

Heat flows adjust local ion concentrations in favor of prebiotic chemistry

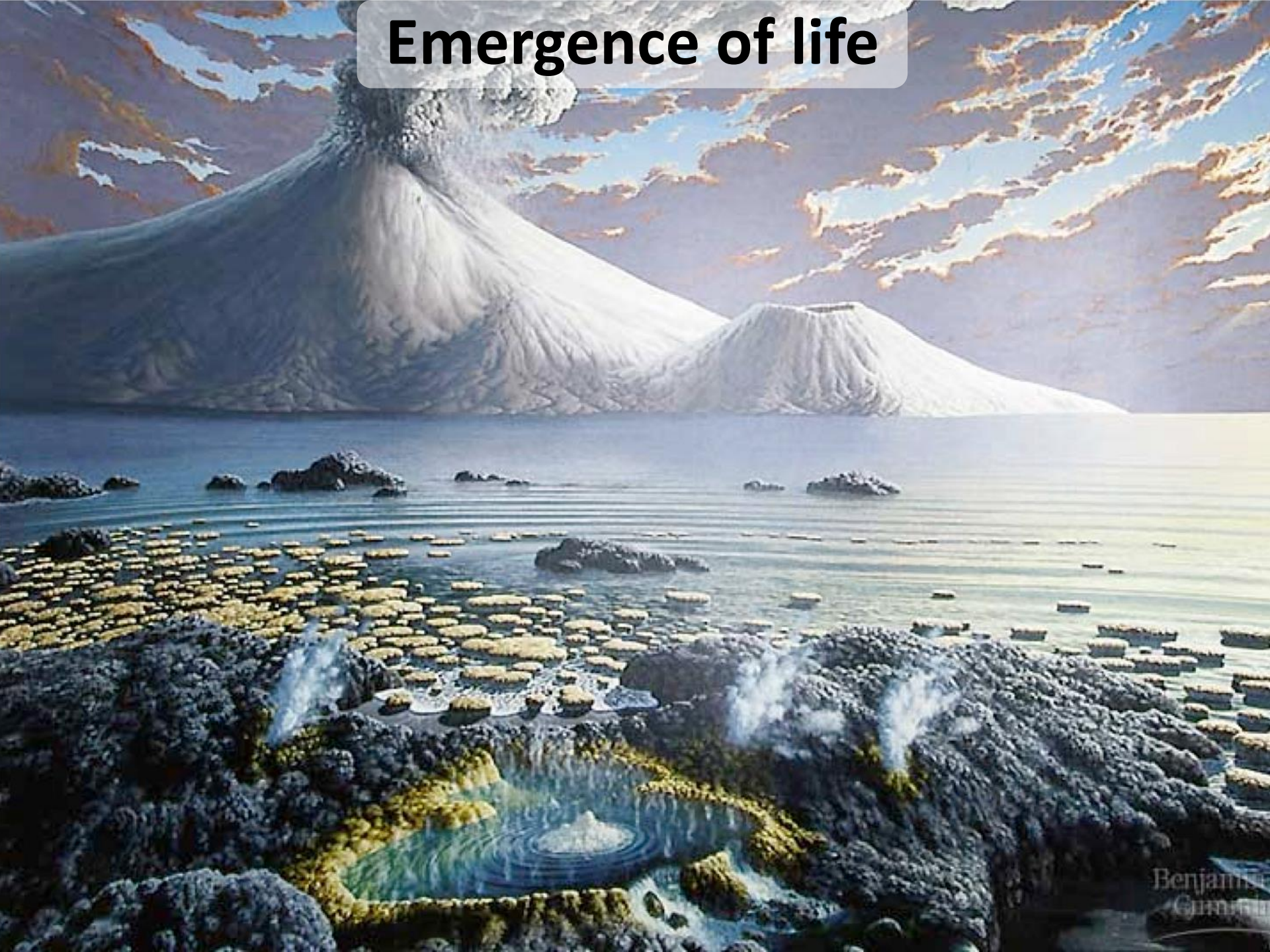
Christof Mast
Systems Biophysics
LMU Munich



Virtual
SMB 2021
Annual Meeting

June 13 - 17, 2021

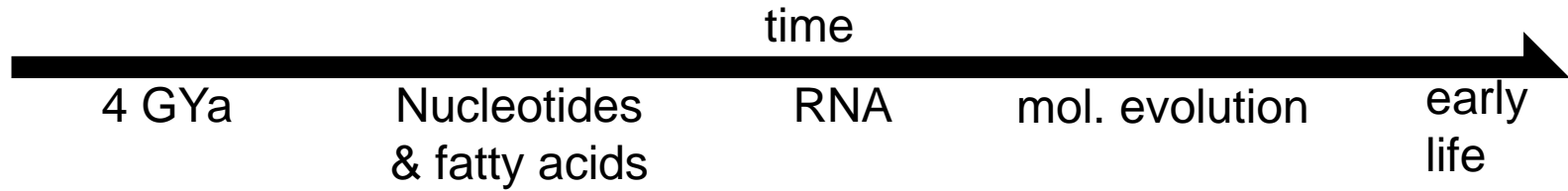
Emergence of life



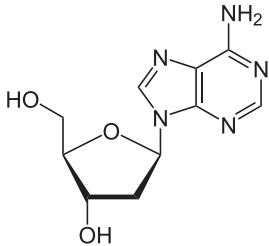
Emergence of life



Prebiotic chemistry



e.g. Nucleoside synthesis



Prebiotic chemistry

time

4 GYa

Nucleotides
& fatty acids

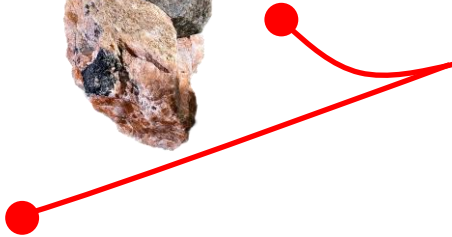
RNA

mol. evolution

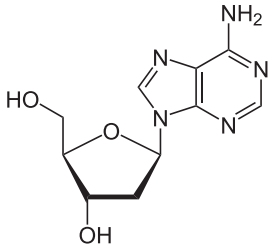
early
life



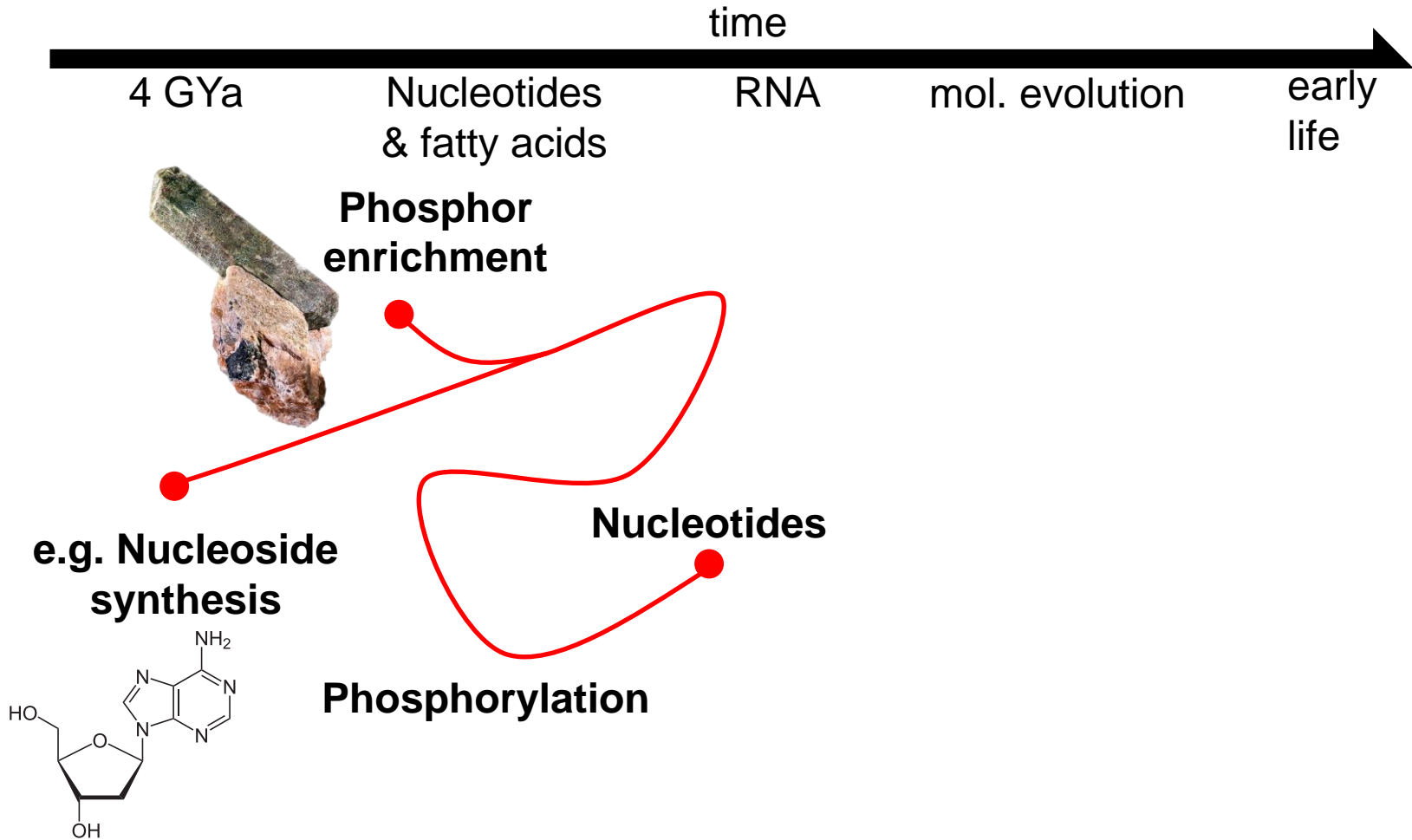
**Phosphor
enrichment**



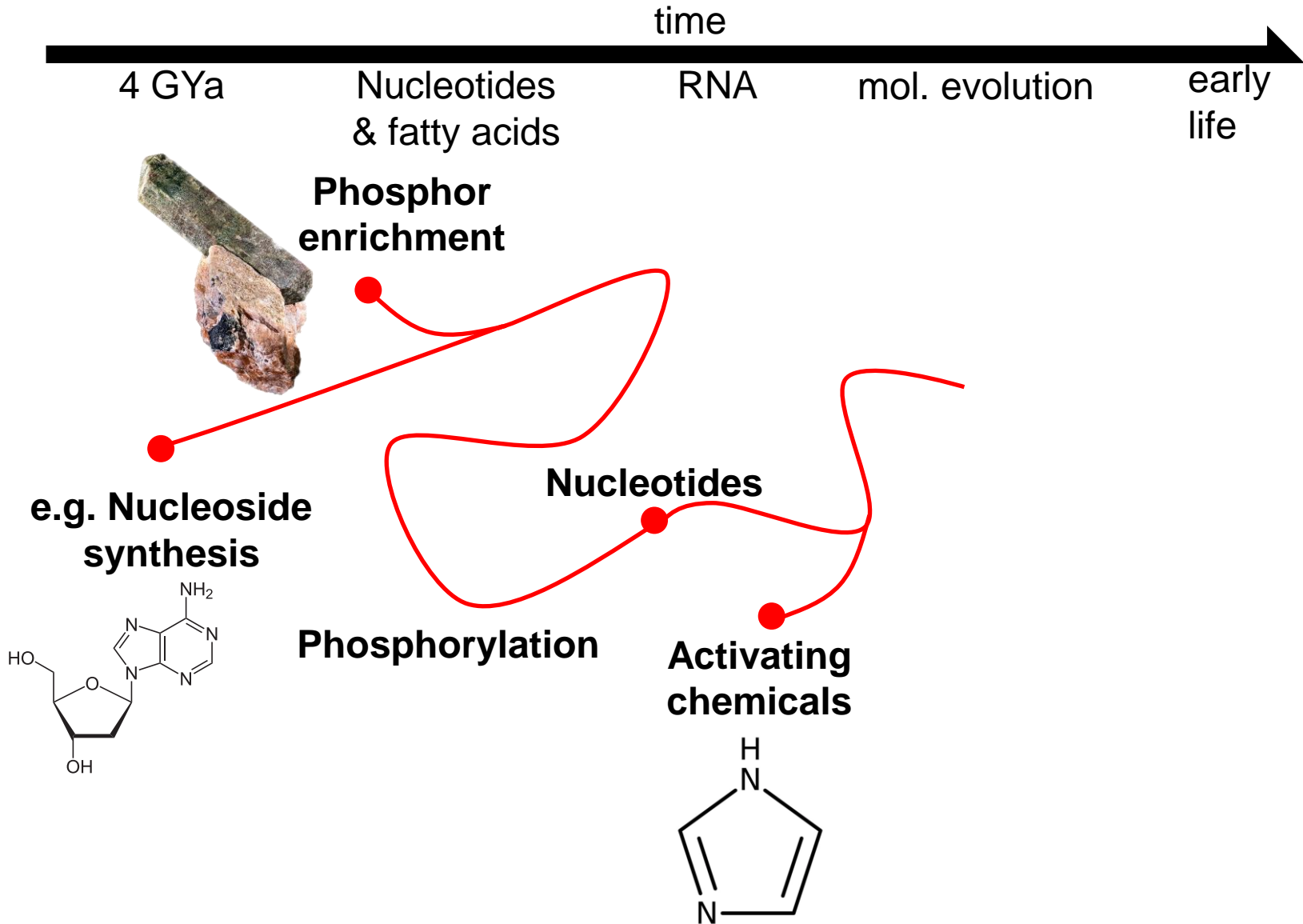
**e.g. Nucleoside
synthesis**



Prebiotic chemistry



Prebiotic chemistry



Prebiotic chemistry

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Nucleotides
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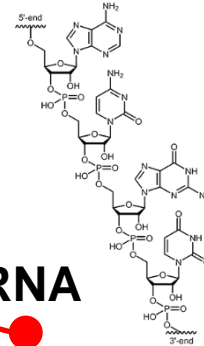
RNA

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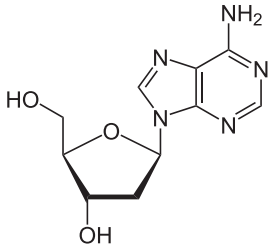


