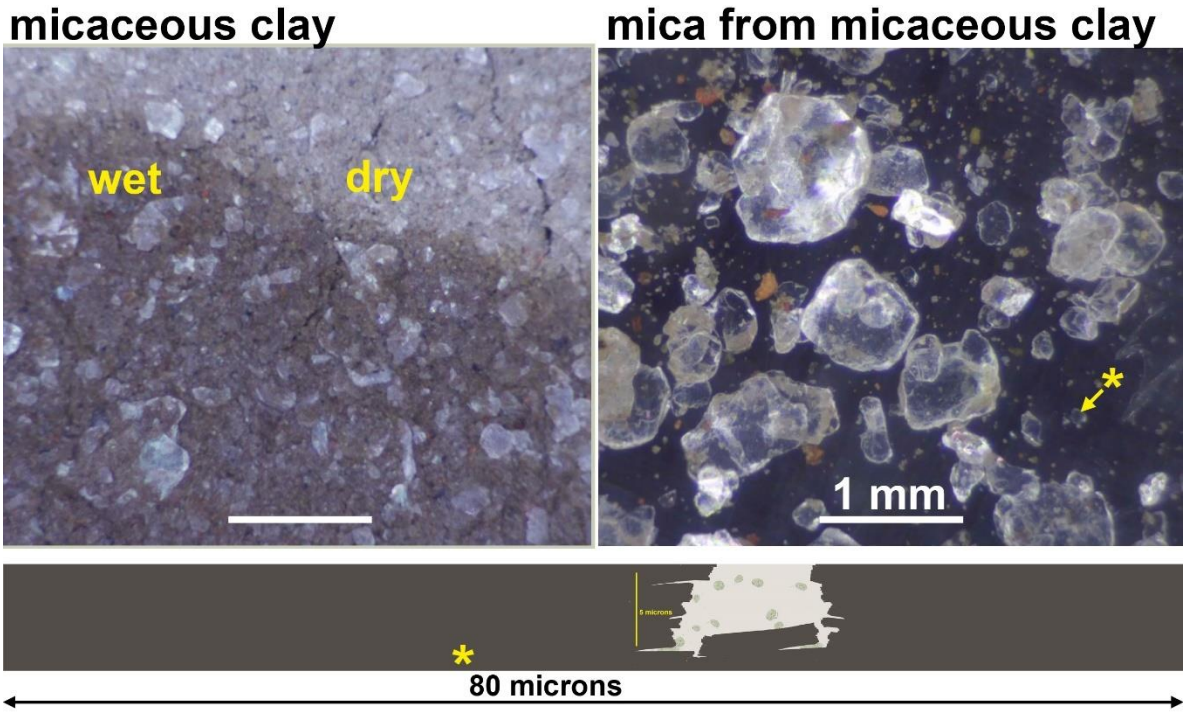

Figure . 4. Micaceous clay and life's origins. Top Left: a brown micaceous clay ("New Mexico Clay") containing pale reflecting pieces of mica, in the middle of a wet-dry cycle. **Top Right:** mica and a few clay particles, washed from the micaceous clay. Yellow asterisk and arrow point to a mica fragment with a diameter of 80 microns. Scale bars are 1 mm. **Bottom:** mica diagram, showing the length of 80 microns, relative to the sizes of protocells and mica structures of Fig. 2.

2.3 Why is biotite a better mica?

Biotite mica has advantages over muscovite mica. Biotite is rich in iron (Fe) and magnesium (Mg) (Fig. 5). The iron is predominately Fe(II) [63]. Especially in the Hadean reducing environment, Fe(II) predominated over Fe(III). Mg(II) is a major inorganic divalent cation in living systems, where it stabilizes DNA and RNA structures and provides the counterions for ATP, among other things. Biotite is the most conductive mica, because of its iron content. Electrical conductivity increases exponentially with the iron content of micas [64, 65]. Biotite's iron is likely to be useful for redox reactions [66] at life's origins, in the redox-active and conducting environment of clay [67, 68] and the reducing atmosphere of the Hadean [69]. In a beautiful piece of work, Muchowska et al. have synthesized 9 of the 11 main components of the TCA cycle, from glyoxylate and pyruvate, with Fe(II), in a test tube at 70°C in only hours [39, 70].

