The Potential Roles of Minerals in the Origins of Life

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Art Credit: Dr. Bakhtiyor Rasulev, Jackson State University
Sahai Research Group
Outline of Presentation

- Time-line of Earth History

- Habitability
  - Early Earth Environments for the Origins of Life (OoL)
  - Modern Earth Environments
  - Other Worlds

- Minimal Definition of “Life.” Common Origin of all Life

- Potential Effects of Minerals on “Protocell” Emergence

- Predictive Model for Mineral Effects?
Time Line of Early Earth Events

- Oldest Zircon Crystal: 4.4 billion years old
- BIFs: Some atm $O_2$
- Liquid Water
- Isua: First Sedimentary Evidence for Oceans and Earliest Isotopic Evidence for Life
- Apex Chert: Earliest Fossils
- First Cells with Nucleus
- First Hard-shelled Animals
- Rise in Atmospheric Oxygen
- Acasta Oldest Rock
- Moon Formation
- Formation of Core
- Hadean Era
- Archaean Era
- Proterozoic Era
- Phanerzoic Era

MINIMAL DEFINITION OF LIFE
A Common Origin: Minimal Protocell

mass transport in and out

genes: reproduction

membrane boundary

metabolism: trans-membrane, catalyzed energy transfer cycles

$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Potential Roles of Minerals in Protocell Evolution

Do the potential mineral effects depend on their properties such as crystal structure, chemical composition, solubility, surface charge, particle size, etc.?

→ enable development a model to predict effects of wide range of minerals?
HABITABILITY
Visualization of Early Earth Environments: 4.5 - 3.9 Ga

Hadean Era 4.5 - ~ 4.4 Ga

Meteorite & comet heavy bombardment
hot, inhospitable, no atmospheric O₂

Archaean Era ~ 4.4 Ga - 4.1 Ga

“Cool” early Earth: temps ~ 80 - 90 °C
liquid H₂O, oceanic crust, no atm. O₂

Archaean Era ~ 4.1 Ga - 3.9 Ga

Continental crust
fresh water, no atm. O₂

Archaean Era: ~ 3.5 Ga

Earliest bacterial fossils?
(compare to modern cyanobacterium)
Deep sea sulfidic hydrothermal vents
pH ~ 3-8, temp. ~ 375 – 4 °C

http://faculty.cascadia.edu/jvanleer/astro%20sum01/Hyrothermal%20Vent%20Final/hydrothermal_vents.htm

Kawah Ijen Volcanic Lake, Java, Indonesia
Sulfuric acid, pH ~ 0.5

http://en.wikipedia.org/wiki/Ijen

Spotted Lake, Canada
pH > 7, Ca, Na, Mg sulfates

http://www.playbull.com/beautiful-places/spotted-lake-canada/

Ice core, Arctic
Temp. = 0 °C, high pressure at depth

http://serc.carleton.edu/microbelife/extreme/cold/index.html
Tree of Extant Life

A Common Origin

EUCARYA
- Animals
- Fungi
- Plants
- Eukaryotes

ARCHAEA
- Sulfolobus
- Desulfurococcus
- Pyrococcus
- Methanococcus
- Archaeoglobus
- other extremophiles

BACTERIA
- Ancyromonas
- Protists
- Thermotoga
- Aquifex
- other bacteria

Extremophiles: acidophiles, thermophiles, halophiles, psychrophiles, piezophiles

protocells

thermophiles, other bacteria
Other Solid Worlds?