**Phosphor
enrichment**



RNA

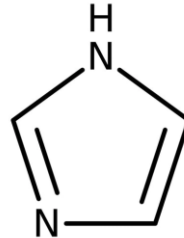
**e.g. Nucleoside
synthesis**



Nucleotides

Phosphorylation

**Activating
chemicals**



Prebiotic chemistry

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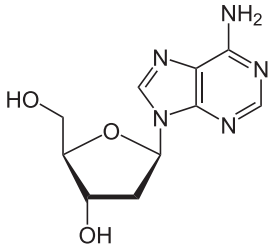
mol. evolution

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**Phosphor
enrichment**

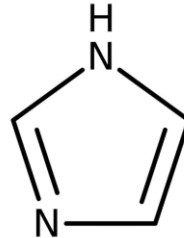
**e.g. Nucleoside
synthesis**



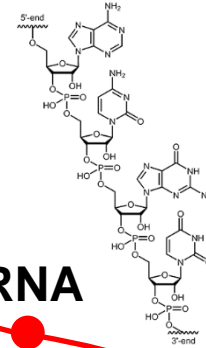
Phosphorylation

Nucleotides

**Activating
chemicals**



RNA



Ribozymes



Prebiotic chemistry

time

4 GYa

Nucleotides
& fatty acids

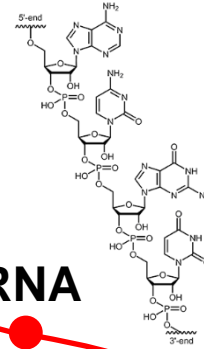
RNA

mol. evolution

early
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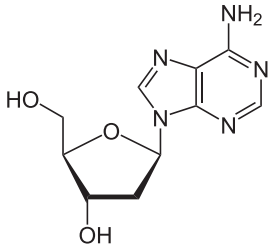
**Phosphor
enrichment**



RNA

**Molecular
evolution**

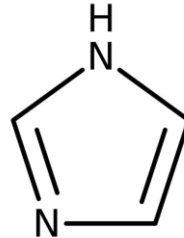
**e.g. Nucleoside
synthesis**



Nucleotides

Phosphorylation

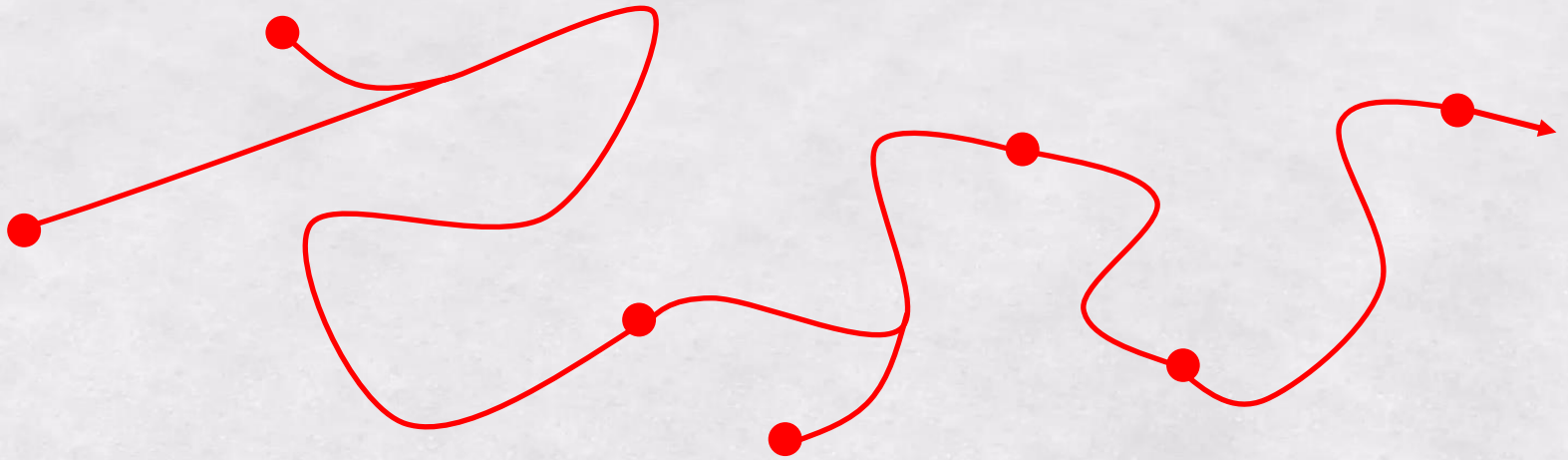
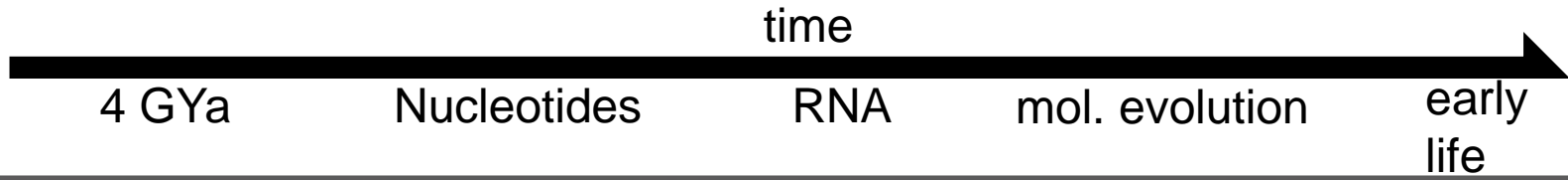
**Activating
chemicals**



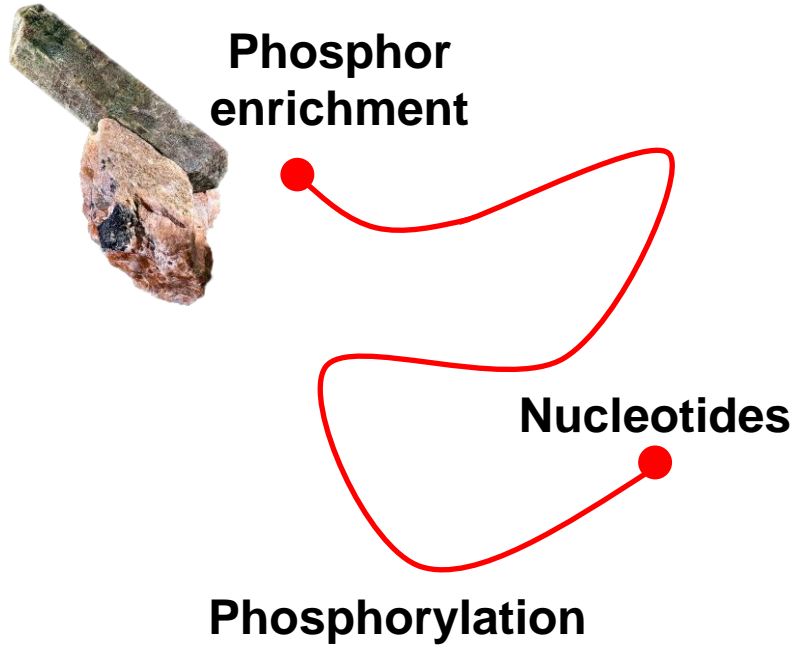
Ribozymes



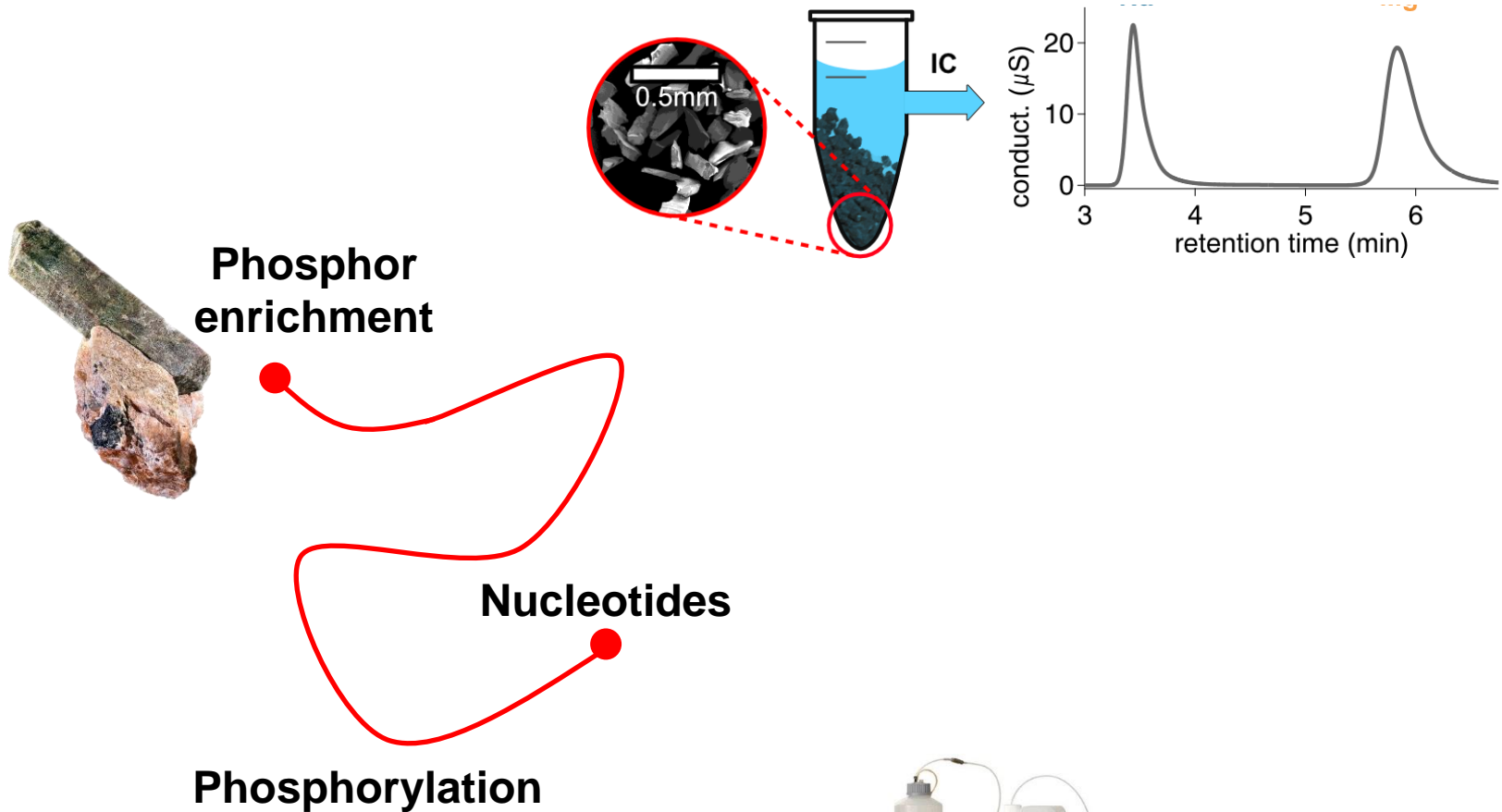
It's hard!



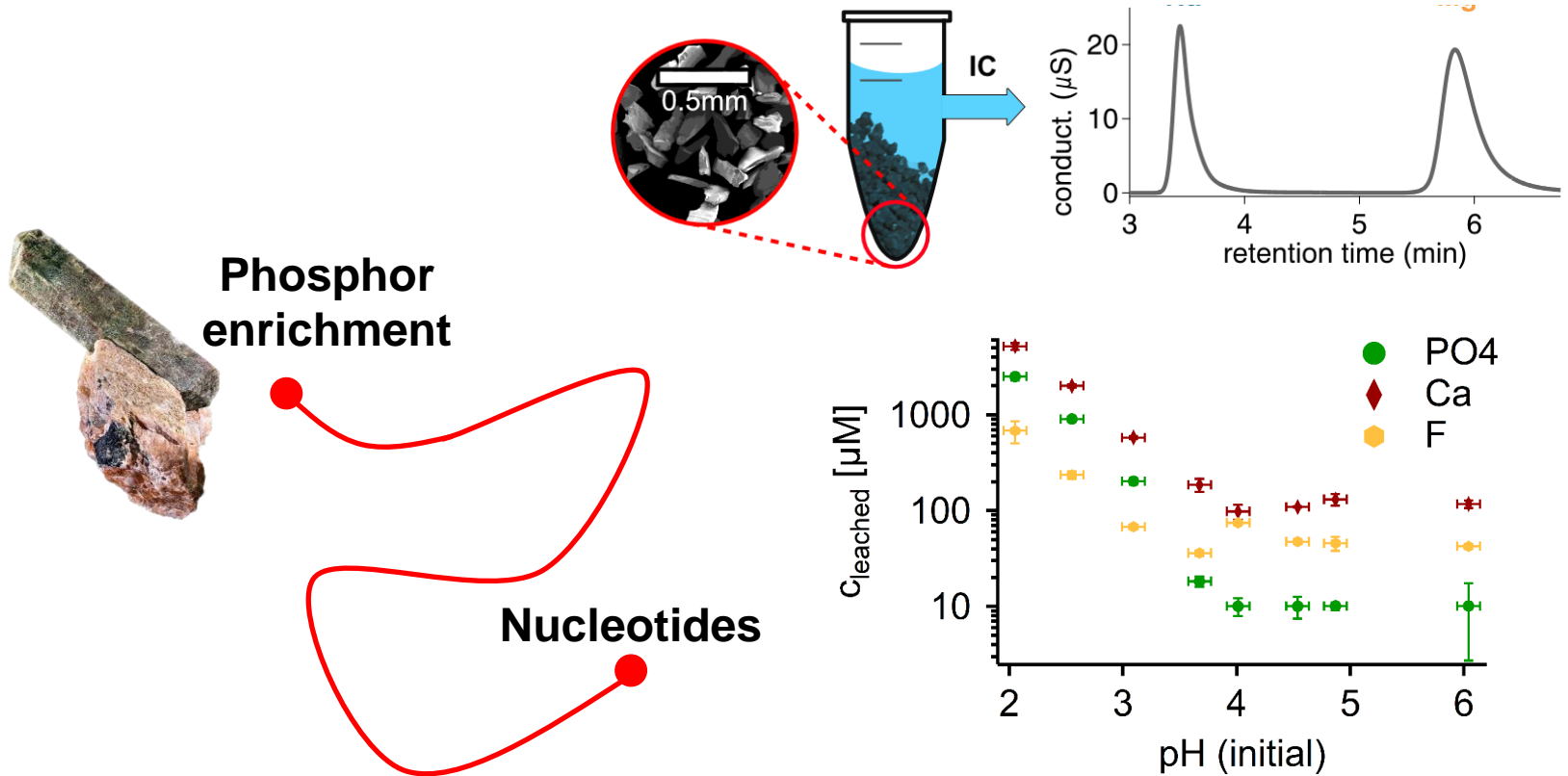
Ionic boundary conditions



Ionic boundary conditions



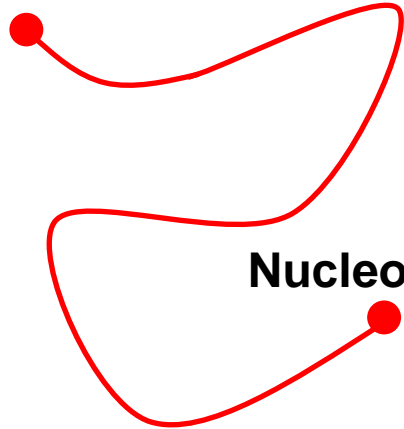
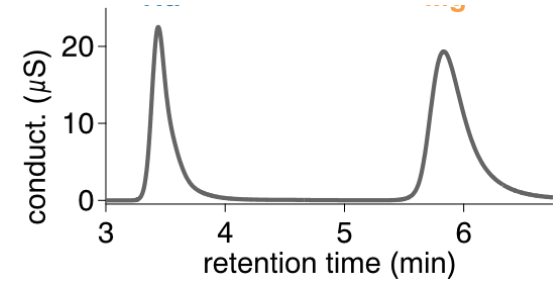
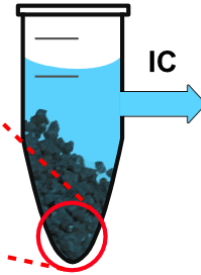
Ionic boundary conditions