Acid accelerates the dissolution of biotite, acting primarily at step edges of biotite sheets and etch pits [71]. Biotite is also found on Mars, which may have been the original source of life in the Solar System, seeding life on earth [72].

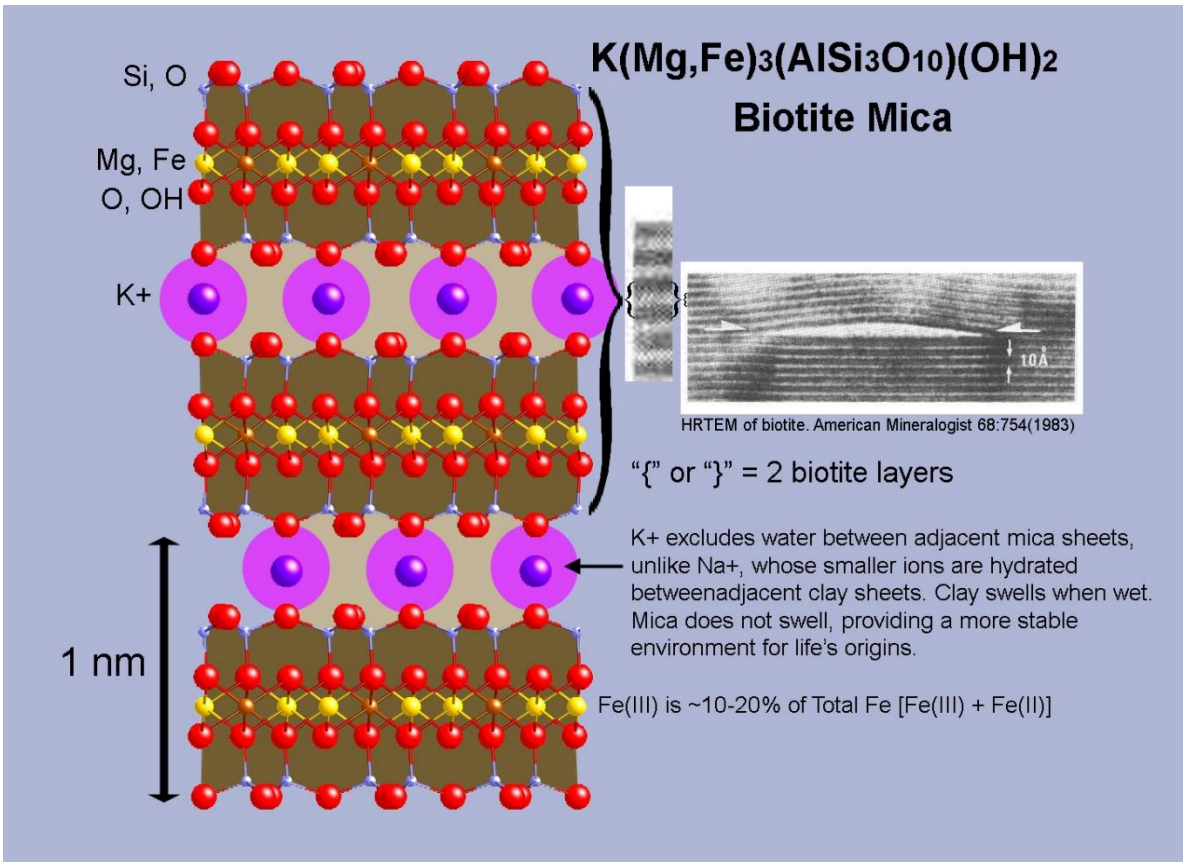

Figure 5. Biotite mineral structure (CrystalMaker image) with HRTEM image of biotite bubble [73] and data (Fe(III) is ~10-20% of total Fe) from [63]. 'Biotite', and 'black mica', are common names used for a subgroup of generally dark-colored, iron-bearing micas, including the species annite, tetraferriannite, ferroceladonite, fluorannite. Biotite is rich in iron (Fe) and magnesium (Mg).

