Mechanical Energy and Mica Sheets at the Origins of Life

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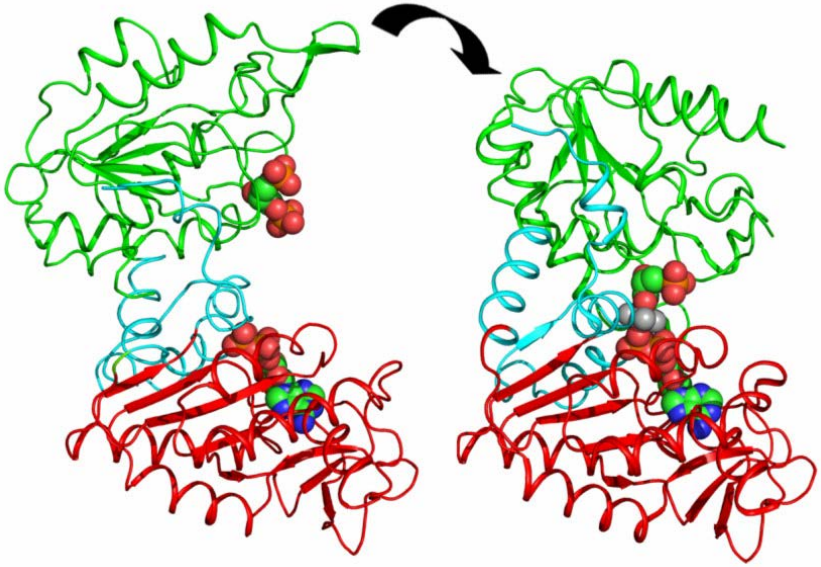
http://web.physics.ucsb.edu/~hhansma/mica.htm

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?



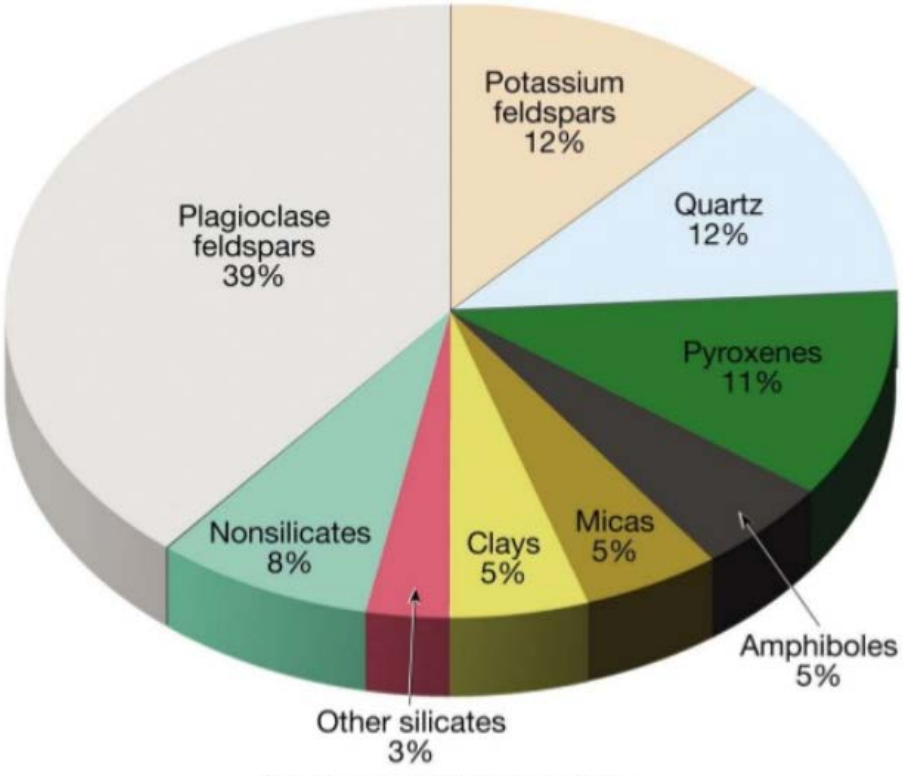
MAYBE mechanical energy came before chemical energy at the origin of life.

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

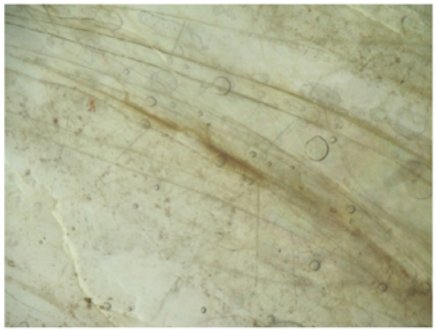


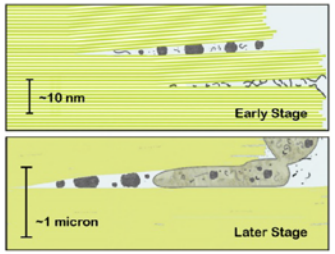
Overview of Origin of life between Sheets of Mica

Origin of Life between the Sheets of Mica

(More about this later)

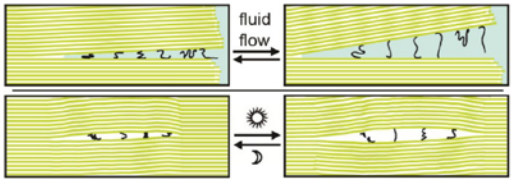
1. This is where the idea started - mica from an abandoned 'mine' with algae growing at edges of mica sheets:

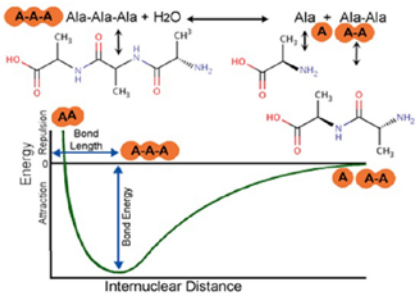




2. In a "Mica World," molecules accumulate between mica sheets, evolving into protocells...

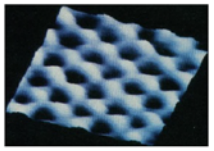
3. Powered by the Mechanical Energy of moving mica sheets:





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

5. On mica's 0.5-nm anionic crystal lattice:



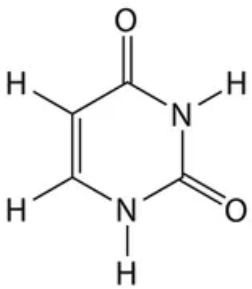
AFM image

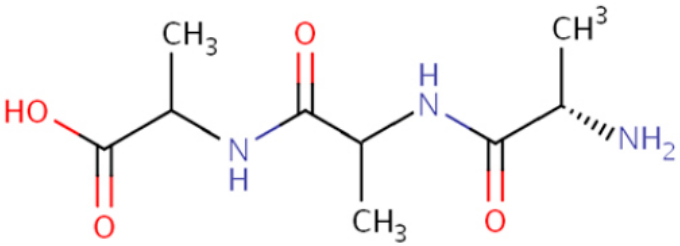
MechanoChemistry in the Lab
&
Testing MechanoChemistry between Mica Sheets