Ionic boundary conditions

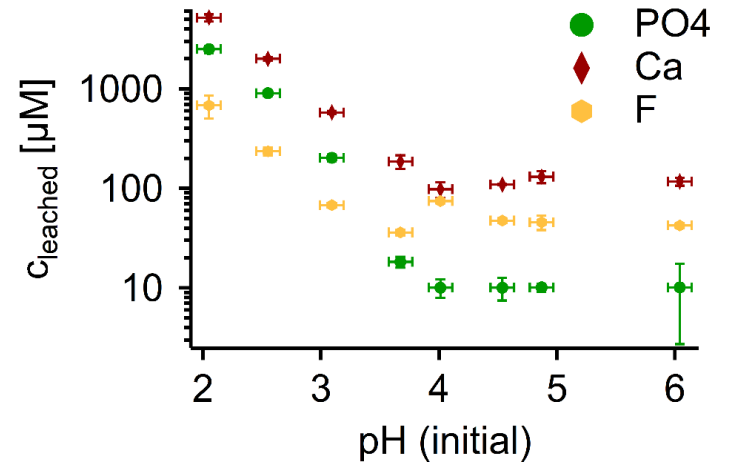


Phosphor enrichment



Nucleotides

Phosphorylation



ThermoFisher
SCIENTIFIC

Type: Public

Traded as: NYSE: TMO, S&P 100 component, S&P 500 component

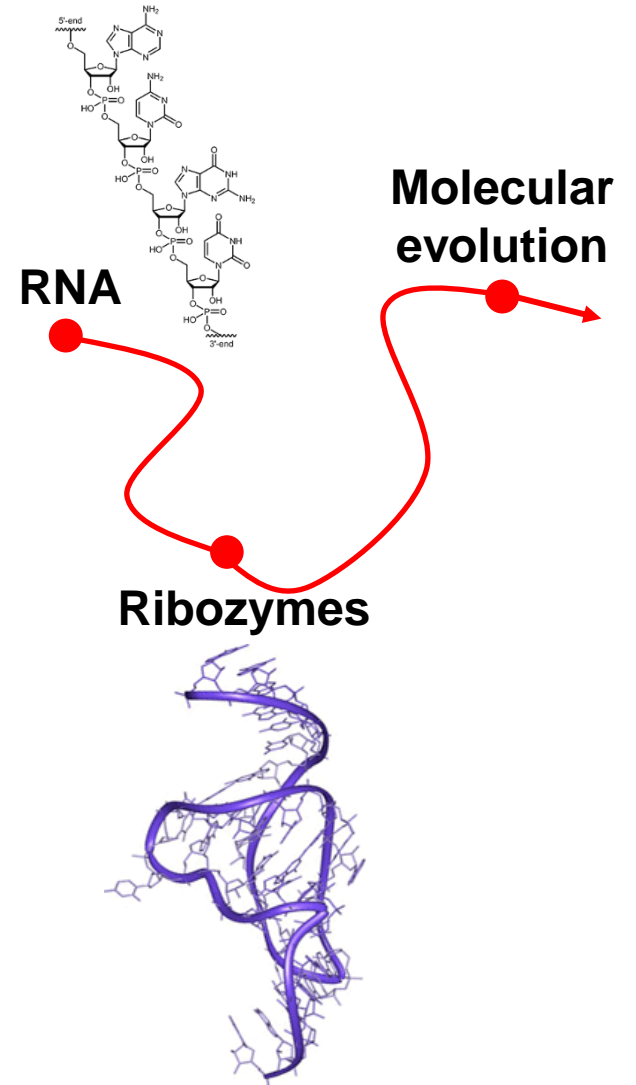
Industry: Laboratory equipment

Founded: 1956^[1]

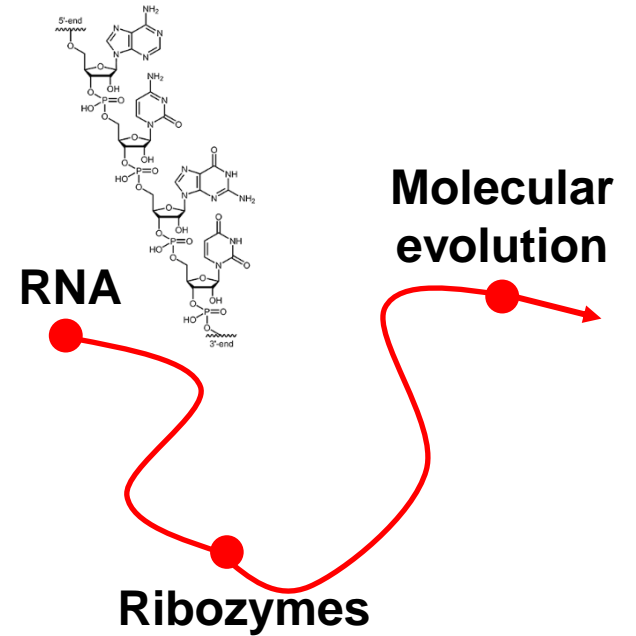
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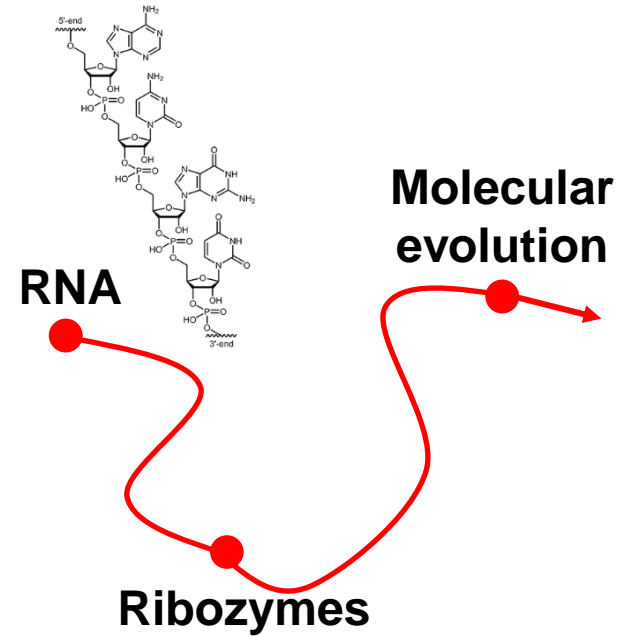
Ionic boundary conditions



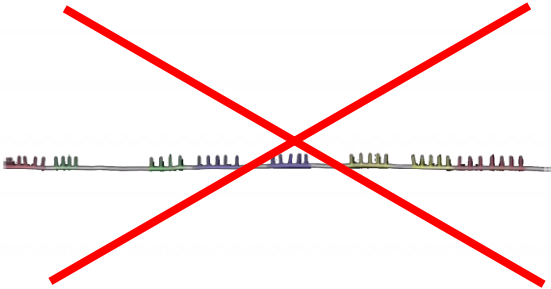
Ionic boundary conditions



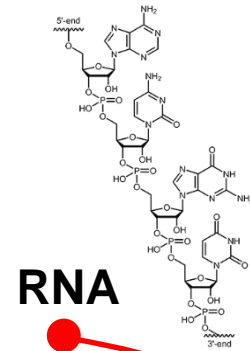
Ionic boundary conditions



Ionic boundary conditions



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

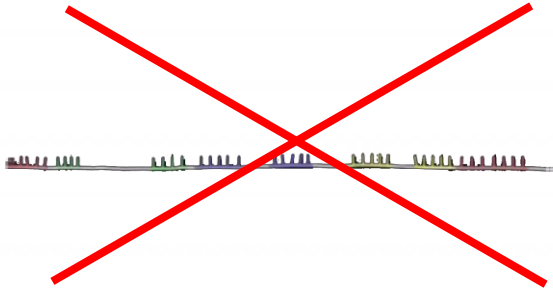


Molecular evolution

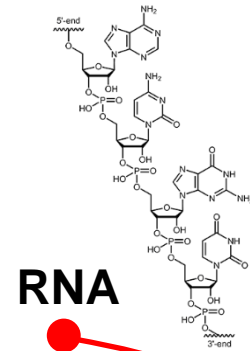
Ribozymes



Ionic boundary conditions



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



Molecular evolution

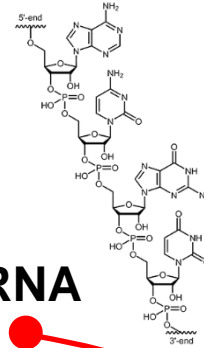
Ribozymes



Ionic boundary conditions



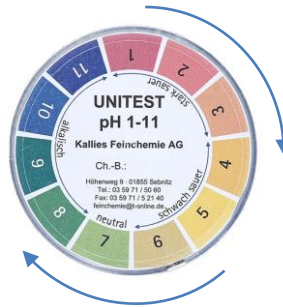
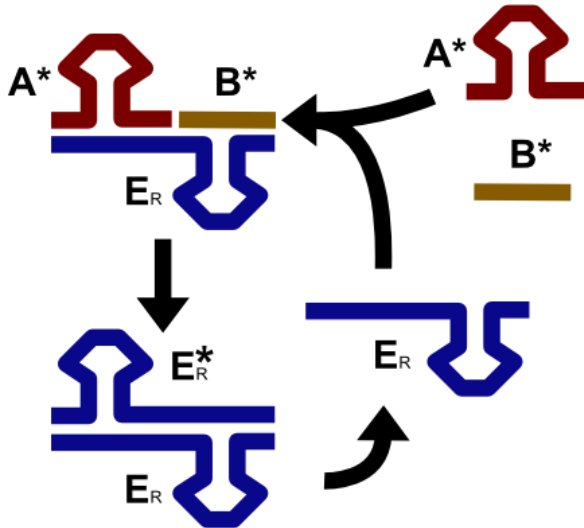
$$\frac{[Mg^{2+}]}{[Na^+]} = 0.001 \text{ to } 0.1$$



