Mechanical Energy and Mica Sheets at the Origins of Life

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http://web.physics.ucsb.edu/~hhansma/mica.htm
Why Mechanical Energy?

- **WHY** do enzymes move, open and shut, using mechanical energy, when this mechanical energy now comes from chemical energy such as ATP?

  **MAYBE** mechanical energy came before chemical energy at the origin of life.
Endless Energy Source

If life originated between the sheets of mica, there was an *endless energy source* from the *mechanical energy* of moving mica sheets.

Black Mica - Biotite
Micas are 5% of Earth’s Minerals
Overview of Origin of life between Sheets of Mica
Origin of Life between the Sheets of Mica

1. This is where the idea started - mica from an abandoned 'mine' with algae growing at edges of mica sheets:

2. In a "Mica World," molecules accumulate between mica sheets, evolving into protocells...

3. Powered by the Mechanical Energy of moving mica sheets:

4. Which can push molecules into the attractive regime of the potential energy curve...

5. On mica's 0.5-nm anionic crystal lattice:
MechanoChemistry in the Lab & Testing MechanoChemistry between Mica Sheets
Mechanical Energy for Mechano-Chemistry

Synthetic organic mechanochemistry has been used to produce organic molecules, including:

- pyrimidines,
- peptides,
- nucleosides,
- optically active products,
- oxidations,
- reductions,
- condensations,
- nucleophilic reactions, and
- cascade reactions

Testing Mechano-Chemistry between Mica Sheets

1. Make a 'sandwich' of split mica sheets with a 'prebiotic' reaction mixture between them.

2. Cycle the mica 'sandwich' through cycles of: wet-dry / temperature / pressure.

(Would need a special chamber for pressure cycles)
Possible Reaction Mixtures:

1. Proto-peptide / depsipeptide [Center for Chemical Evolution]
2. Vesicle-forming mixtures [Deamer - Damer]
3. Formose reaction for sugar syntheses from formaldehyde
4. Ester that fluoresces when enzymatically cleaved [Deamer]
5. Other?
Analyzing the Results

- Use a fluorometer for fluorescent products
- Otherwise, use XPS [X-ray Photoelectron Spectroscopy] or SIMS [Secondary Ion Mass Spectroscopy]


In all cases, the duration of the experiments will be short, relative to the time elapsed during the actual origins of life. Vanishingly small quantities of product will be formed. Thus, this is bleeding edge research.
Problems with the Formose Reaction
Tar Problem in the Formose Reaction for Sugar Syntheses

The tar problem

Biomolecules plus heat and time
The tar problem

Biomolecules plus heat and time

- How can formation of wasteful byproducts like tars be prevented?
Confined in a ‘Mica World’ – Formose Reaction with No Tar Problem?

\[
\begin{array}{c}
\text{H}_2\text{C} = \text{O} \quad \text{H}_2\text{C} = \text{O} \\
\text{H}_2\text{C} = \text{H} \quad \text{H}_2\text{C} = \text{H}
\end{array}
\xrightleftharpoons{\text{Ca}^{++}\text{OH}^-} \text{Formaldehyde}
\]

In confined spaces, chemical reactions produce smaller and fewer reaction products.
More about ‘Mica World’
Origin of life between the sheets of the black mica, Biotite?
“Biotite Mica World” - better than what?

Arrows show same location at both stages

Better than

Muscovite Mica World

Early stage

~10 nm

~1 micron

Early stage

~10 nm

~1 micron
Why is Biotite Mica better than Muscovite Mica for the Origins of Life?

- High in iron (Fe), biotite is capable of **redox reactions**, which were essential for life’s origins.
- It’s the most electrically conductive mica.
- It’s found on Mars.

Biotite, soaked several days in Water: Chlorox (NaOCl):

\[
\text{Fe(II)} \xrightarrow{\text{Chlorox}} \text{Fe(III)} + e^- \]

1 cm
Biotite has anionic mineral sheets, bridged by cations, is like living systems, which have anionic polymers and mobile counterions.

\[ \text{K(Mg,Fe)}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2. \]

Biotite Mica

K+ excludes water between adjacent mica sheets, unlike Na+ whose smaller ions are hydrated between clay sheets. Clay swells when wet. Mica doesn’t swell, providing a more stable environment for life’s origins.