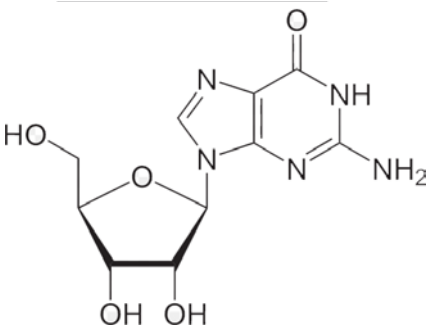
Mechanical Energy for Mechano-Chemistry

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





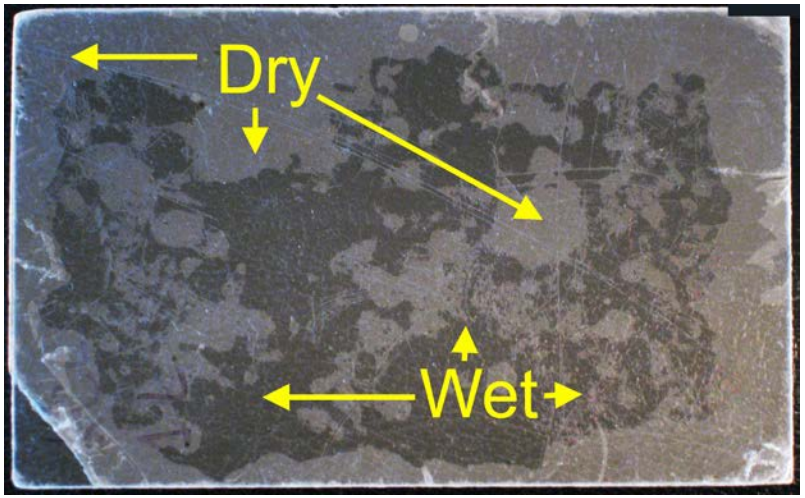


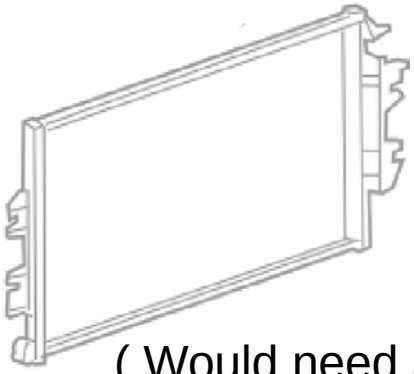
- Wang, G.-W. Mechanochemical organic synthesis. Chem. Soc. Rev. **2013**, 42, 7668–7700.
- Raj, T.; Sharma, H.; Mayank; Singh, A.; Aree, T.; Kaur, N.; Singh, N.; Jang, D.O. “Solvent-Less Mechanochemical Approach to the Synthesis of Pyrimidine Derivatives. ACS Sustain. Chem. Eng. **2017**, 5,1468–1475.

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?

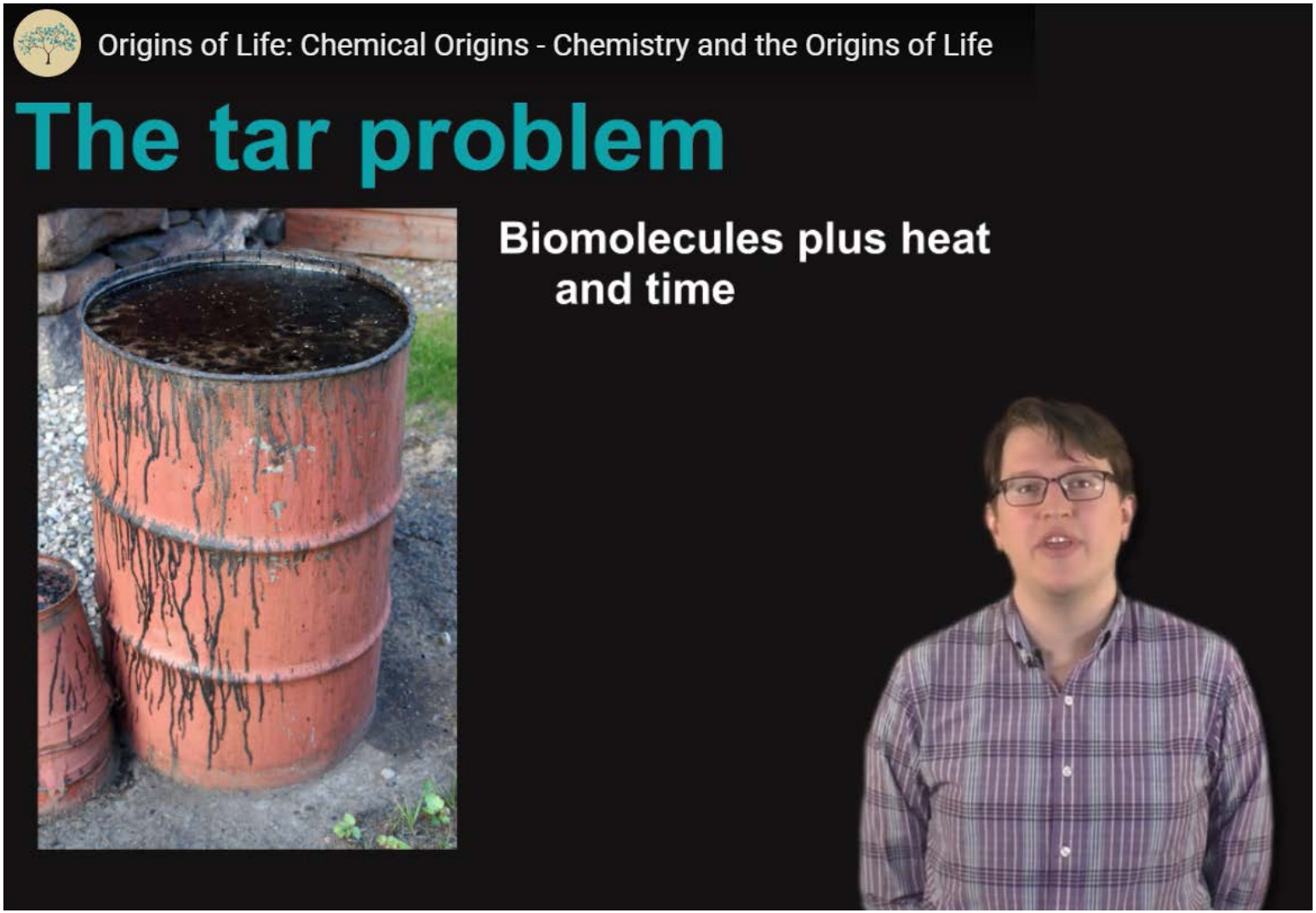
Analyzing the Results

- Use a fluorometer for fluorescent products
- Otherwise, use XPS [X-ray Photoelectron Spectroscopy] or SIMS [Secondary Ion Mass Spectroscopy] http://www.virginia.edu/ep/SurfaceScience/comparison_of_surface_analysis_techniques.htm