Molecular evolution

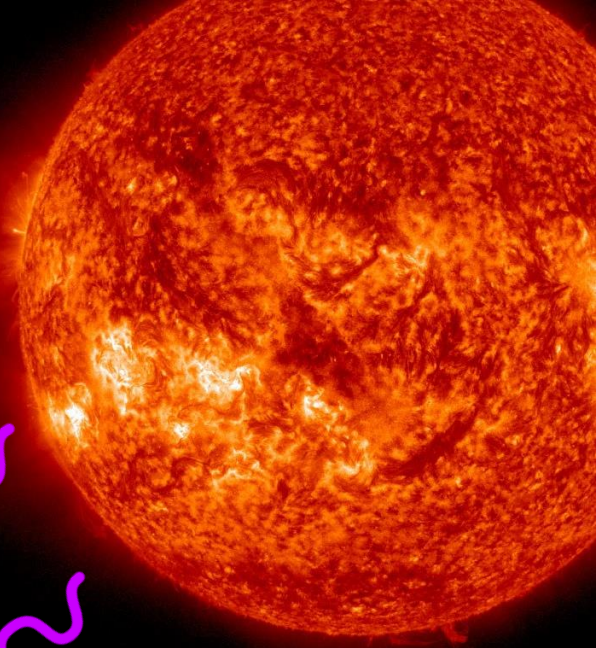
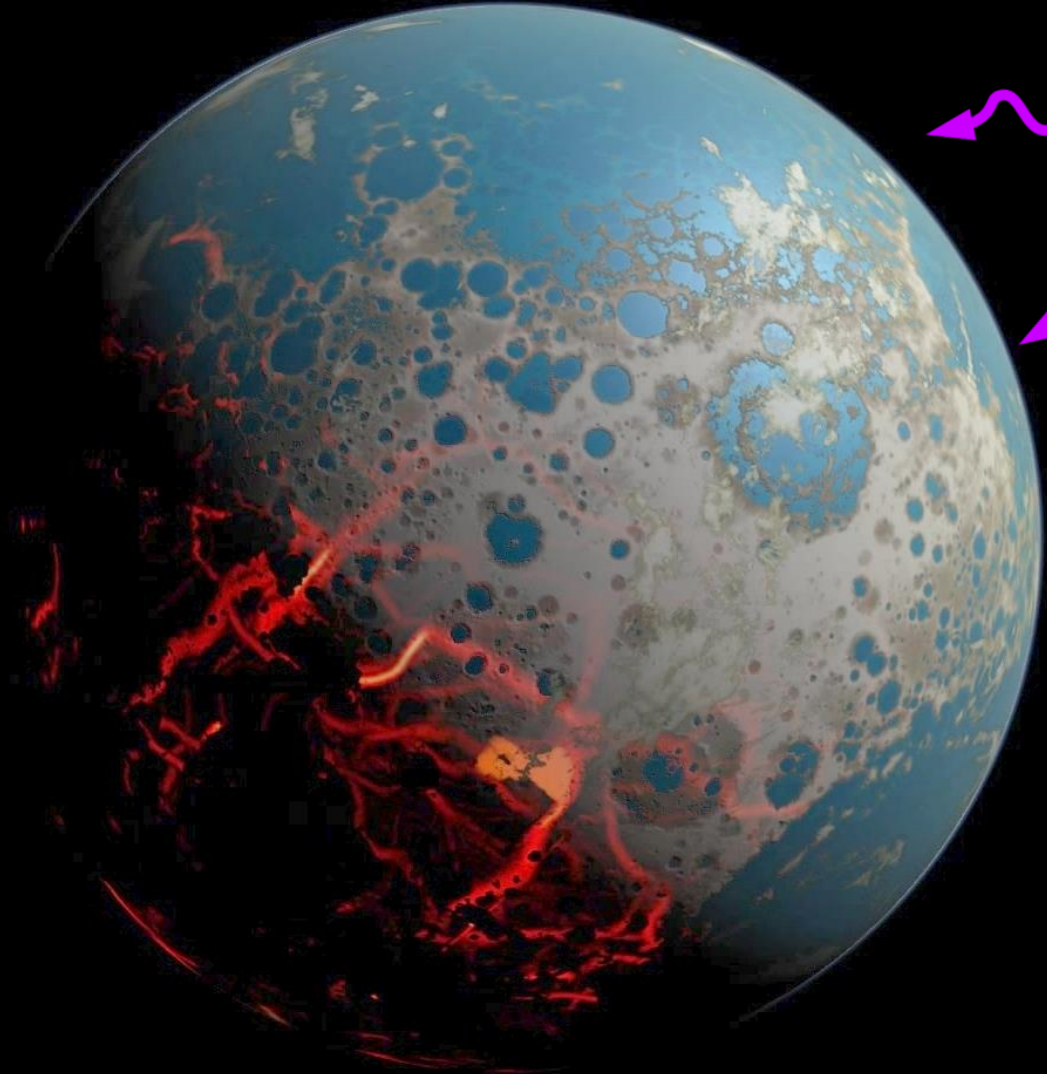
RNA

Ribozymes



Systems Pre-Biophysics

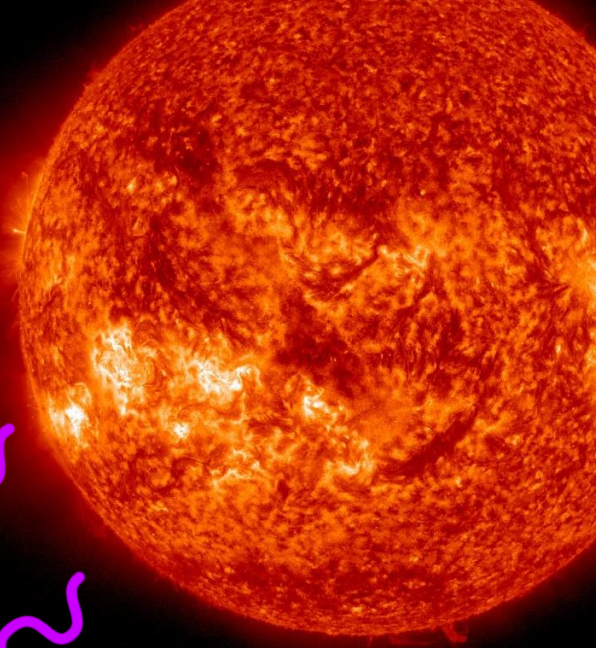
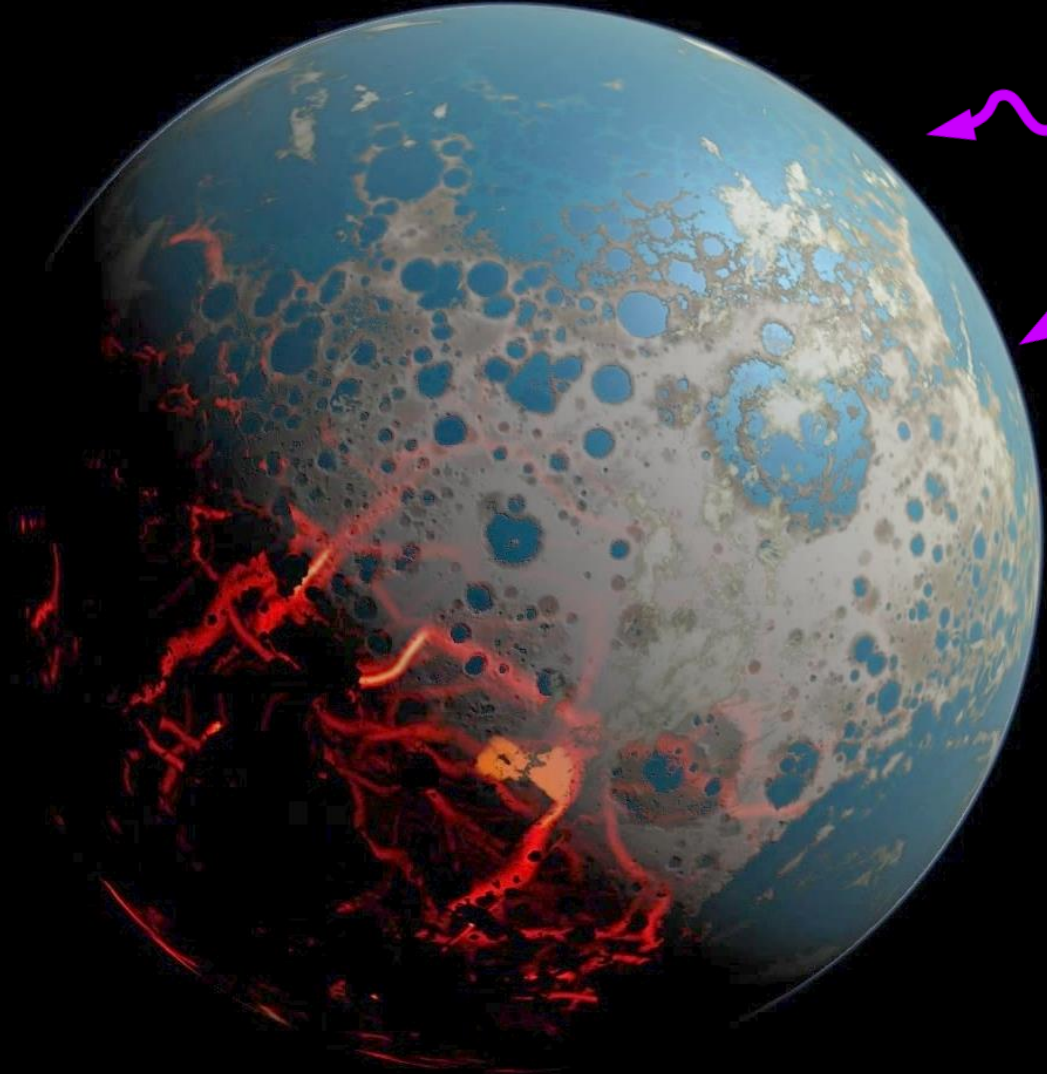
Coupling between physical non-equilibria and prebiotic chemistry & geology



scale not correct

Systems Pre-Biophysics

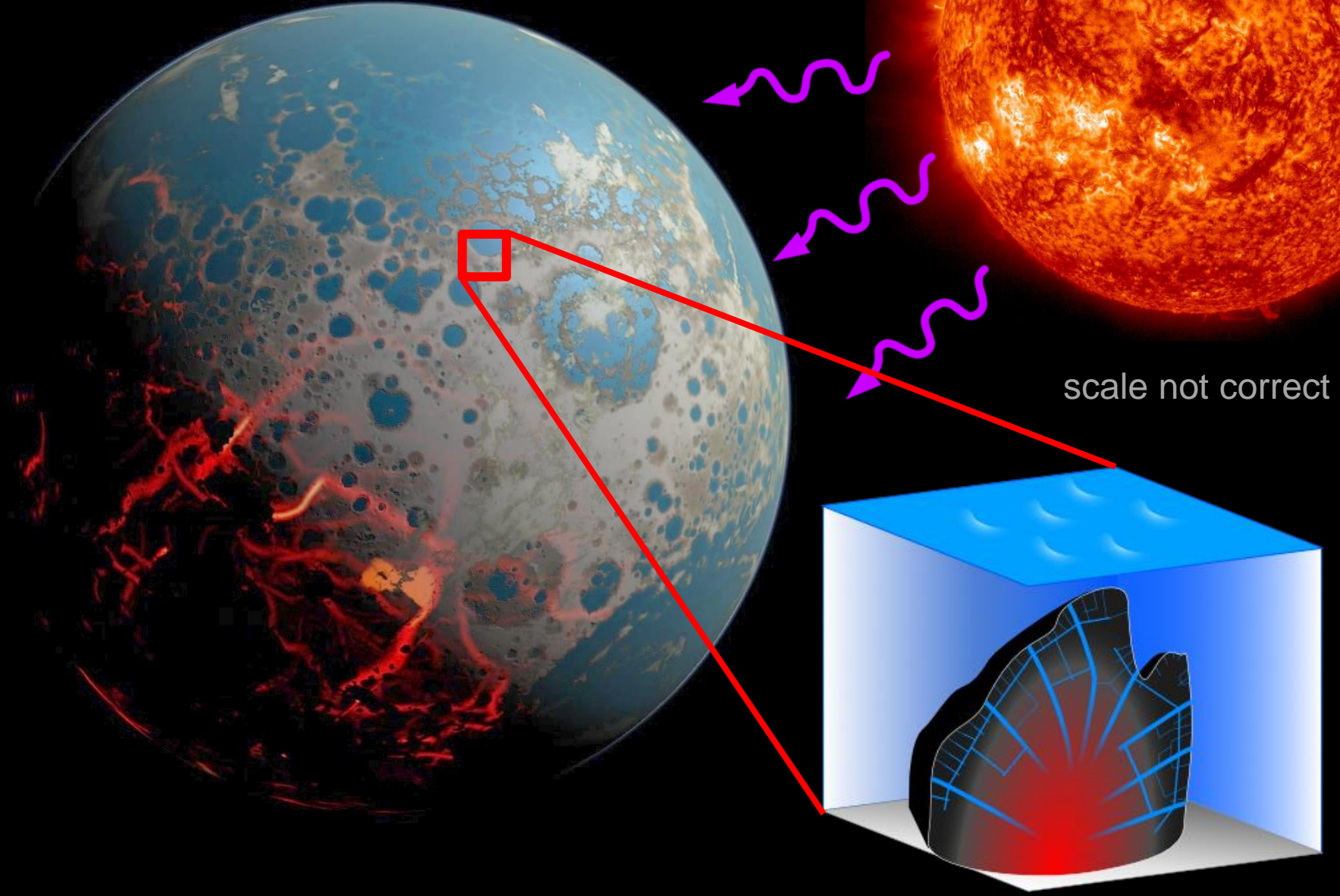
Coupling between physical non-equilibria and prebiotic chemistry & geology



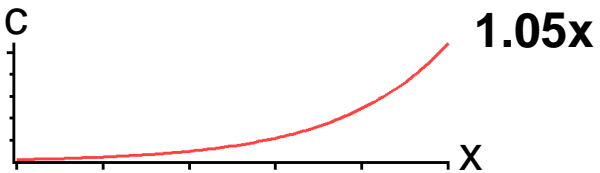
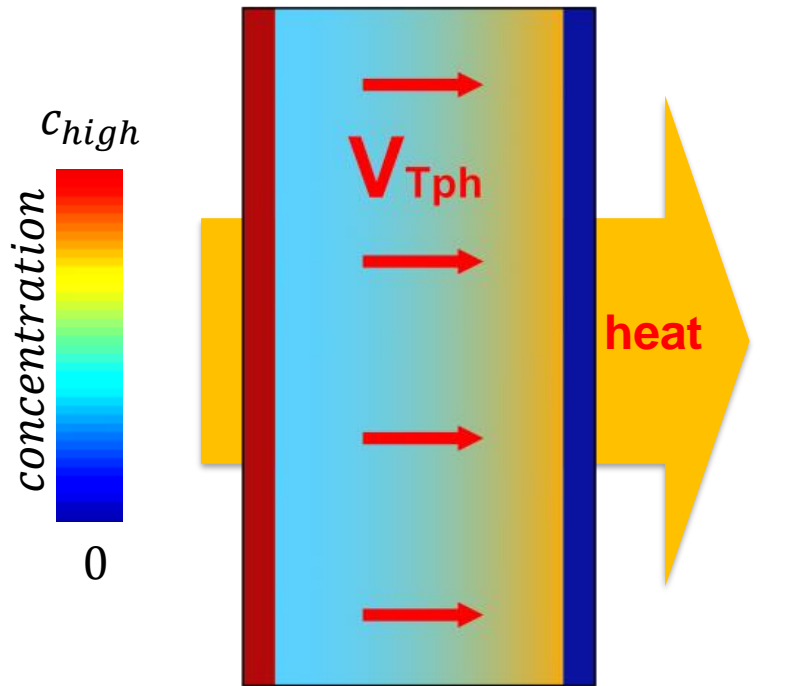
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Systems Pre-Biophysics