3. Biology, mica, and clay

3.1 Membranes and the origins of life

Membranes on mica have been observed by Atomic Force Microscopy [74-76]. Vesicles on mica fuse to form extended bilayers and multilayers. Even without lipids, however, mica sheets could have provided partially enclosed spaces for emerging life, before the molecules of emerging life were enclosed in membranes. Membranes can be fragile. They leak, acquire and lose molecules, swell, and rupture. Membranes of living cells are highly evolved structures that provide more extensive support for their contents than primitive vesicles and membranes.

Lipid membranes might not have been essential at the early stages of the origins of life [77]. "The evolution of … membranes would … be [a] late development" say Root-Bernstein et al. in their paper about 'prebiotic ecology [77]. An 'ecosystems first' perspective is proposed by Baum and others, based on their intriguing research involving chemical selection on mineral surfaces [78]. "If even one enzyme were missing, all metabolic processes would cease," according to a skeptic about abiogenesis [79].

Perhaps, instead of membranes, protolife evolved as an acellular ecosystem, sharing all the necessary enzymes in an open system. Imagine pieces of this ecosystem periodically encapsulating in membranes. Nearly all of these membrane-encapsulated protocells would lack some essential component of life or enzyme. Occasionally a membrane-encapsulated protocell would contain all the essential components of life and became alive. Occasionally one of these living protocells would reproduce and begin seeding Earth with Life. On the

other hand, there is also a school of thought in which membranes are the enclosed spaces where proto-life first evolved, e.g., [80].

3.2 Membraneless biomolecular condensates

There is an increasingly popular alternative to membranes at the origins of life – 'membraneless biomolecular condensates' or 'membraneless organelles'. Peptides/proteins and RNA interact in membraneless condensates in living cells, as nucleoli and other particles [81-83]. These particles form by liquid-in-liquid phase separation (LLPS) [84]. Membraneless biomolecular condensates are increasingly of interest to origins-of-life researchers [55, 85-89].

Ribosomes are ancient biomolecular condensates, composed of proteins and RNA, and are now necessary for translating nucleic acids into proteins. Ribosomes were present in the Last Universal Common Ancestor of life (LUCA) [90]. When life was coming into being, in the pre-LUCA stages, ribosomes and their precursors may have been early 'membraneless organelles', protected within mica sheets [55]. Prokaryotic ribosomes are ~20 nm in diameter, comparable to the thickness of 20 mica sheets (see Fig. 1 for scale).

3.2 DNA and RNA on mica

RNA polymers form, non-enzymatically, on a mica surface during wet-dry cycles. Nucleotide monophosphates of Adenine (A), Guanine (G), Cytosine (C) and Uracil (U) on mica were cycled through wet-dry cycles at 80^{o}C and imaged by Atomic Force Microscopy (AFM) [91]. This simple process, with no enzymes or activated nucleotides, produced RNA on bare mica. RNA lengths were ~100-1000 nucleotides, which is about an order of magnitude longer than the RNA lengths obtained when polymerization occurred in the presence of lipids [20]. It makes sense that mica's anionic crystal lattice is a better substrate than lipids, for polymerizing RNA, because RNA has the same periodicity – 0.5 nm – as mica's crystal lattice. Mica may have been a template for RNA polymerization at life's origins. Perhaps nucleic acid linkages are 3'-5' and not 2'-5' because mica sheets served as a template that favored 3'-5' linkages. Perhaps nucleotide templating on mica prevented diphosphate linkages, which form a bent polymer.