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

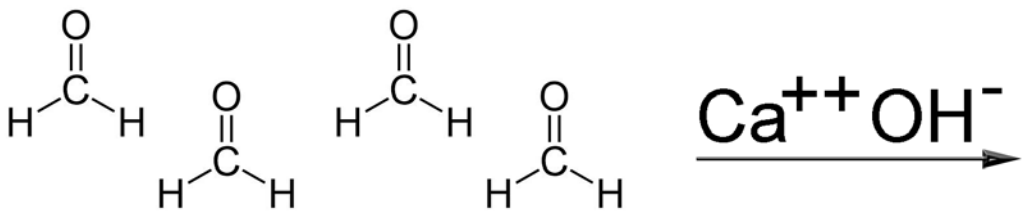


The tar problem

Biomolecules plus heat and time

- How can formation of wasteful byproducts like tars be prevented?

Confined in a ‘Mica World’ – Formose Reaction with No Tar Problem?

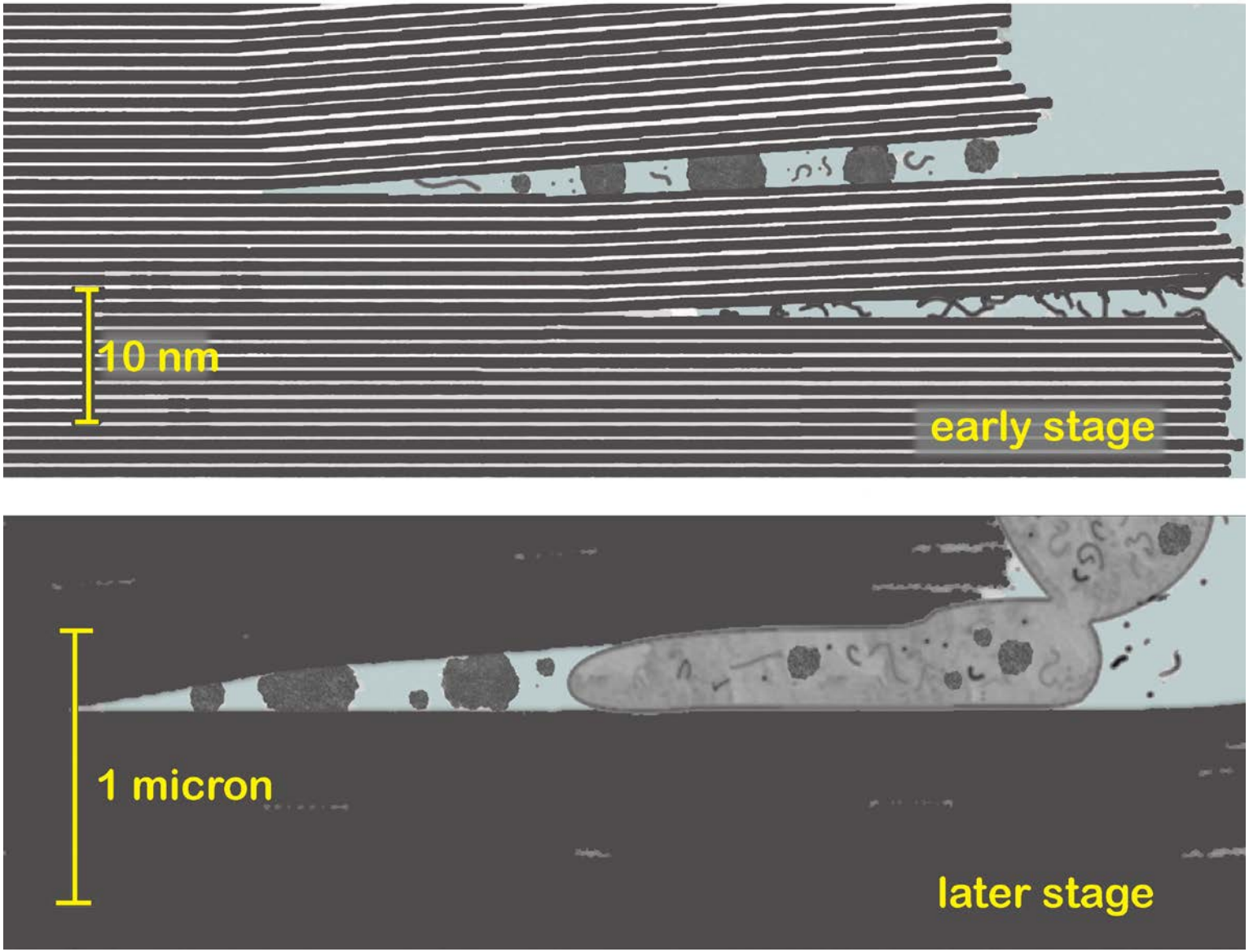


Formaldehyde

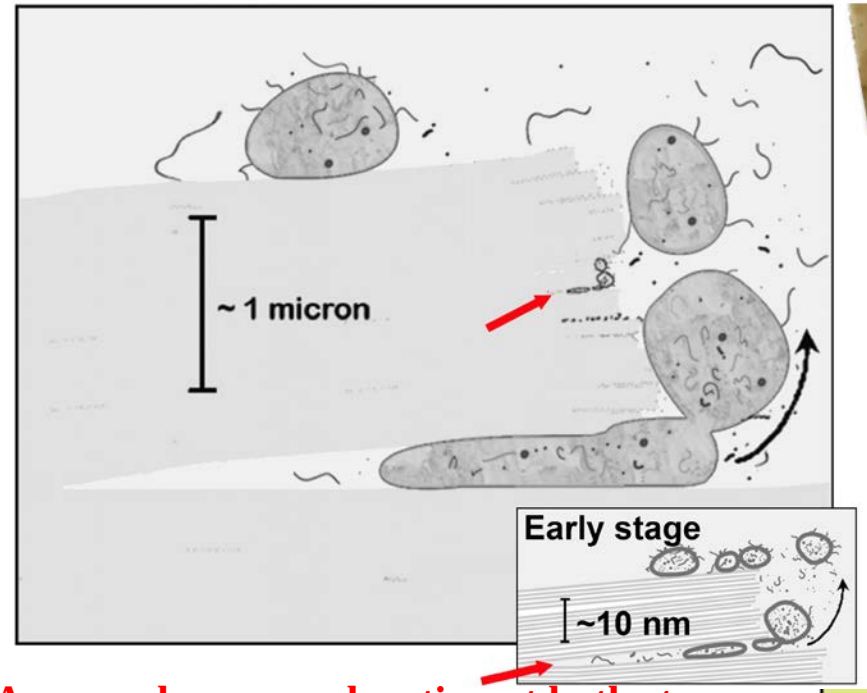
In confined spaces, chemical reactions produce smaller and fewer reaction products.