Coupling between physical non-equilibria and prebiotic chemistry & geology

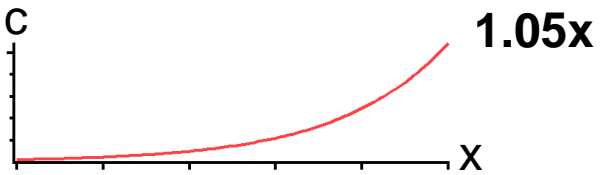
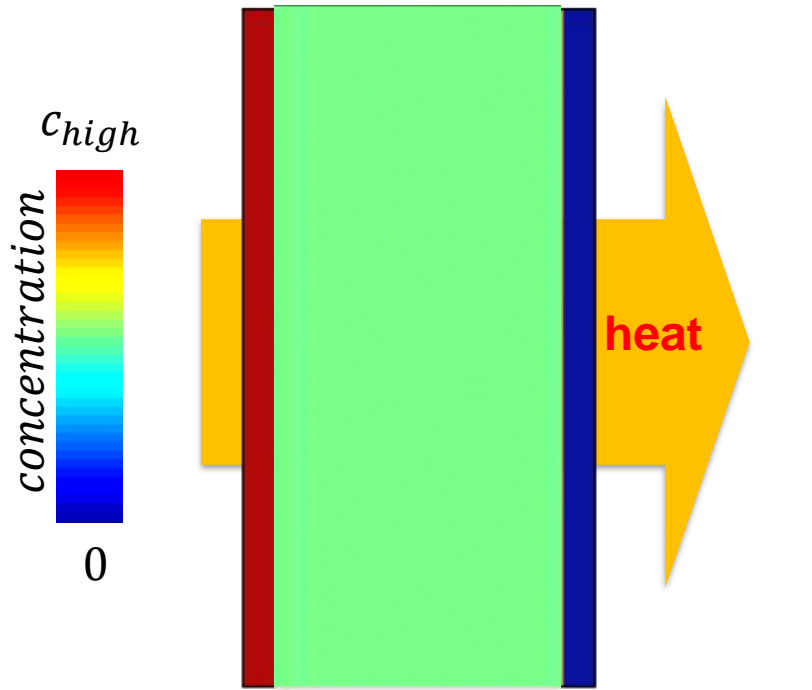


Thermophoresis: The „capacitor effect“



$$\frac{C_{hot}}{C_{cold}} = \exp(-S_T \cdot \Delta T)$$

Thermophoresis: The „capacitor effect“

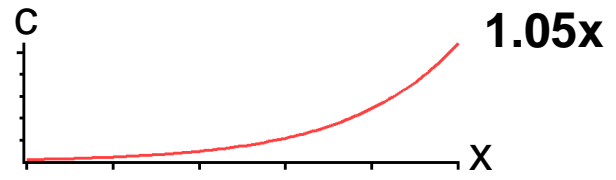
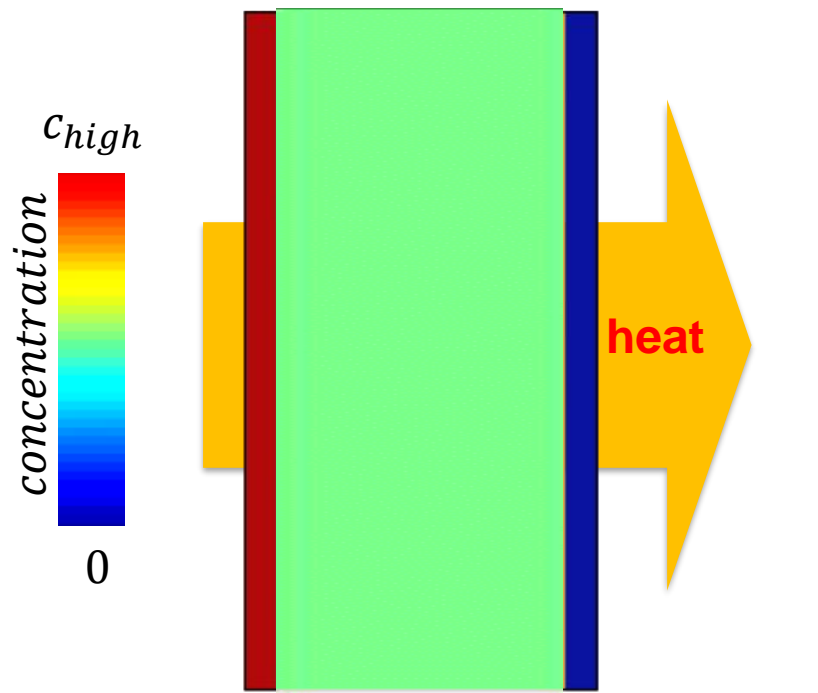


$$\frac{C_{hot}}{C_{cold}} = \exp(-S_T \cdot \Delta T)$$

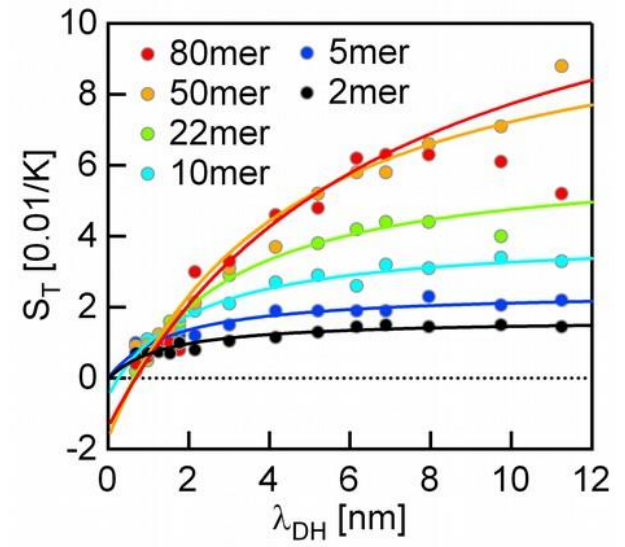
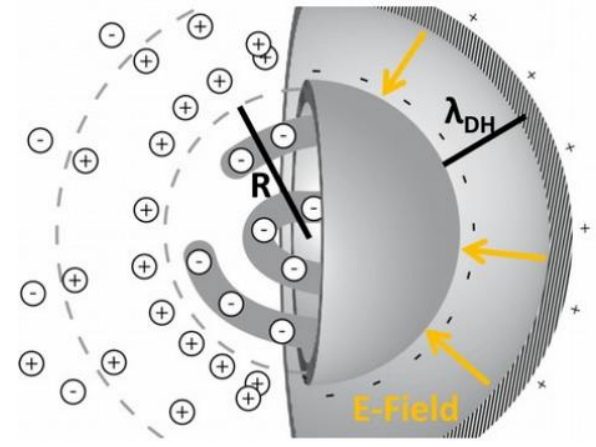
Thermophoresis: The „capacitor effect“

$$S_T = \frac{Q^2 \beta \lambda_{DH}}{4A \epsilon \epsilon_0 k T^2} \rightarrow \frac{Q^2}{16 \pi \epsilon \epsilon_0 k T^2 [\lambda_{DH} [1 + R/\lambda_{DH}]^2]} \left[1 - \frac{T \partial \epsilon}{\epsilon \partial T} \left[1 + 2 \frac{\lambda_{DH}}{R} \right] \right]$$

[Dhont]



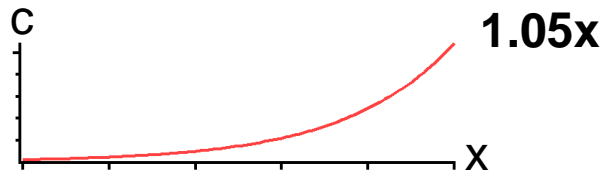
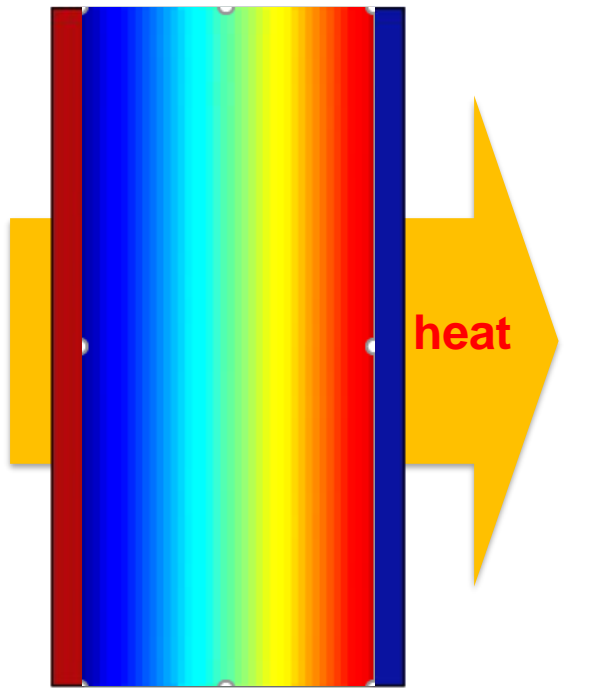
$$\frac{C_{hot}}{C_{cold}} = \exp(-S_T \cdot \Delta T)$$



Increase thermophoretic effect by convection

Thermophoresis only:

(no g , thin vessel, g & ∇T same direction..)

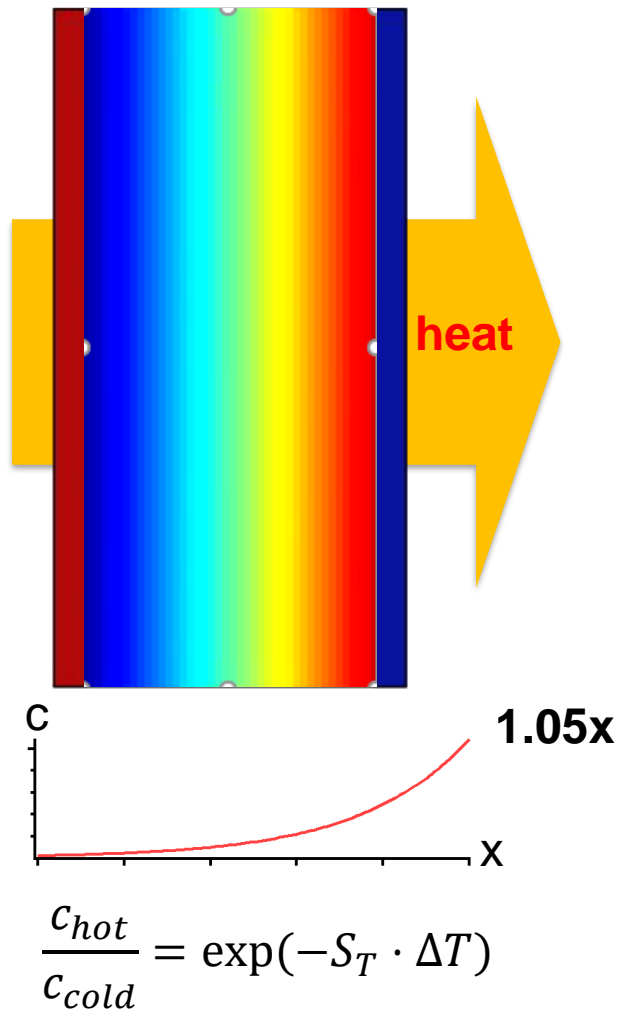


$$\frac{C_{hot}}{C_{cold}} = \exp(-S_T \cdot \Delta T)$$

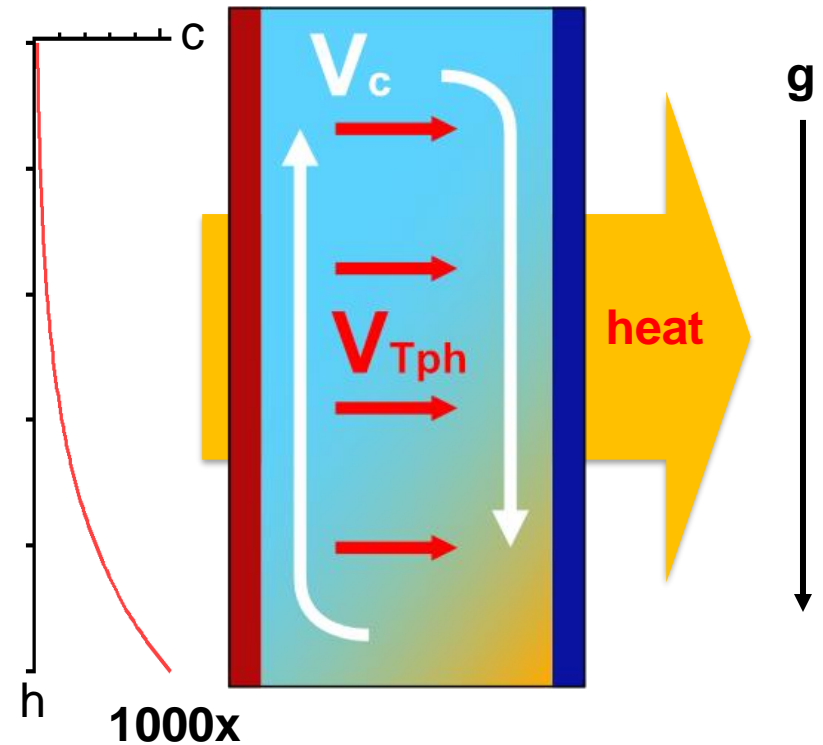
Increase thermophoretic effect by convection

Thermophoresis only:

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Thermophoresis + convection:

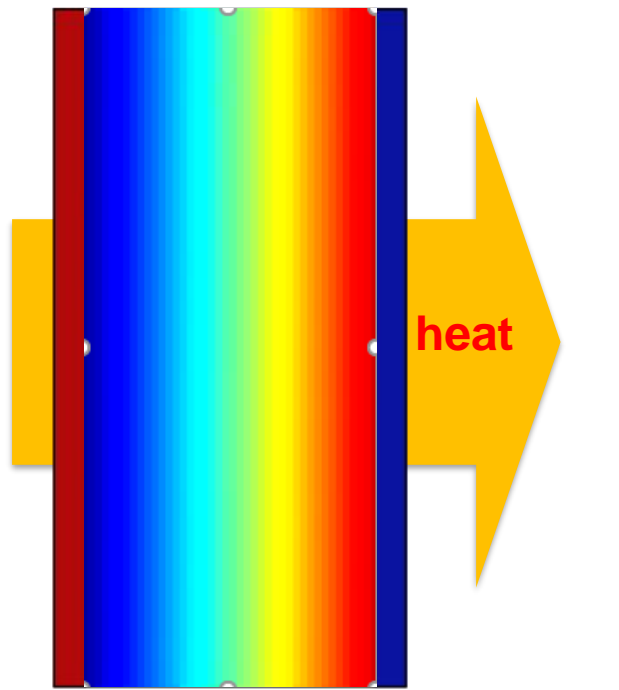


$$\frac{c_{bottom}}{c_{top}} = \exp\left(\alpha \cdot S_T \cdot \Delta T \cdot \frac{h}{w}\right)$$