DNA binds reversibly to mica in the presence of various divalent inorganic cations. For example, freshly cleaved mica was soaked in 33 mM magnesium acetate to bind DNA to mica for early imaging by AFM in air [92] (Fig. 6). With AFM in aqueous fluid, stable DNA imaging on mica was observed when Ni^{++}, Co^{++}, and Zn^{++} salts were present; in contrast, DNA binding was not strong enough for AFM imaging when salts of Mn^{++}, Cd^{++}, Hg^{++}, or K^{+} were used [93]. DNA transcription by RNA polymerase was observed by AFM when Zn^{++} was alternately added, to bind the DNA to mica, and removed, to allow polymerase activity [94].

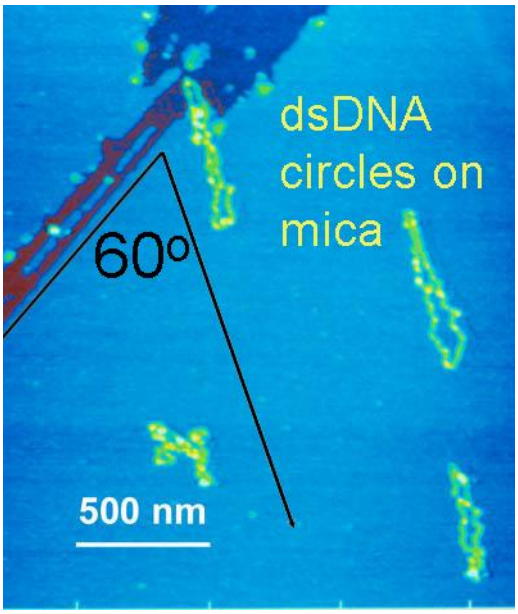

Figure 6. Atomic Force Microscopy of double-stranded DNA (dsDNA) circles on mica with cracks (dark streaks at upper left). Three of the 4 dsDNA circles form a 60-degree angle with the mica crack, consistent with alignment on mica's hexagonal crystal lattice.

3.3 Sugars

Sugars, especially ribose, are a major biomolecule in living systems. A plausible prebiotic reaction for forming sugars is the formose reaction, in which formaldehyde reacts to form sugars [95]. In a test tube, the end products become increasingly large polymers of sugars, branched sugar polymers, and eventually a tarry mess. Monosaccharides are the desirable product, at the origins of life [96]. If the reaction is the tightly confined between mica sheets, simpler sugars might predominate. Mica's anionic hexagonal lattice may also favor linear oligosaccharides over branched or bent ones. The formose reaction produces a simple sugar when the reactants are confined in vesicles [97].

4. Mica, clays, and life

Mica sheets, and clays, have similarities with life, as would be expected for places where life might have originated (Table 1) [48, 53]. Mica sheets, clay sheets, and nucleic acid polymers are all anionic, with exchangeable inorganic cations. The anionic sites on the surfaces of mica and clay sheets have a periodicity of 0.5 nm, which is also the spacing of phosphate groups in single-stranded nucleic acids. Hydrogen bonds (H-bonds) form in vast numbers in living (and non-living) systems. H-bonds form between organic molecules and the mica surface [98]. Both mica sheets and enzymes have open and shut motions that do work on the molecules between them. As the title of a recent article says, 'Enzymes at work are enzymes in motion' [99]. The motion of enzymes is powered by chemical energy, primarily ATP. The motion of mica sheets is powered primarily the thermal disequilibria.