More about
‘Mica World’

Origin of life between the sheets of the black mica, Biotite?

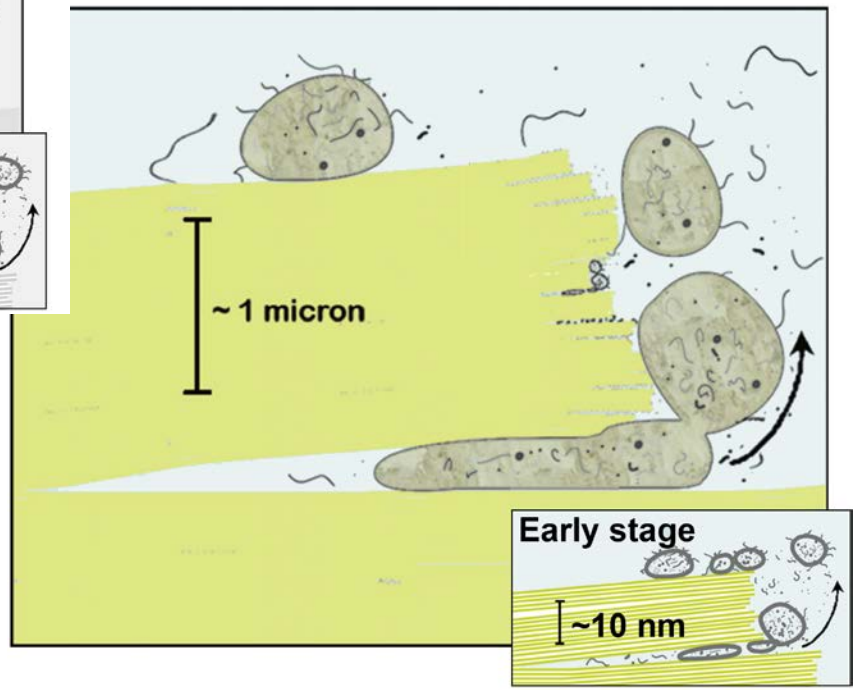


“Biotite Mica World” - better than what?