Mars
- Alluvial Fans
- Fe₂O₃ Concretions

Titan - Moon of Saturn
- Craters

Europa - Moon of Jupiter
- Ice Rafts
MINERAL EFFECTS ON MEMBRANE STABILITY
Model Protocell Membranes

extracted lipids ...

meteorite: carbonaceous chondrite

fatty acid molecule (e.g. decanoic acid)

vesicle (membrane)

... form vesicles

synthetic vesicles
Model Protocell Membrane (Fatty Acid Vesicle) Dynamics

stop video at 7:77 seconds

http://www.molecularmovies.com/showcase/
Rocks Types Present on Early Earth (4.4 - 3.9 Ga)

Archaean Era
~ 4.4 Ga - 4.1 Ga

Oceanic Crustal Rocks: Komatiite

Archaean Era
~ 4.1 Ga - 3.9 Ga

Continental Crustal Rocks: Tonalite

Weathering of these Rocks

Minerals Formed: Oxides, Carbonates, Sulfides, Clays (Aluminosilicate)
Some Rocks and Minerals Relevant to Early Earth Environments

- **komatiite**
- **tonalite**
- **amorphous silica** \((\text{SiO}_2)\)
- **\(\gamma\)-\(\text{Al}_2\text{O}_3\)** (diaspore analog)
- **montmorillonite**
  \[ (\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O} \]
- **siderite** \((\text{FeCO}_3)\)
- **pyrite** \((\text{FeS}_2)\)
Transmission Electron Microscopy of Minerals and Rocks

- Amorphous silica ($\text{SiO}_2$)
- Tonalite
- Komatiite
- Montmorillonite clay
- Pyrite ($\text{FeS}_2$)
- Siderite ($\text{FeCO}_3$)
- Zincite ($\text{ZnO}$)
- $\gamma$-Alumina ($\text{Al}_2\text{O}_3$)
1. Do Minerals Disrupt Vesicles Membranes?

a. Visualization by Cryo-Transmission Electron Microscopy

- Montmorillonite (aluminosilicate)
- Zincite (ZnO)
- Anatase ($\beta$-TiO$_2$)
- Goethite ($\alpha$-FeOOH)
1. Do Minerals Disrupt Vesicles Membranes?

b. Quantitation by Calcein (Fluorescent Self-Quenching Dye) Leakage Assay
Membrane Disruption or Total Rupture (Leakage)

12 minerals and rocks studied:
- wide range of composition, crystal structure, surface charge
- did not destabilize membranes compared to no mineral present

→ Excellent news!
Vesicle Formation from Fatty Acid Micelles

http://www.molecularmovies.com/showcase/
12 minerals and rocks significantly promoted formation rate.

Effect varies systematically with mineral properties (charge, particle size)

have developed model to predict effect of minerals not tested here

--- surface charge

+++ surface charge
Isoelectric Point (Surface Charge) Depends on Crystal Structure and Chemical Composition

\(\alpha\text{-SiO}_2\) Crystal System: trigonal; Spacegroup \(P 3_2 2 1\); Unit cell: \(a = 4.914 \text{ Å}, c = 5.401 \text{ Å}\)

Pauling bond strength, \(s_{\text{Si, SiO}_2} = 4/IV = 1.0\) \(r_{\text{Si-O, SiO}_2} = 1.64 \text{ Å}\) \(\varepsilon_{\text{SiO}_2} = 3.81\)

\(\alpha\text{-Al}_2\text{O}_3\) Crystal System: trigonal; Spacegroup \(R -3 c\); Unit cell: \(a = 4.762 \text{ Å}, c = 12.994 \text{ Å}\)

\(s_{\text{Al, } \alpha\text{-Al}_2\text{O}_3} = 3/IV = 0.50\) \(r_{\text{Al-O, } \alpha\text{-Al}_2\text{O}_3} = 1.93 \text{ Å}\) \(\varepsilon_{\gamma\text{-Al}_2\text{O}_3} = 10.4\)

\(s_{\text{Al, tet}} = 3/IV = 0.75\) \(r_{\text{Al-O, tet}} = 1.81 \text{ Å}\)

Sverjensky & Sahai, 1996
Summary: Mineral and Rock Effects on Membranes

- ✗ destabilize (disrupt) membranes?
- ✓ promote formation rate of membranes?
- ✓ mineral effects depend on chemical composition, crystal structure, surface charge, particle size
  → predictive model for rate effects

membrane stability on other worlds?
Potential Roles of Minerals in Protocell Evolution

Minerals as Catalysts ("Prebiotic Enzymes")?

