Heat flows adjust local ion concentrations in favor of prebiotic chemistry

Christof Mast
Systems Biophysics
LMU Munich
Emergence of life
Prebiotic chemistry

4 GYa Nucleotides & fatty acids RNA mol. evolution early life
e.g. Nucleoside synthesis

Powner, Gerland, Sutherland, Nature vol 459, 239-242 (2009)
Prebiotic chemistry

4 GYa
Nucleotides & fatty acids
Phosphor enrichment

E.g. Nucleoside synthesis

RNA
mol. evolution
early life

Prebiotic chemistry

4 GYa: Nucleotides & fatty acids

Phosphor enrichment

e.g. Nucleoside synthesis

Phosphorylation

RNA

mol. evolution

early life

Powner, Gerland, Sutherland, Nature vol 459, 239-242 (2009)
**Prebiotic chemistry**

- 4 GYa
- Nucleotides & fatty acids
- RNA
- mol. evolution
- early life

**Phosphor enrichment**

**e.g. Nucleoside synthesis**

**Phosphorylation**

**Activating chemicals**

Prebiotic chemistry

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Nucleotides & fatty acids
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e.g. Nucleoside synthesis
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Powner, Gerland, Sutherland, Nature vol 459, 239-242 (2009)
Prebiotic chemistry

4 GYa | Nucleotides & fatty acids | RNA | mol. evolution | early life

Phosphor enrichment

e.g. Nucleoside synthesis

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Activating chemicals

Ribozymes

Prebiotic chemistry

4 GYa
Nucleotides & fatty acids

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Phosphorylation

Nucleotides

Activation chemicals

RNA

Ribozymes

Molecular evolution

Powner, Gerland, Sutherland, Nature vol 459, 239-242 (2009)
It’s hard!

- 4 GYa
- Nucleotides
- RNA
- mol. evolution
- early life

Time line diagram showing the evolution from nucleotides to early life.
Ionic boundary conditions

Ionic boundary conditions

Phosphor enrichment

Nucleotides

Phosphorylation

Ionic boundary conditions

Phosphor enrichment

Nucleotides

Phosphorylation

Ionic boundary conditions

Phosphor enrichment

Nucleotides

Phosphorylation


**ThermoFisher Scientific**

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Not available
Ionic boundary conditions

RNA

Ribozymes

Molecular evolution
Ionic boundary conditions
Ionic boundary conditions

RNA

Ribozymes

Molecular evolution
Ionic boundary conditions

\[
\frac{[Mg^{2+}]}{[Na^+]}
\approx 0.001 \text{ to } 0.1
\]
Ionic boundary conditions

\[ \frac{[Mg^{2+}]}{[Na^+]} = 0.001 \text{ to } 0.1 \]
Ionic boundary conditions

\[
\frac{[Mg^{2+}]}{[Na^+]^2} = 0.001 \text{ to } 0.1
\]
Systems Pre-Biophysics
Coupling between physical non-equilibria and prebiotic chemistry & geology

scale not correct
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scale not correct
Thermophoresis: The "capacitor effect"

\[
\frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T)
\]
Thermophoresis: The „capacitor effect“

\[ \frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T) \]
Thermophoresis: The "capacitor effect"

\[
S_T = \frac{Q^2 \beta \lambda_{DH}}{4A\varepsilon_0 kT^2} \rightarrow \frac{Q^2}{16\pi\varepsilon_0 kT^2[\lambda_{DH}[1 + R/\lambda_{DH}]]^2} \left[ 1 - \frac{T \partial \varepsilon}{\varepsilon \partial T} \left[ 1 + 2 \frac{\lambda_{DH}}{R} \right] \right]
\]

\[
\frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T)
\]

[Dhont]
Increase thermophoretic effect by convection

Thermophoresis only:
(no \( \textbf{g} \), thin vessel, \( \textbf{g} \) & \( \nabla T \) same direction..)

\[
\frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T)
\]
Increase thermophoretic effect by convection

Thermophoresis only:
(no \( g \), thin vessel, \( g \) & \( \nabla T \) same direction.)

\[ \frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T) \]

Thermophoresis + convection:

\[ \frac{c_{\text{bottom}}}{c_{\text{top}}} = \exp \left( \alpha \cdot S_T \cdot \Delta T \cdot \frac{h}{w} \right) \]
Increase thermophoretic effect by convection

Thermophoresis only:
(no $g$, thin vessel, $g \& \nabla T$ same direction..)

\[
\frac{c_{\text{hot}}}{c_{\text{cold}}} = \exp(-S_T \cdot \Delta T)
\]

Thermophoresis + convection:

\[
\frac{c_{\text{bottom}}}{c_{\text{top}}} = \exp\left(\alpha \cdot S_T \cdot \Delta T \cdot \frac{h}{w}\right)
\]
Scenario

\[
Mg^{2+} + Na^+ = 0.001 \text{ to } 0.1
\]

Basalt:
\[
\frac{[Mg^{2+}]}{[Na^+]} = 0.001 \text{ to } 0.1
\]