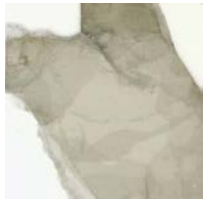


Better than

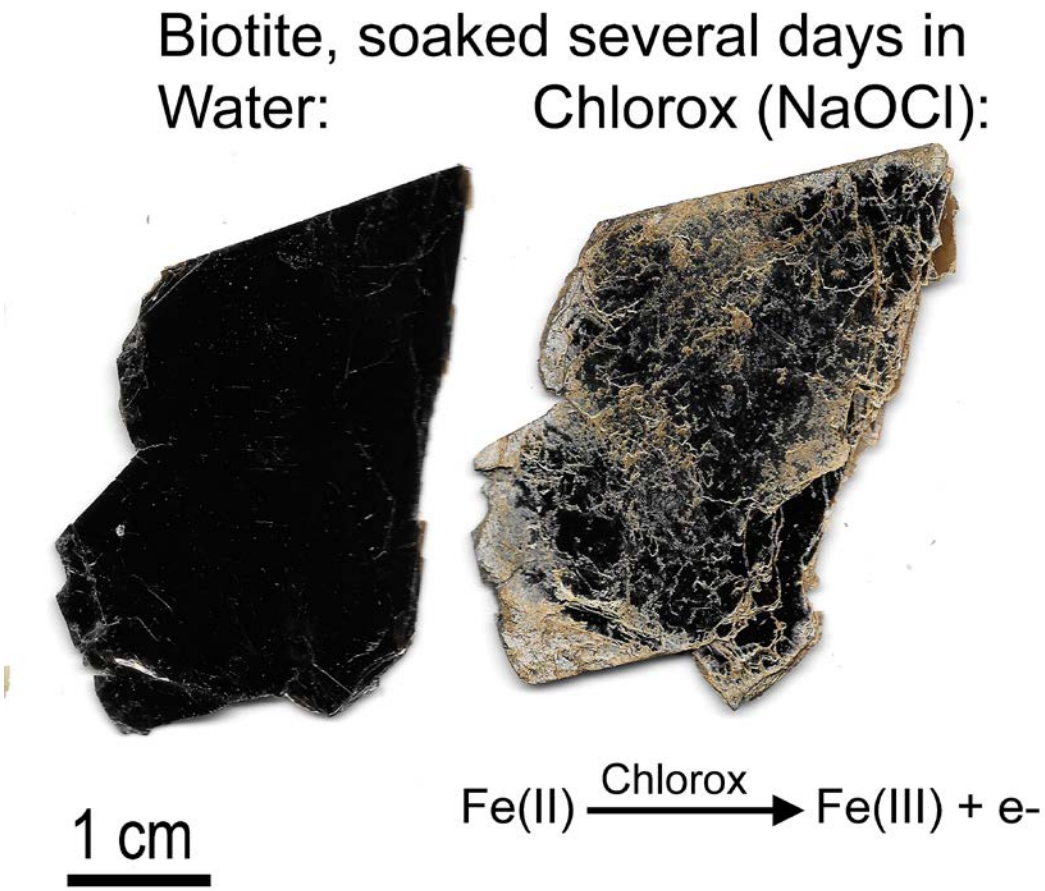
Muscovite Mica World



Arrows show same location at both stages



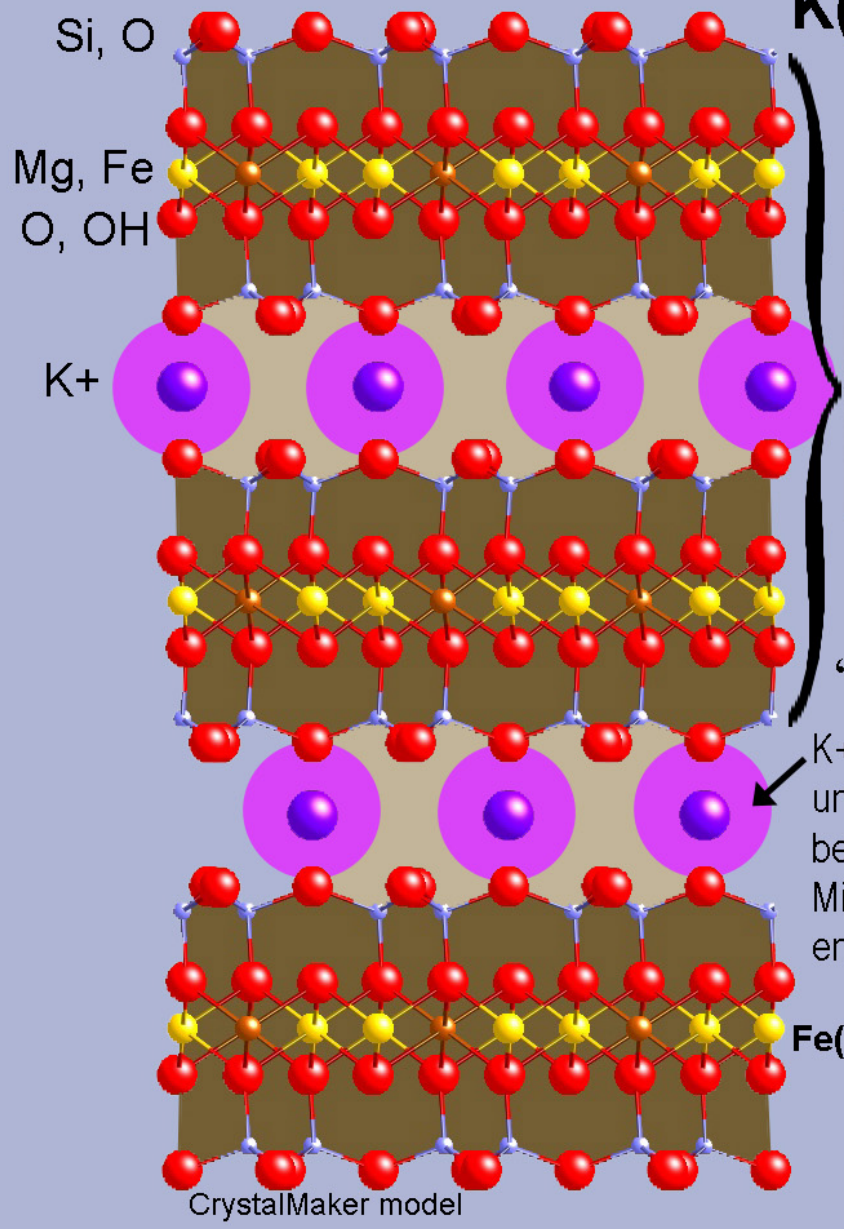
Why is Biotite Mica better than Muscovite Mica for the Origins of Life?



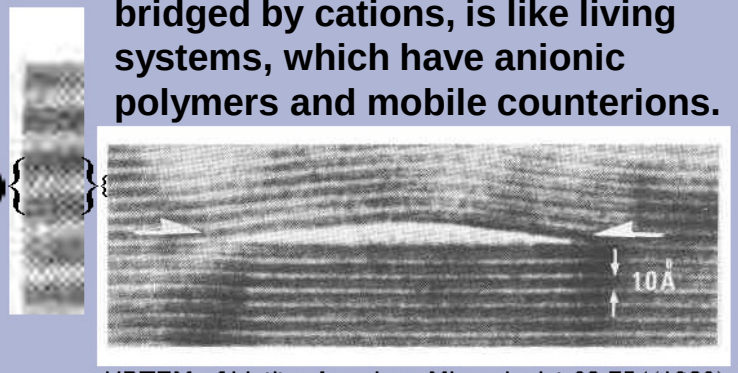
- High in iron (Fe), biotite is capable of **redox reactions**, which were essential for life's origins.
- It's the most electrically conductive mica.
- It's found on Mars

K(Mg,Fe)3(AlSi3O10)(OH)2.

Biotite Mica



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



HRTEM of biotite. American Mineralogist 68:754(1983)