- Mass transport
- Membrane stability
- Genes: replication
- Mineral

FeS_2

hv e^-
h^+

CO_2 + H_2O → CH_2O + O_2

Metabolism: catalyzed energy transfer cycles
Concluding Remarks

• The Earth’s atmospheric, oceanic and rock compositions have evolved over time.

• Life probably originated early in Earth history.

• Earth’s environment and life co-evolved after the origin of life.

• Minerals do not rupture membranes and promote membrane formation rate.

• Minerals as “prebiotic enzymes” remains to be examined.

• Life on other worlds?
• The Sahai Research Group

• Dr. Jack Szostak,
   Harvard University

• Funding:

   The Simons Foundation, NY
   NSF
   NASA
Proposed Mechanism of Mineral Effects on Lipid Membranes

1) or or + negative mineral $\leftrightarrow$ negative mineral

2) or or $\rightarrow$ positive mineral $\rightarrow$ positive mineral
Summary: Mineral Crystal Chemistry Affects Model Protocell Viability

micelle $\rightarrow$ vescicle

transition rates

CVC

Mineral Surface Charge

$\Delta G_{ads}^0, \ H^+ = c_1 \left( \frac{1}{\varepsilon_k} \right) + c_2 \left( \frac{s}{r_{M-O}} \right) + c_3$

Crystal Chemistry
Ion Leaching from Rocks and Minerals in Bicine Buffer (pH 8)

- Low siderite loading: cations may bridge vesicle head groups → vesicle formation rate ↑
- High siderite concentrations: cations precipitate out the lipid → no vesicles
# Characterization of Minerals and Rocks

## Table 1. Mineral characterization

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Isoelectric point (IEP)</th>
<th>B.E.T. surface area (m²/g)</th>
<th>Primary particle size, secondary particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (Aerosil-300)</td>
<td>SiO₂</td>
<td>1.5 – 2.5</td>
<td>288 ± 5</td>
<td>15 ± 5, 50 – 500</td>
</tr>
<tr>
<td>Quartz (Minusil-5)</td>
<td>SiO₂</td>
<td>2 – 3</td>
<td>6 ± 0.5</td>
<td>50 – 100, 200 – 400</td>
</tr>
<tr>
<td>Montmorillonite (Volclay SP-200)</td>
<td>Na₀.₂Ca₀.₁Al₂Si₄O₁₀(OH)₂(H₂O)₁₀</td>
<td>1.5 – 2.5</td>
<td>33 ± 1</td>
<td>50 – 100, 200 – 400</td>
</tr>
<tr>
<td>Komatiite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tonalite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>4 – 5</td>
<td>0.7 ± 0.2</td>
<td>200 – 400, 600 – 1000</td>
</tr>
<tr>
<td>Anatase</td>
<td>TiO₂</td>
<td>5.4 – 6</td>
<td>54 ± 2</td>
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<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>6.3 – 7.3</td>
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<td>Zincite</td>
<td>ZnO</td>
<td>8.3 – 8.7</td>
<td>3 ± 0.3</td>
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<tr>
<td>γ-Alumina</td>
<td>γ-Al₂O₃</td>
<td>8.3 – 9.3</td>
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<td>Goethite</td>
<td>FeO(OH)</td>
<td>8.7 – 9.3</td>
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# determined by measuring ζ-potential of minerals at different pH in water;  
§§ measured using nitrogen adsorption-desorption isotherm at 77 k (Micromeritics Tristar II 3020 analyzer)  
* Measured in 200 mM Bicine pH 8;  
£ Estimated from the TEM images (Figure S1)
Peptide-Catalyzed RNA Polymerization

RNA nucleotide monomers

peptides

polymerization

RNA oligomer

polymer → folding → functional RNA (e.g., riboswitch)

Lipid-Catalyzed RNA Polymerization

RNA nucleotide monomers → lipid membranes → RNA oligomer → polymerization

polymer → folding → functional RNA (e.g., riboswitch)

Amphiphiles Investigated

**Single-Chain Amphiphiles**

- Decanoic Acid, C10 (DA)
- 1-Decanol, C10 (DOH)
- Oleic Acid, C18 (OA)