Increase thermophoretic effect by convection

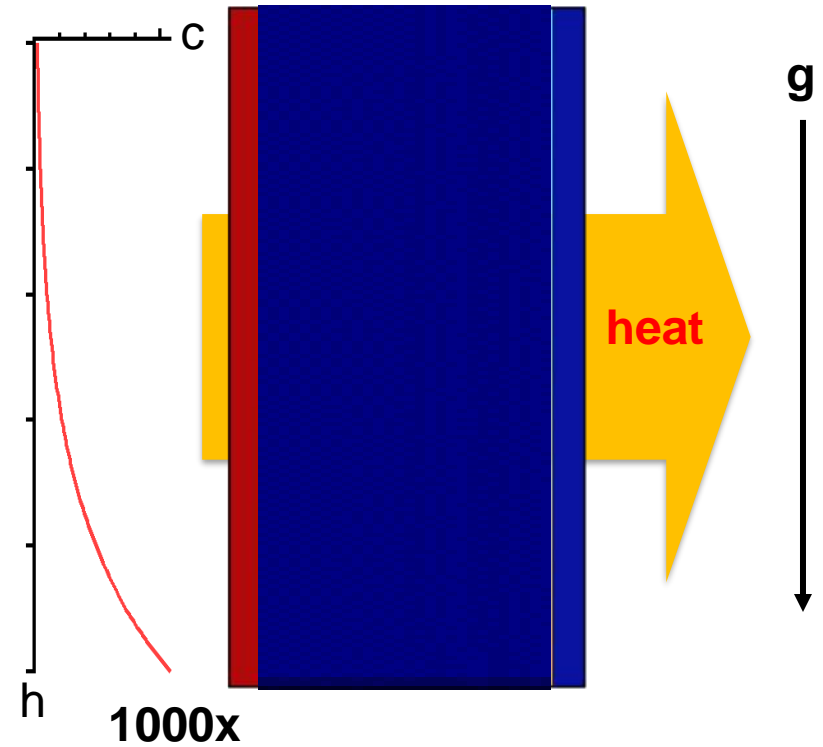
Thermophoresis only:

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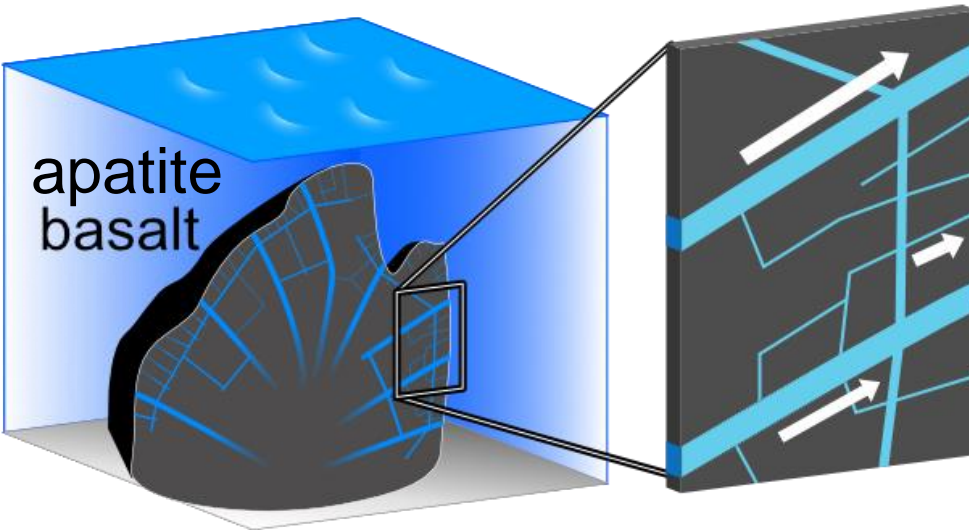
$$\frac{C_{hot}}{C_{cold}} = \exp(-S_T \cdot \Delta T)$$

Thermophoresis + convection:



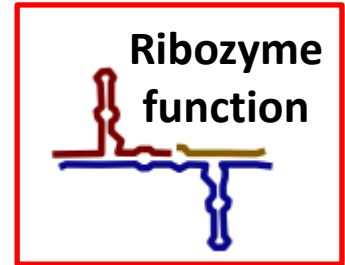
$$\frac{C_{bottom}}{C_{top}} = \exp\left(\alpha \cdot S_T \cdot \Delta T \cdot \frac{h}{w}\right)$$

Scenario



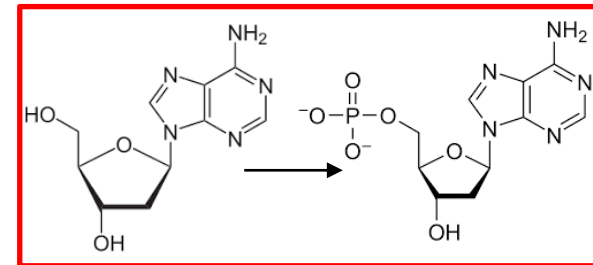
Basalt:

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

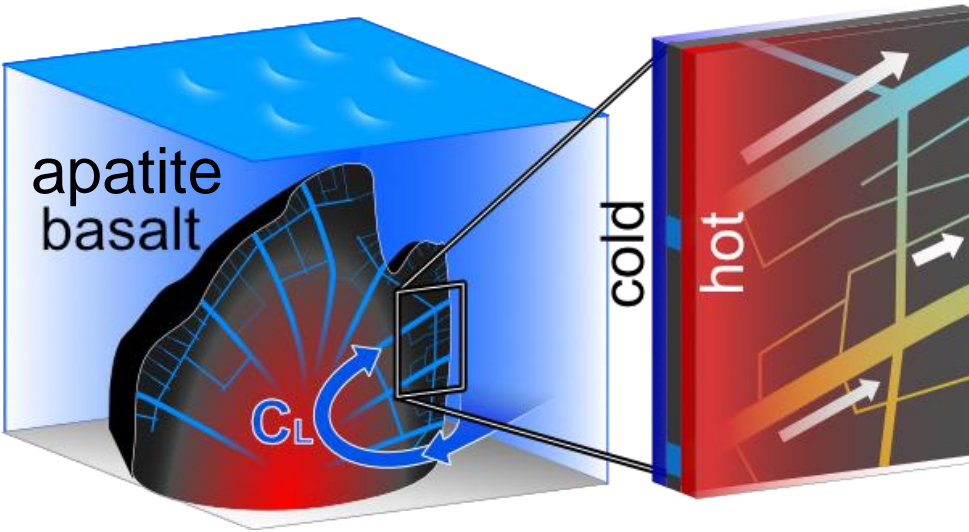


Apatite @pH2:

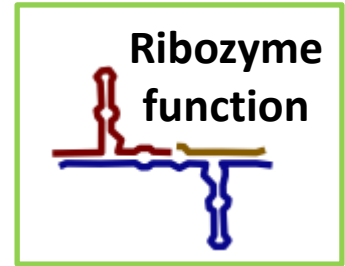
$$\frac{6[PO_4]}{10[Ca^{2+}]} \sim 1$$



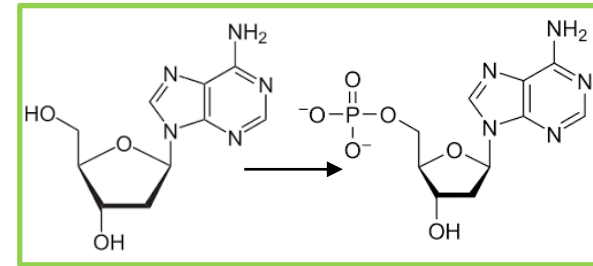
Scenario



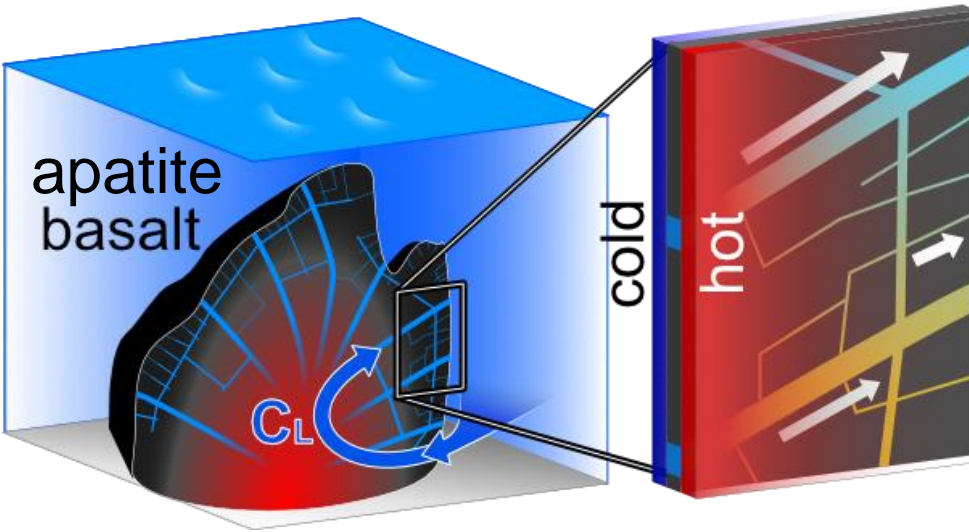
Basalt:
$$\frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100$$



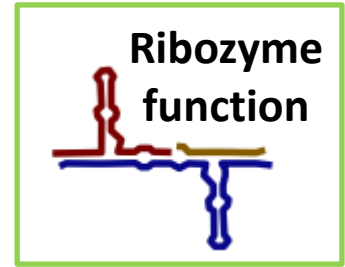
Apatite @pH2:
$$\frac{6[PO_4]}{10[Ca^{2+}]} > 10$$



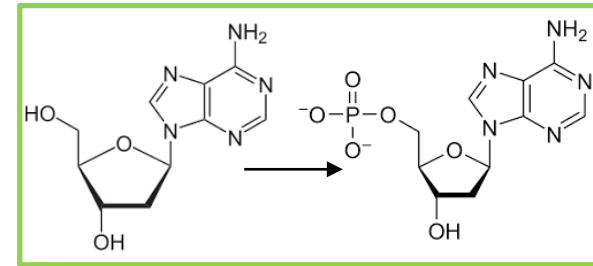
Scenario



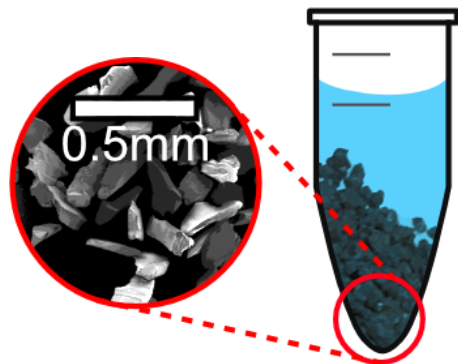
Basalt:
$$\frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100$$



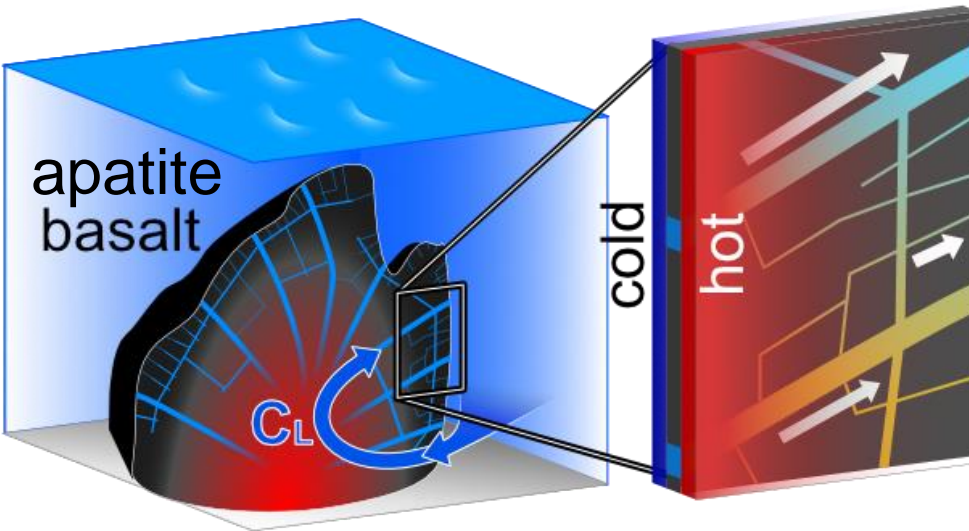
Apatite @pH2:
$$\frac{6[PO_4]}{10[Ca^{2+}]} > 10$$



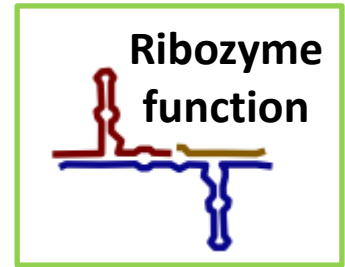
Experiment



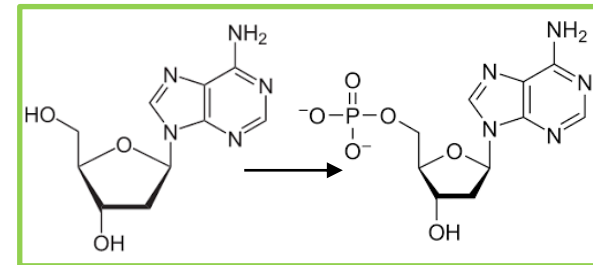
Scenario



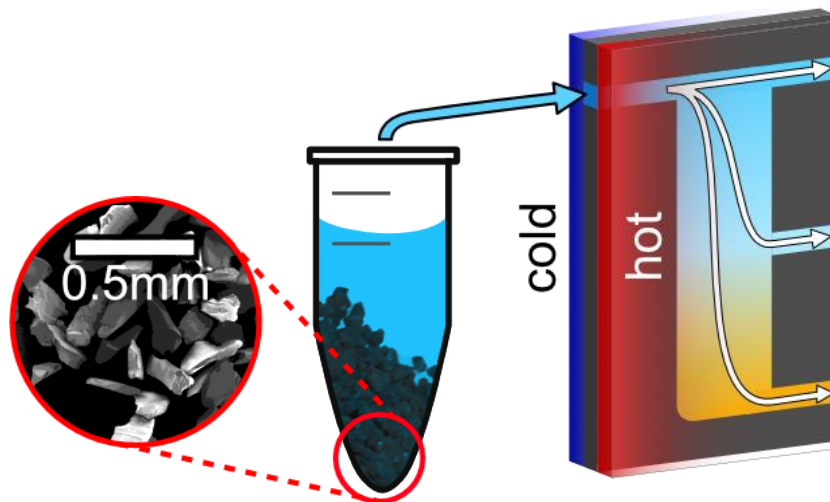
Basalt:
$$\frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100$$