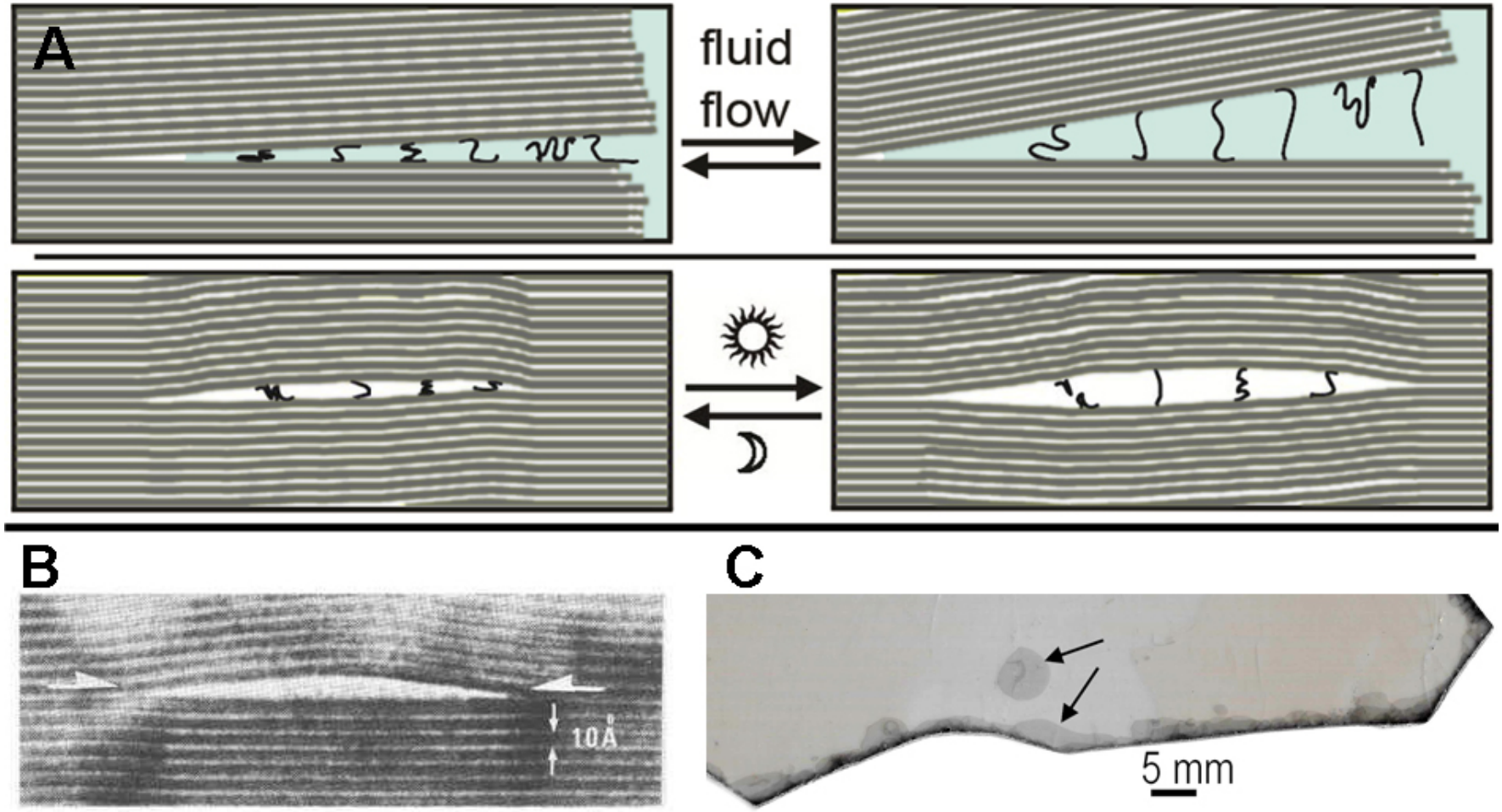
"{" or "}" = 2 biotite layers

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)]*

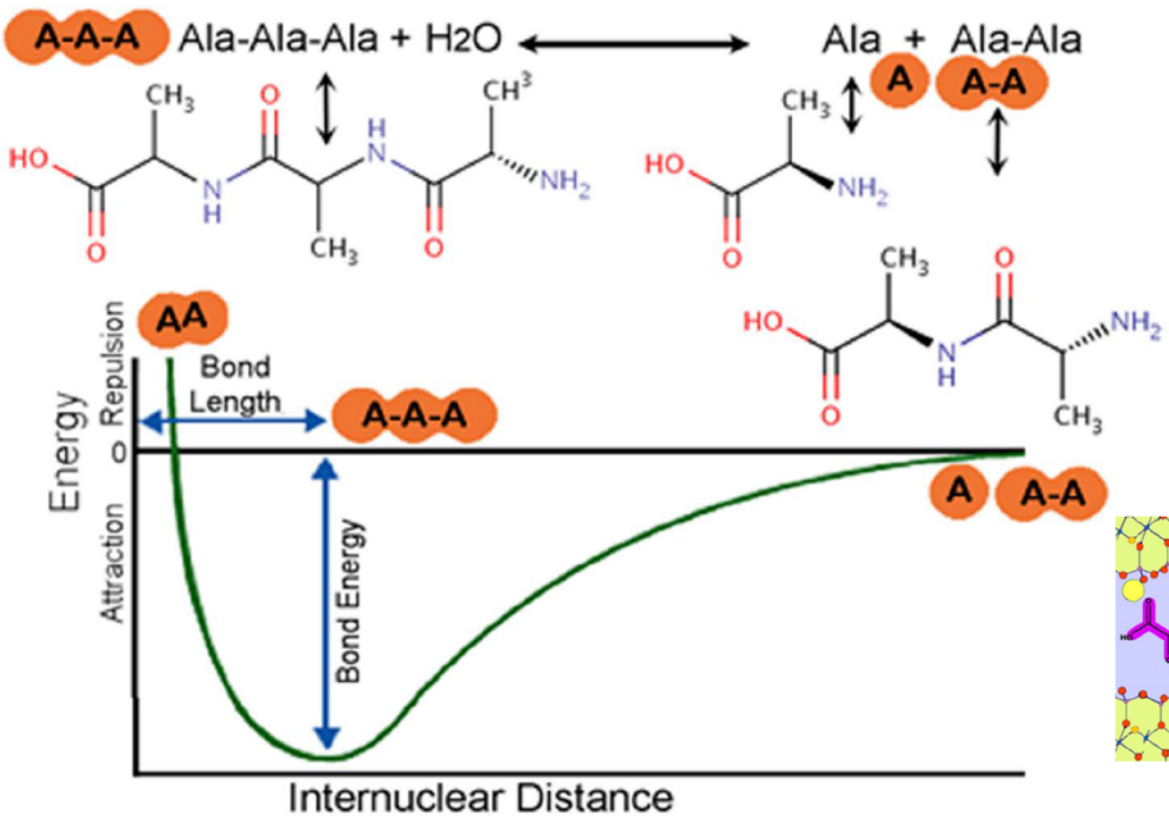
*Quaternary Research 59 (2003) 262–270

Moving Mica Sheets do Work on Molecules

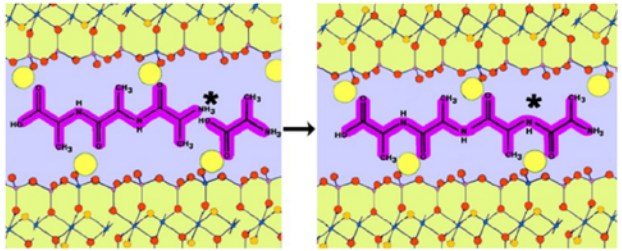


Air bubbles in mica

The Ultimate in Crowding: Mechanochemical Synthesis