Fe(II) is \(~80-90\%\) of Total Fe [Fe(III) + Fe(II)]

*Quaternary Research 59 (2003) 262–270
Moving Mica Sheets do Work on Molecules

Air bubbles in mica
The Ultimate in Crowding: Mechanochemical Synthesis

- Peptide bond free energy of hydrolysis, $\Delta G \sim -2.4$ kcal/mole or
- $\sim 170$ pN x 1Å as work for peptide bond synthesis

MechanoChemistry has been used to synthesize pyrimidines, peptides, nucleosides, optically active products, oxidations, reductions, condensations, nucleophilic reactions, and cascade reactions [by grinding...] Wang, G.-W., Chemical Society Reviews, 2013.
Biomolecules adsorb to mica

DNA on mica in atomic force microscope and Lipid Vesicles

‘Swimming’ DNA

Ni\textsuperscript{2+}, Co\textsuperscript{2+} & Zn\textsuperscript{2+} hold DNA on mica under fluid.
Mica Lattice Oriented Molecules

- DNA molecules
- aligned with the hexagonal lattice of mica
- in the Atomic Force Microscope (AFM)

0.5-nm anionic hexagonal lattice of mica in AFM
dsDNA circles on mica

60°
Hydrogen Bonds (H-Bonds) on Mica!

- H-bonds form between biological molecules and the surface of mica.
- H-bonds are essential for life.

Water layers on surfaces don’t screen charges

- Bulk water insulates charged molecules 40 times better than water in the first 2-3 water layers above a surface.
- Water molecules on mica provide almost no screening of charges
- Charged molecules on mica will interact strongly with mica’s surface charges.

Could Mica Schist have enough mechanical energy to power a ‘Mica World’?

Maybe…

Mica flakes

3.5 cm
Biology from Biotite Schist?

Schist

Flakes from mica schist
- = left rock in Schist photo
- Largest flake ~600 microns
- Smallest flakes ~70 microns

Biotite world on the scale of Schist:

~ 1 micron long biotite flake
## Properties of Life & Mica


<table>
<thead>
<tr>
<th>Life:</th>
<th>Mica:</th>
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</thead>
<tbody>
<tr>
<td>Cellular</td>
<td>Stacks of thin mineral sheets separating ‘cellular’ spaces</td>
</tr>
<tr>
<td>High in Potassium, K⁺</td>
<td>High in potassium, K⁺</td>
</tr>
<tr>
<td>([K^+]_{\text{cytoplasm}} \sim 100 \text{ mM})</td>
<td>([K^+] \sim 100 \text{ mM between mica sheets }\sim0.7 \text{ nm apart})</td>
</tr>
<tr>
<td>Full of anionic polymers such as DNA &amp; phospholipids</td>
<td>Anionic surfaces</td>
</tr>
<tr>
<td>Low in entropy</td>
<td>Low in entropy</td>
</tr>
<tr>
<td>0.5 nm spacing of anionic ssRNA phosphates &amp; sugar residues in carbohydrates</td>
<td>0.5 nm grid of anionic sites</td>
</tr>
<tr>
<td>Inorganic cations bridge anionic sites on molecules such as DNA</td>
<td>Inorganic cations bridge anionic sites</td>
</tr>
<tr>
<td>Forms H-bonds</td>
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<tr>
<td>Water-filled</td>
<td>Hydrophilic</td>
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<tr>
<td>Filled &amp; covered with lipid membranes</td>
<td>Supports lipid membranes &amp; vesicles</td>
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<tr>
<td>Mechanical energy of enzymes</td>
<td>Mechanical energy of moving mica sheets</td>
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<tr>
<td>Synthesizes biomolecules in confined spaces, on surfaces</td>
<td>Chemistry of confinement &amp; solid phase synthesis</td>
</tr>
<tr>
<td>Eats &amp; excretes</td>
<td>Fluid flow between sheets brings in ‘food.’ removes ‘wastes’?</td>
</tr>
<tr>
<td>Evolves</td>
<td>Provides isolation as needed for Darwinian evolution</td>
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Acknowledgments

Thank you to my brother Jim Greenwood for raising the question of Biotite – and for leading the hike to the mica mine in 2006!

And to my many other colleagues for their interest and input.