Apatite @pH2:
\[
\frac{6[PO_4]}{10[Ca^{2+}]} \sim 1
\]

Ribozyme function
Scenario

**Basalt:**
\[
\frac{[Mg^{2+}]}{[Na^+]}
\]
= 1 to 100

**Apatite @pH2:**
\[
\frac{6[PO_4]}{10[Ca^{2+}]}
\] > 10
Scenario

Basalt: \[
\frac{[Mg^{2+}]}{[Na^+]}
\] = 1 to 100

Apatite @\(pH2\): \[
\frac{6[PO_4]}{10[Ca^{2+}]}
\] > 10

Experiment
Scenario

**Basalt:**
\[ \frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100 \]

**Apatite @pH2:**
\[ \frac{6[PO_4]}{10[Ca^{2+}]} > 10 \]

Experiment

---

Ribozyme function

[Chemical structures and reactions]
Scenario

Basalt:
\[
\frac{[Mg^{2+}]}{[Na^+] = 1 \text{ to } 100}
\]

Apatite @pH2:
\[
\frac{6[PO_4]}{10[Ca^{2+}] > 10}
\]

Ribozyme function

Experiment

Apatite

[Diagram of apatite formation and reactions]

[Chemical reactions]

[Diagram of experimental setup]

[0.5mm scale]
Scenario

Basalt:
\[
\frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100
\]

Apatite @ pH 2:
\[
\frac{6[PO_4]}{10[Ca^{2+}]} > 10
\]

Experiment

Ion chromatography:
Setup
Setup
Setup

- Oil flows through the syringe pumps.
- The sample is heated in the heat flow chamber.
- Oil is directed to the top outlet.
- Pressure is monitored at the mid outlet.
- Flow direction is indicated by arrows.
Results: Heat flows boost Mg/Na

Leaching only:

Matreux, LeVay, .., Scheu, Dingwell, Braun, Mutschler, Mast, *Heat flows in rock cracks naturally optimize salt compositions for ribozymes*, under final review
Results: Heat flows boost Mg/Na

Leaching only:

Ribozyme function:

Results: Heat flows boost Mg/Na

Ribozyme function in the trap:

<table>
<thead>
<tr>
<th>[Mg]</th>
<th>Na</th>
<th>ΔT</th>
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<tr>
<td></td>
<td>1000x</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10x</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0x</td>
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</table>

<table>
<thead>
<tr>
<th>Mg concentration (mM)</th>
<th>Processed substrate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mM</td>
<td></td>
</tr>
<tr>
<td>1 mM</td>
<td></td>
</tr>
<tr>
<td>4 mM</td>
<td></td>
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Results: Heat flows boost Mg/Na

Ribozyme function in the trap:

<table>
<thead>
<tr>
<th>0.5 mM</th>
<th>1 mM</th>
<th>4 mM</th>
<th>[Mg]</th>
<th>Na/</th>
<th>Mg</th>
<th></th>
</tr>
</thead>
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<tr>
<td>1000 10 0 0</td>
<td>1000 10 0 0</td>
<td>1000 10 0 0</td>
<td>[Na]</td>
<td>[Mg]</td>
<td>ΔT</td>
<td></td>
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<tr>
<td>1 2 3 4</td>
<td>5 6 7 8</td>
<td>9 10 11 12</td>
<td>lane</td>
<td></td>
<td></td>
<td></td>
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</tbody>
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Matreux, LeVay, ..., Scheu, Dingwell, Braun, Mutschler, Mast, *Heat flows in rock cracks naturally optimize salt compositions for ribozymes*, under final review
Results: Heat flows boost Mg/Na

Cascade of thermal traps:

Ribozyme function in the trap:

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Ribozyme function in the trap:

Matreux, LeVay, ..., Scheu, Dingwell, Braun, Mutschler, Mast, Heat flows in rock cracks naturally optimize salt compositions for ribozymes, under final review
Results: Heat flows boost PO4/Ca

Apatite dissolves

PO4

Ca2+

Acidic

neutral

re-precipitation free Ca2+

re-precipitation free PO4
Ionic boundary conditions: pH

RNA

Ribozymes

Molecular evolution

Ion boundary conditions: pH
Proton Gradient and pH oscillations emerge from heat flow at the microscale
Proton Gradient and pH oscillations emerge from heat flow at the microscale
Proton Gradient and pH oscillations emerge from heat flow at the microscale
Separation of oxonium/hydroxid

Proton Gradient and pH oscillations emerge from heat flow at the microscale
Proton Gradient and pH oscillations emerge from heat flow at the microscale

Inversion of pH gradient: formic acid

Effective thermal diffusion of H

Initial concentration of formic acid [mol/l]

Initial NaOH concentration [mol/l]

ΔpH

HCOOH
Proton Gradient and pH oscillations emerge from heat flow at the microscale
Combination with DNA/RNA

Proton Gradient and pH oscillations emerge from heat flow at the microscale
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