Life	Mica
Cellular	Stacks of thin mineral sheets separate 'cellular' spaces
High in Potassium ions $[K^+]_{cytoplasm}$ ~ 100 mM	Potassium ions bridge mica sheets $[K^+]$ ~ 100 mM for mica sheets ~ 0.7 nm apart*
Nucleotides polymerize to DNA & RNA	Nucleotides polymerize to RNA in wet/dry cycles**
0.5 nm spacing of anionic phosphates in ssDNA & sugars in carbohydrates	0.5 nm anionic crystal lattice on mica surface
Exchangeable inorganic cations bridge anionic sites on molecules such as DNA	Exchangeable inorganic cations bridge anionic sites between mica sheets
Low in entropy	Low in entropy
Water-rich	Hydrophilic
Forms H-bonds	Forms H-bonds
Mechanical energy of enzyme motion	Mechanical energy from moving mica sheets*
Synthesis of biomolecules in confined spaces & on surfaces	Supports chemistry of confinement & solid phase synthesis
Filled and covered with lipid membranes	Supports lipid membranes & vesicles

Table 1. Ways in which life imitates mica

Mica shares these characteristics with clays and some other minerals, except for the following characteristics:

*Not in swelling clays

**Demonstrated at present only on a mica substrate, when non-activated nucleotide monophosphates were used [91].

5. Dielectric constant at surfaces

The Dielectric constant, or permissivity, of water is 80 for bulk water but only ~2 for the first 2 or 3 water layers above a surface (ca. 2 nm) [100, 101]. This means that the charges on charged molecules will become progressively unscreened as the charged molecules approach the mica surface. Electrostatic forces will be strong, pulling cations and cationic molecules to surfaces such as those of micas and clays, and forming bridges between anionic organic molecules and the mineral surface.

6. Crowding

"There is a growing consensus that confinement may have facilitated the transformation of inanimate matter into living organisms … Compartments of various sizes exist between the sheets of mica; these compartments may have provided confined spaces for the isolation and stabilization of supramolecular assemblies and protocells …" [102].

Molecules in cells are crowded. The space between protein molecules in cells is typically only 10 nm [103]. Crowding speeds up the rates of reactions that are diffusion limited [104]. Crowding may even be the

origin of homochirality [54]. Given the molecular crowding in living cells, molecular crowding at life's origins is a desirable scenario for hypotheses about the origins of life. Molecules in wet-dry cycles become crowded during the drying phase. Molecules that bind to a surface, e.g., the mica surface, will become concentrated and crowded. Molecules in narrow spaces between mica sheets will typically be crowded, by the mica sheets above and below, in addition to crowding by other molecules. Clays will also crowd molecules between their sheets, but clay's swelling will then dilute molecules. Swelling to even 2 layers of water molecules between Na-montmorillonite clay sheets reduces the interaction energy between sheets to near zero, according to molecular modeling [105]. Thermophoresis is another way to concentrate molecules, in a spatially confined thermal gradient, and even to escalate nucleotide polymerization [106, 107].

Confinement chemistry would occur between mica's sheets and during drying and during the compression stage of mechanochemistry. Chemistry in confined spaces produces fewer different molecules and simpler molecules [108, 109]. Confined spaces also help proteins fold [110, 111]. Enzymes confine their substrates to facilitate the enzymatic reactions. Zeolites mimic enzymes in some respects [112]. Confinement chemistry is likely to be a characteristic of any good hypothesis for the origins of life.

7. Conclusions

Dyson says error tolerance is essential for life's origins [113]. With the redundancy of the vast areas between biotite mica sheets, in micaceous clay, almost everything can go wrong, and life can still emerge. If not from micaceous clay, life emerged from some other habitat with vast error tolerance.

The experimental method traditionally starts with a hypothesis, followed by experimentally testing the hypothesis. Testable hypotheses are presented here. Experimental results will show what is possible today. The origins of life, however, are partly a historical science in which much will remain hypothetical, both experiments and ideas [114]. Experimental results give us ideas about how life might have originated, but they cannot absolutely prove how life originated, though strong experimental results are seen as convincing evidence [70]. On the other hand, the strong experimental results of Miller and Urey in 1953 [115] are now primarily an inspiration for origins research, not a major part of abiogenesis [116].

Biology may have emerged from the spaces between biotite sheets in micaceous clay. We will probably never know for certain whether this is true or not.

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