**Double-Chain Amphiphiles: Phospholipids**

- 1-Palmitoyl-2-oleoylphosphatidylcholine, C42 (POPC)
RNA versus DNA Differences

RNA
Ribonukleinsäure

DNA
Desoxyribonukleinsäure

Stickstoffbasen der RNA

Stickstoffbasen der DNA

Cytosin

Guanin

Adenin

Uracil

Stickstoffbasen

Helix aus Zuckerphosphat

Basenpaar

C

G

A

T

Cytosin

Guanin

Adenin

Thymin
Nucleotide Bases (NBs)

DNA

RNA

Adenine (A)  Guanine (G)  Cytosine (C)  Thymine (T)

Adenine (A)  Guanine (G)  Cytosine (C)  Uracil (U)
Nucleotide Polymerization (Single Chain)

Nucleotide Polymerization (Single Chain)
Amino Acid Polymerization: Peptide (Amide) Bond Formation

Glycine (G)    Serine (S)    Phenylalanine (F)

Amino Acids

Arginine (R)    Glutamate (E)

Dipeptide
The Central Paradigm of Biology

deoxyribonucleic acid

DNA polymerase

RNA

ribonucleic acid

Enzymes

DNA

transcription

enzymes

replication

enzymes

translation

enzymes

metabolic cycles

NADP reductase

& Other Proteins
The Central Problem

How to Make One without the Other?

GENETIC CODE

RNA

PROTEIN
DNA Replication

http://www2.le.ac.uk/departments/genetics/vgec/diagrams/95-DNA-replication.gif
DNA Replication
Mineral Surface Charge Depends on Crystal Structure & Composition

$\text{> } MOH^0 + H^+ = \text{> } MOH_2^+$

\[ \log K_{a1} \]

$\text{> } MO^- + H^+ = \text{> } MOH^0$

\[ \log K_{a2} \]

$\text{> } MO^- + 2H^+ = \text{> } MOH_2^+$

\[ \log K_{PZC} \]

\[ PZC = \frac{1}{2} (\log K_{a1} + \log K_{a2}) \approx IEP \]

\[ \Delta G_{ads, H^+}^0 = \Delta G_{solv}^0 + G_{elec}^0 + G_{chem}^0 \]

\[ \Delta G_{ads, H^+}^0 = f_1 \left( \frac{1}{\varepsilon_k} \right) + f_2 \left( \frac{1}{\varepsilon_{int}} \right) + f_3 \left( \frac{1}{\varepsilon_w} \right) + f_4 \left( \frac{-2}{r_{O-H}} \right) + f_5 \left( \frac{Z_{M-OH}}{r_{M-OH}} \right) + f_{6, chem} \]

\[ \Delta G_{ads, H^+}^0 = c_1 \left( \frac{1}{\varepsilon_k} \right) + c_2 \left( \frac{s}{r_{M-O}} \right) + c_3 \]

Pauling bond strength: $s = \text{valence/coordination number}$

Sverjensky (1994); Sverjensky & Sahai (1996); Sahai & Sverjensky (1997a, b); Sahai (2002)
\[ \Delta pK = \log K_2 - \log K_1 \]

\[ \text{SO}^- + \text{SOH}_2^+ = 2 \text{SOH} \]
Importance of Early Earth Environments

e.g., Non-Enzymatic RNA Nucleotide Synthesis

Laboratory Synthesis

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<tr>
<th>Property</th>
<th>Present Earth</th>
<th>Early Earth</th>
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<tbody>
<tr>
<td>$\text{PO}_4$</td>
<td>$1\text{ M}$</td>
<td>$1/1000\text{ M}$</td>
</tr>
<tr>
<td>pH</td>
<td>1 – 12</td>
<td>??</td>
</tr>
<tr>
<td>$T$</td>
<td>-50 to 140 °C</td>
<td>??</td>
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T = 25 °C
Initial Rate of Vesicle Formation Depends on Mineral Surface Charge

Function of adsorption energy of H\(^+\) and OH\(^-\)
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