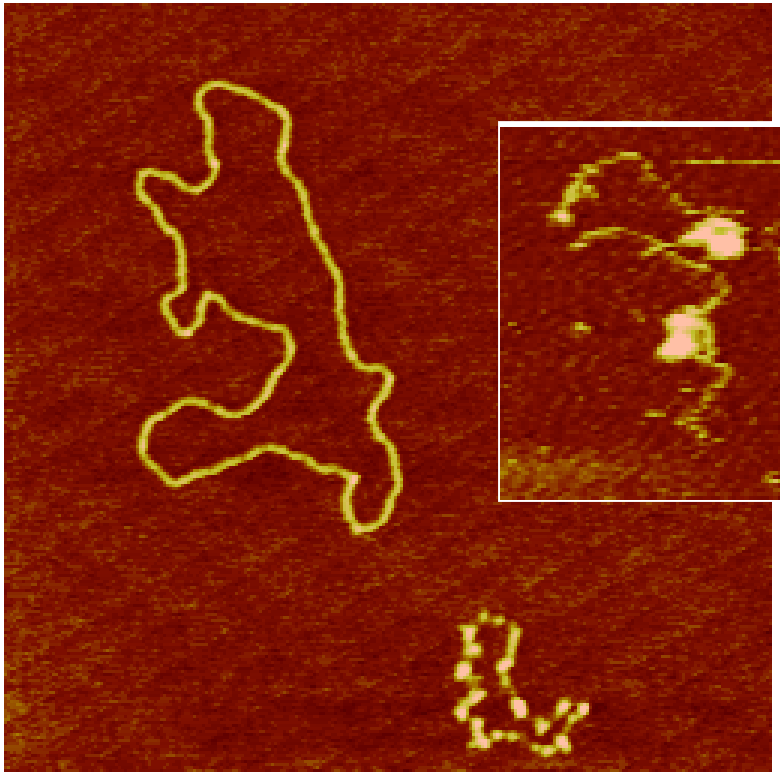
- Peptide bond free energy of hydrolysis, ΔG ~ -2.4 kcal/mole or
- ~170 pN x 1Å as work for peptide bond synthesis



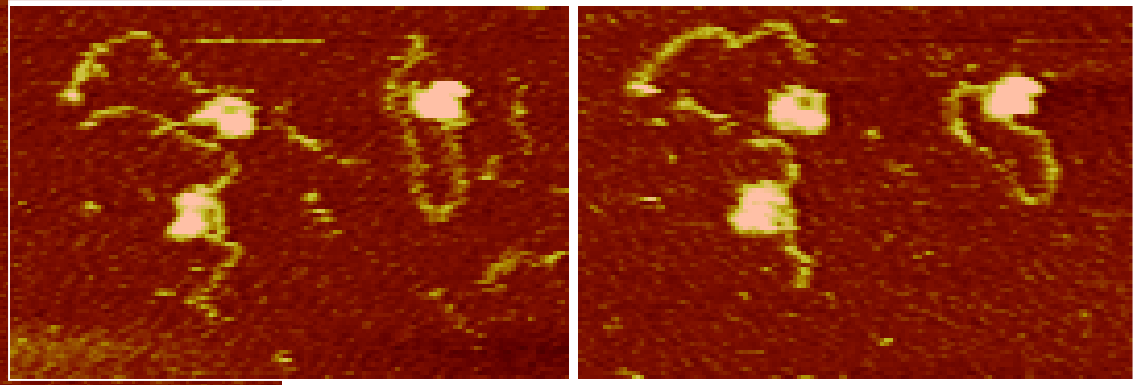
[Hansma 2010]

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



‘Swimming’ DNA



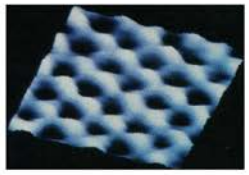
Ni^{2+}, Co^{2+} & Zn^{2+} hold DNA on mica under fluid.

DNA on mica in atomic force microscope

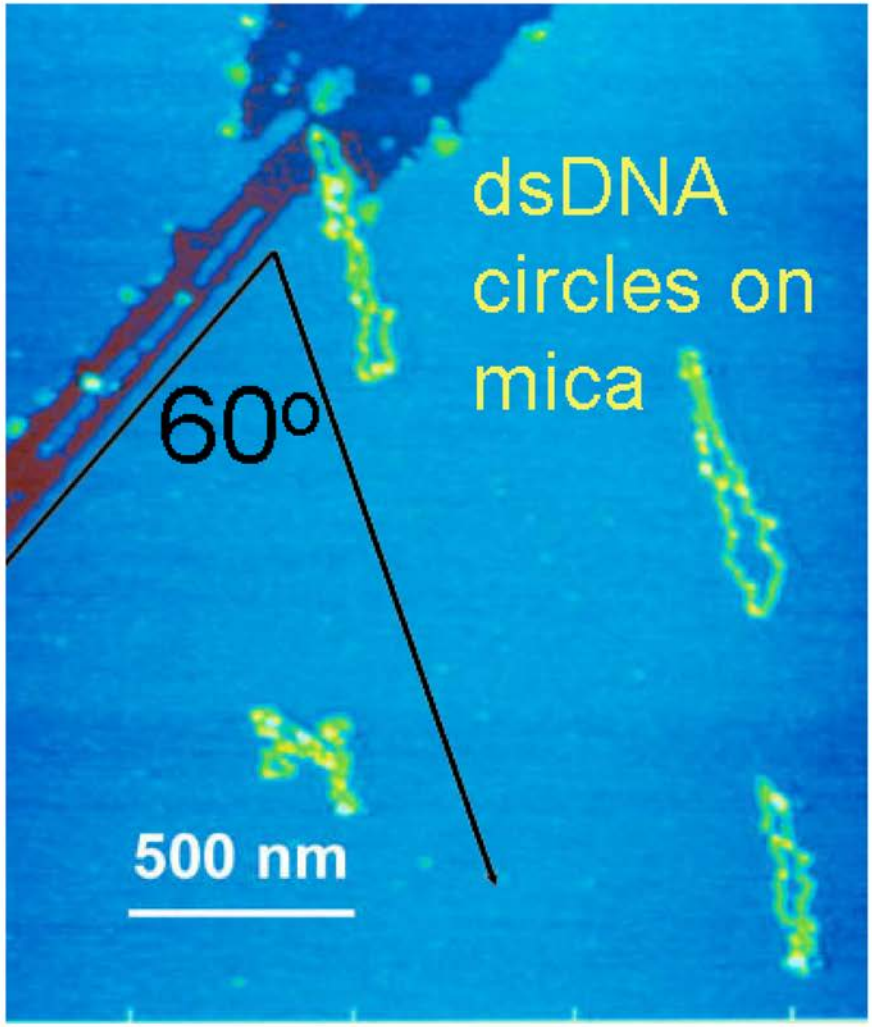
and Lipid Vesicles

Mica Lattice Orients Molecules

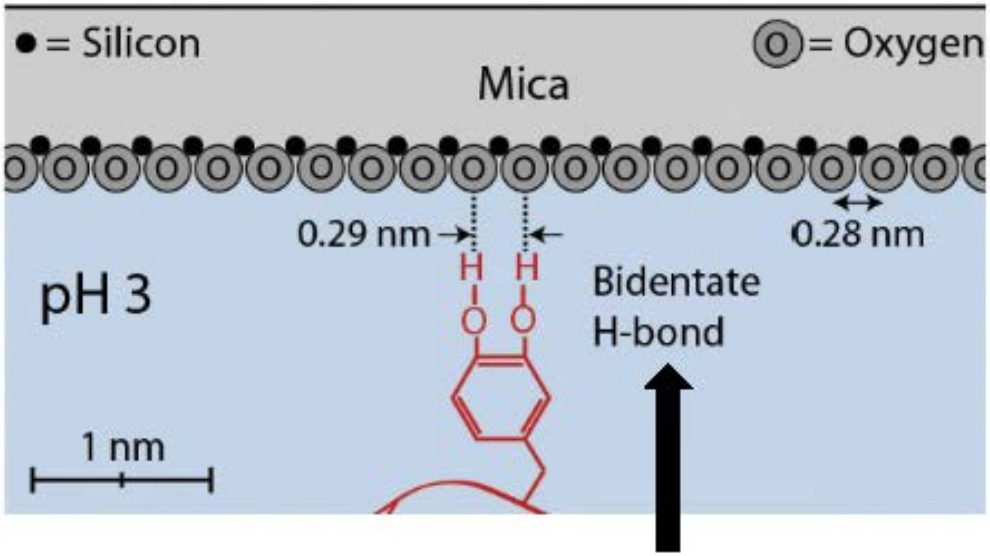
- DNA molecules
- aligned with the hexagonal lattice of mica
- in the Atomic Force Microscope [AFM]



0.5-nm anionic hexagonal lattice of mica in AFM



Hydrogen Bonds (H-Bonds) on Mica!



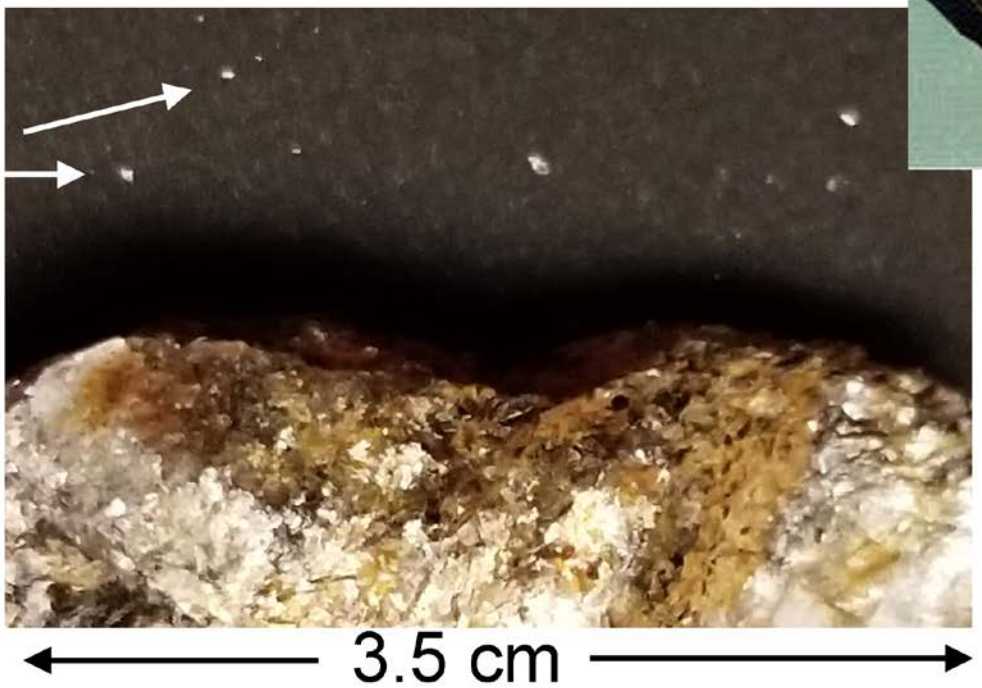
Modified from Yu, Jing, et al. "Adaptive hydrophobic and hydrophilic interactions of mussel foot proteins with organic thin films." *Proceedings of the National Academy of Sciences* 110.39 (2013): 15680-15685.

- **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.
- Fumagalli, L., et al. "Anomalously low dielectric constant of confined water“; Kalinin, S. V. **"Feel the dielectric force" Science (2018).** Dielectric constant of bulk water = 80; confined water = 2

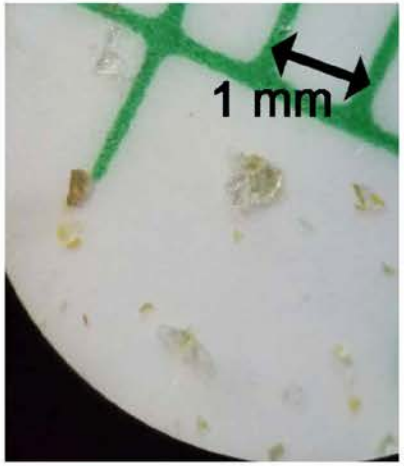
Could Mica Schist have enough mechanical energy to power a ‘Mica World’?



Maybe …

Biology from Biotite Schist?

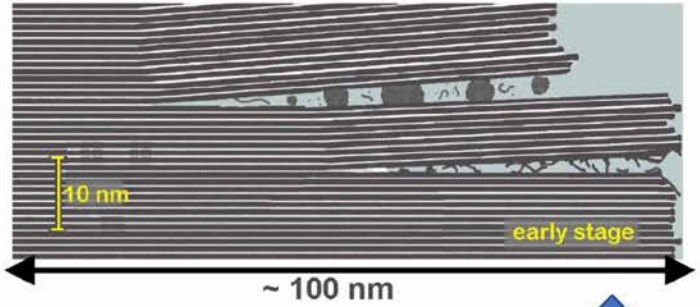
Schist



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

http://web.physics.ucsb.edu/~hhansma/mica.htm

Life:	Mica:
Cellular	Stacks of thin mineral sheets separating 'cellular' spaces
High in Potassium, K^+ $[K^+]_{cytoplasm}$ ~ 100 mM	High in potassium, K^+ $[K^+]$ ~ 100 mM between mica sheets ~0.7 nm apart
Full of anionic polymers such as DNA & phospholipids	Anionic surfaces
Low in entropy	Low in entropy
0.5 nm spacing of anionic ssRNA phosphates & sugar residues in carbohydrates	0.5 nm grid of anionic sites
Inorganic cations bridge anionic sites on molecules such as DNA	Inorganic cations bridge anionic sites
Forms H-bonds	Forms H-bonds
Water-filled	Hydrophilic
Filled & covered with lipid membranes	Supports lipid membranes & vesicles
Mechanical energy of enzymes	Mechanical energy of moving mica sheets
Synthesizes biomolecules in confined spaces, on surfaces	Chemistry of confinement & solid phase synthesis
Eats & excretes	Fluid flow between sheets brings in 'food.' removes 'wastes'?
Evolves	Provides isolation as needed for Darwinian evolution

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.