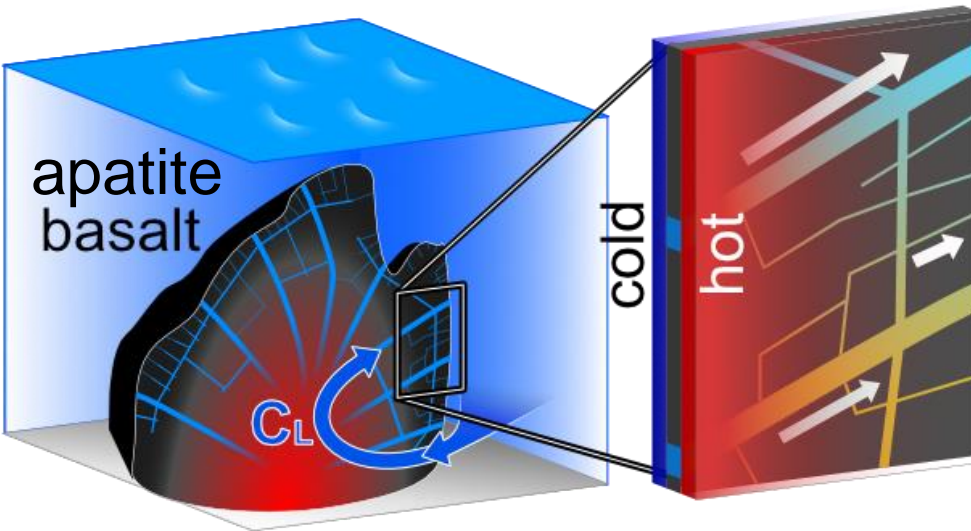
Apatite @pH2:
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Experiment

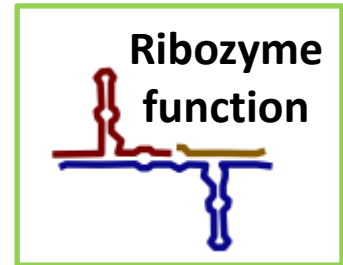


Scenario



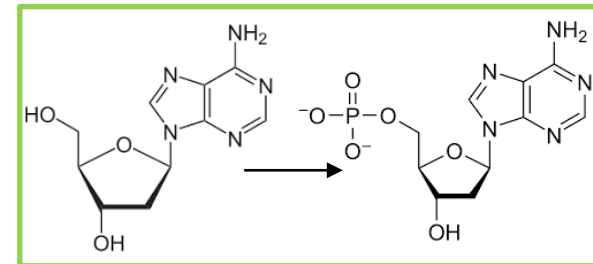
Basalt:

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

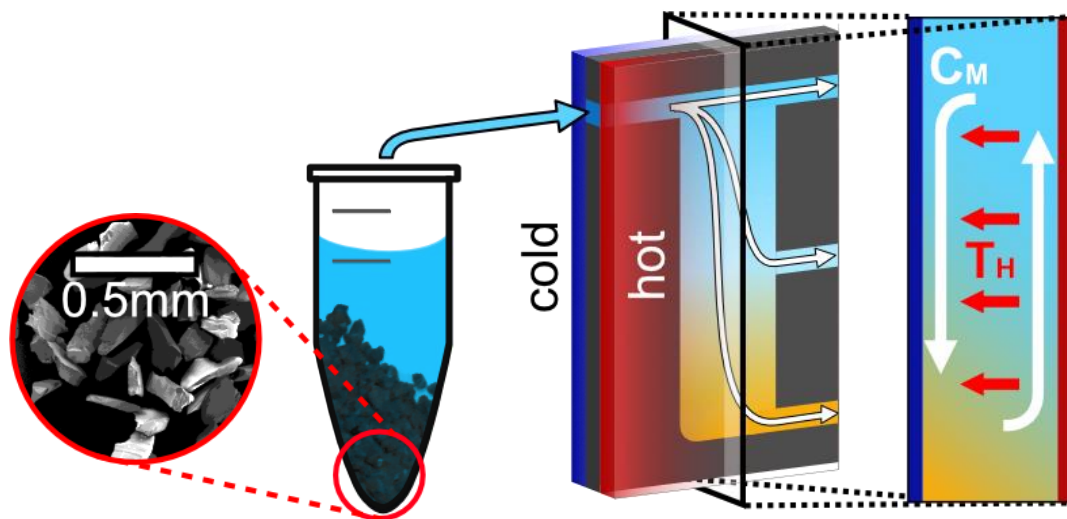


Apatite @pH2:

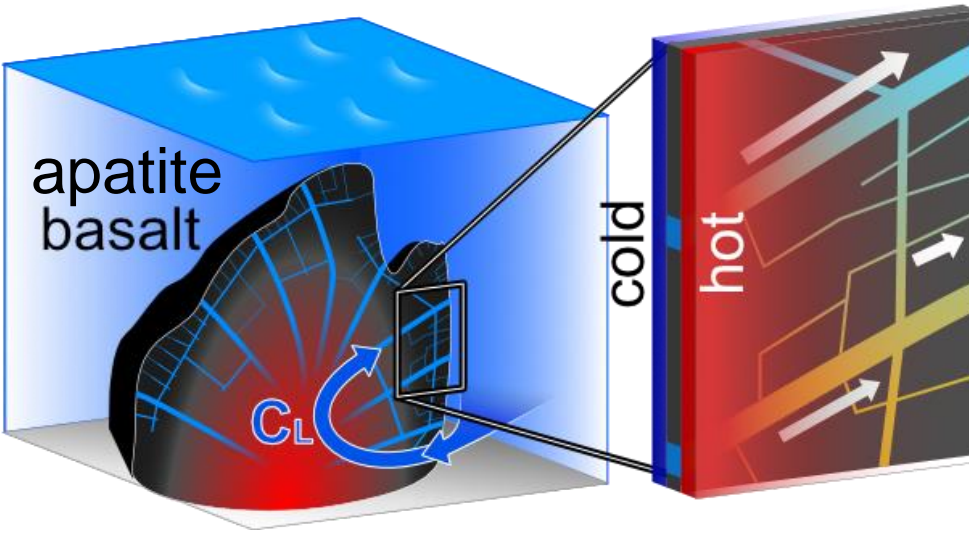
$$\frac{6[PO_4]}{10[Ca^{2+}]} > 10$$



Experiment



Scenario

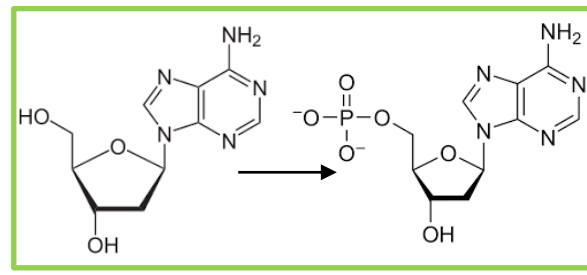
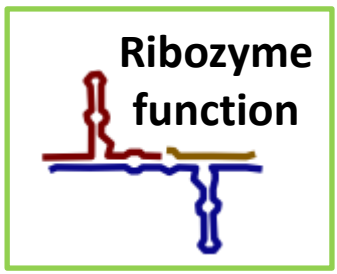


Basalt:

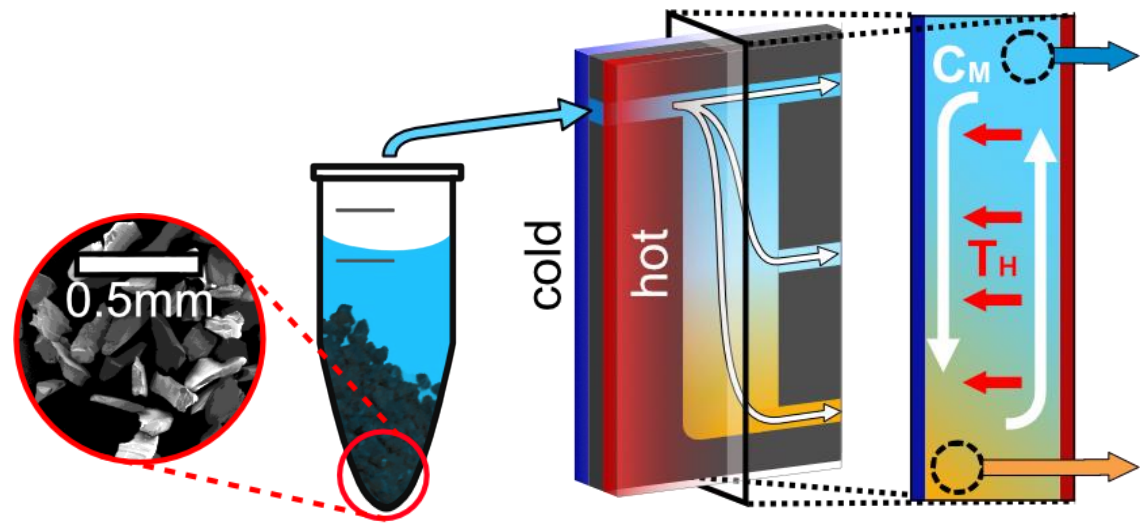
$$\frac{[Mg^{2+}]}{[Na^+]} = 1 \text{ to } 100$$

Apatite @pH2:

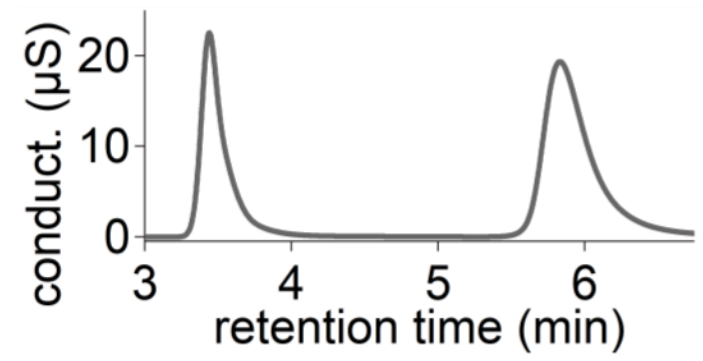
$$\frac{6[PO_4]}{10[Ca^{2+}]} > 10$$



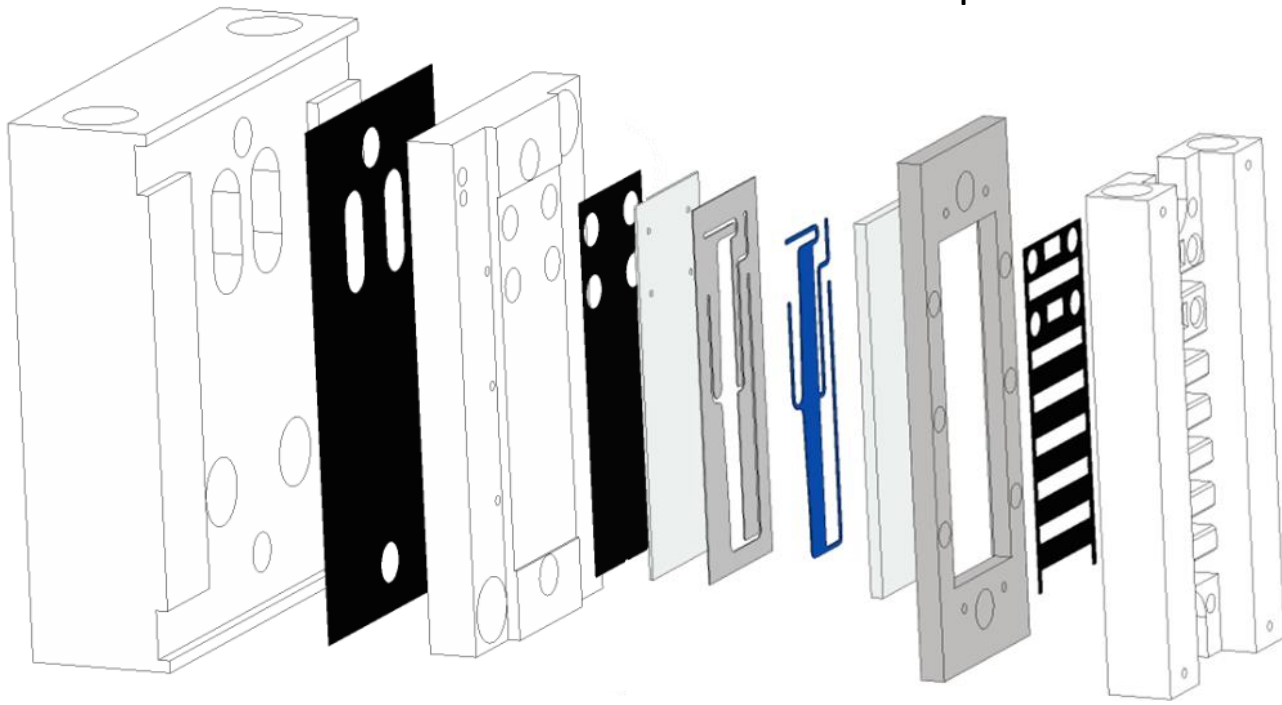
Experiment



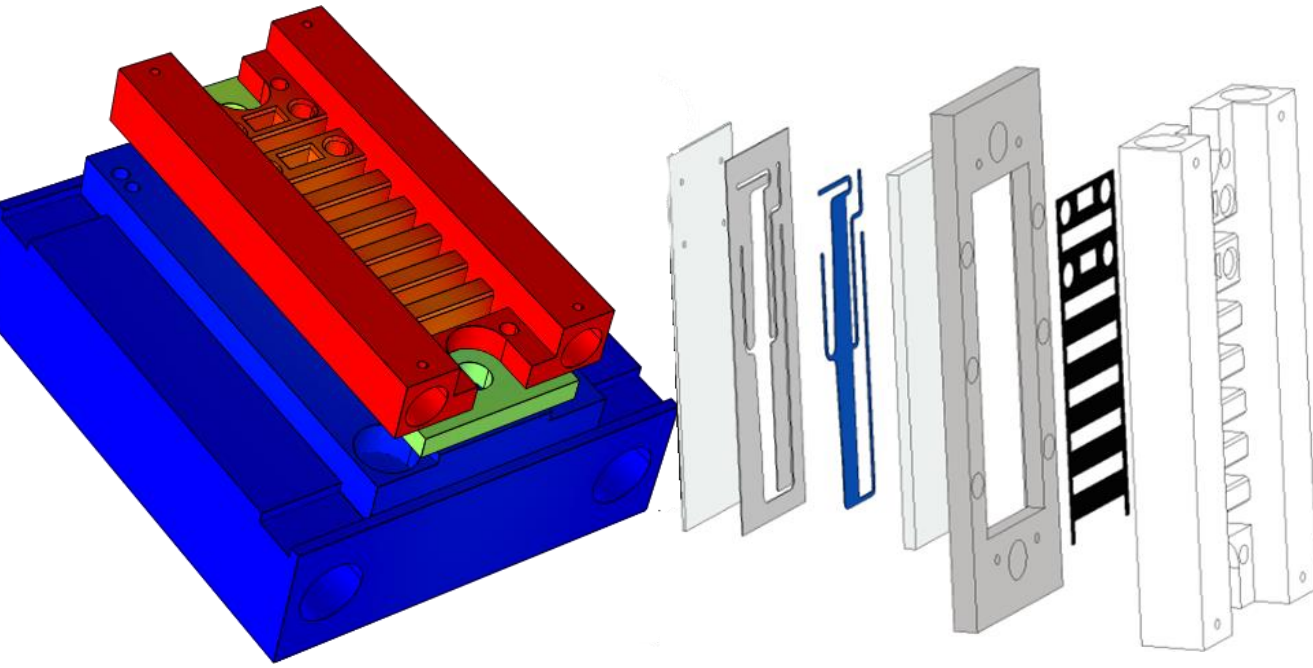
Ion chromatography:



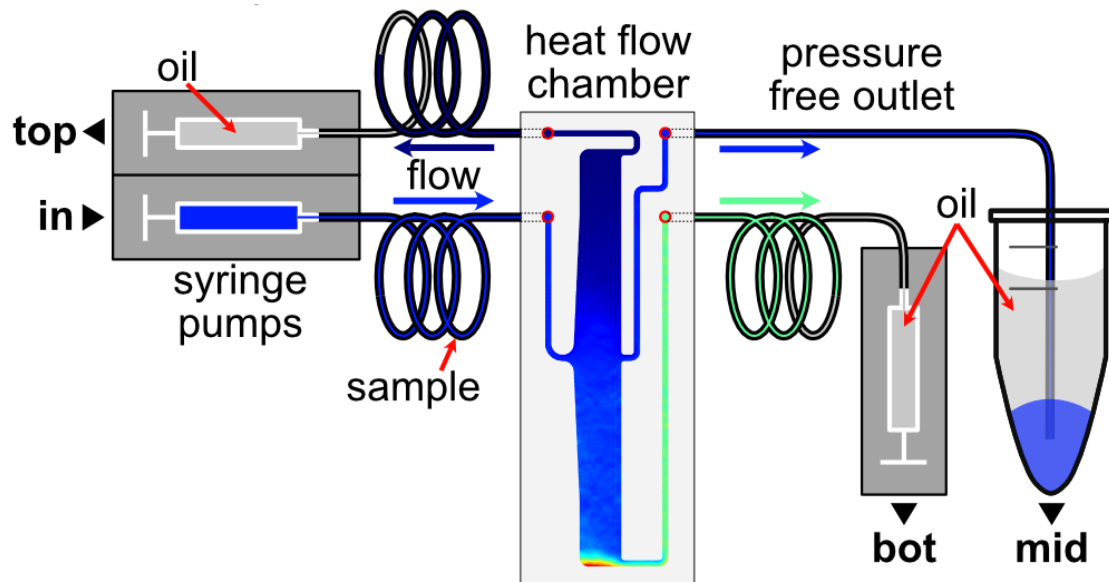
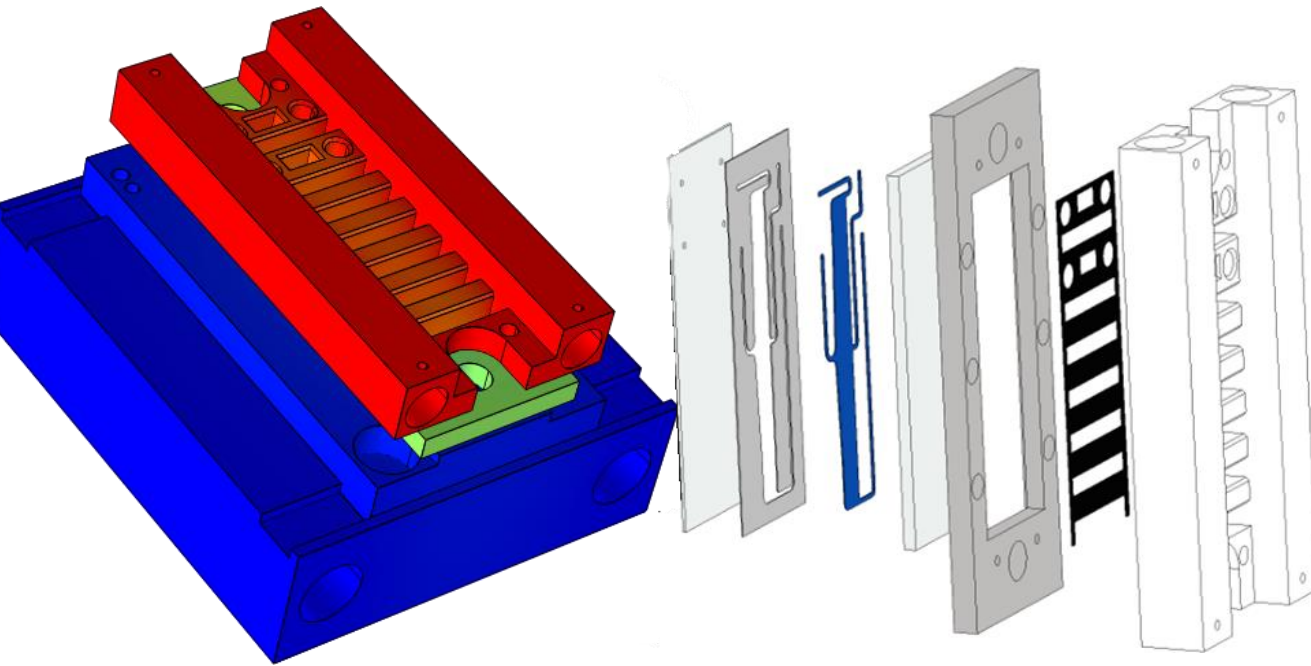
Setup



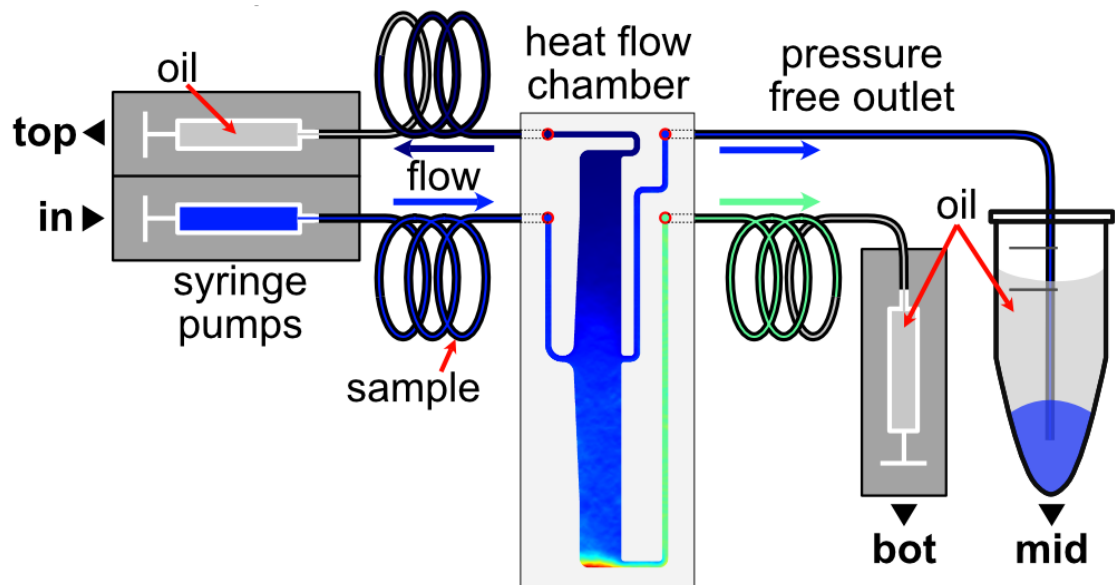
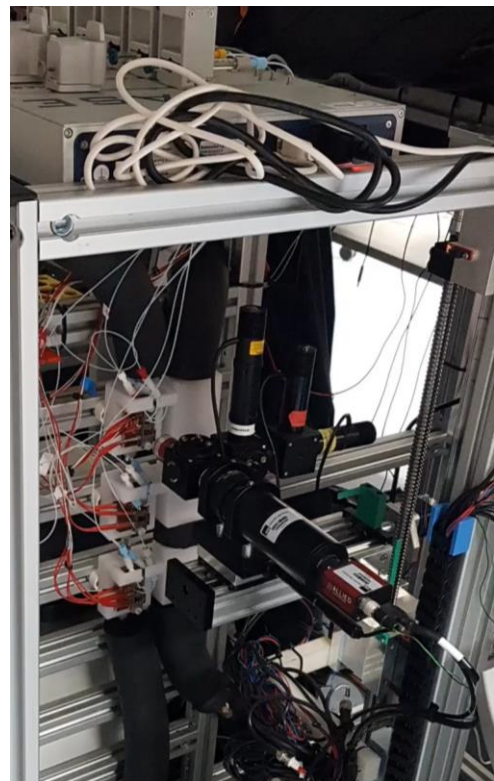
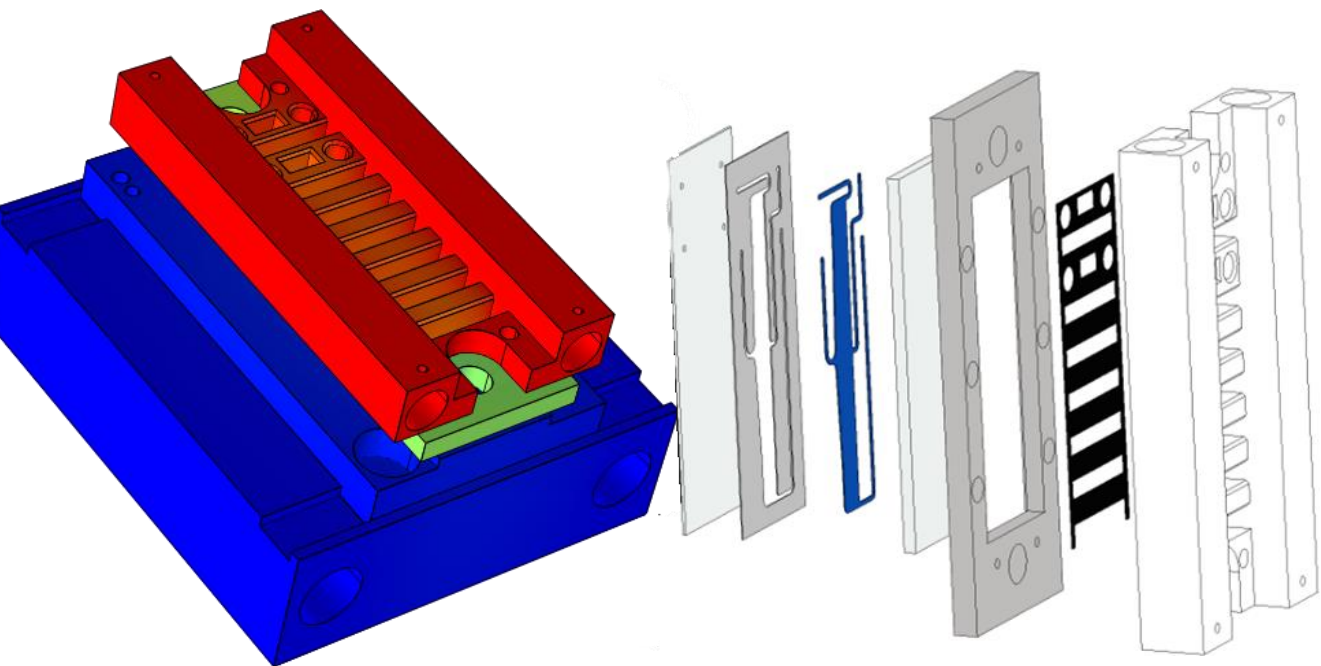
Setup



Setup

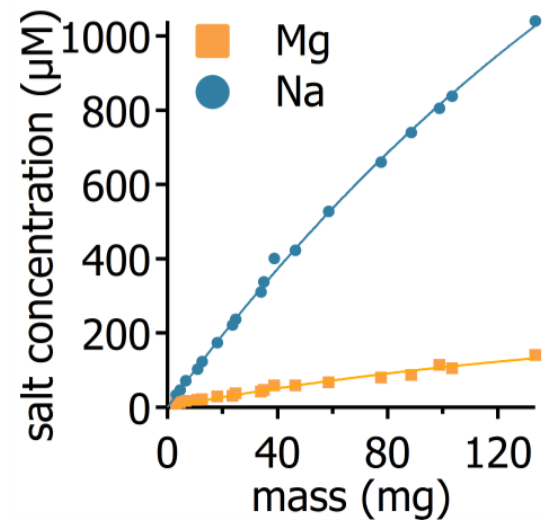
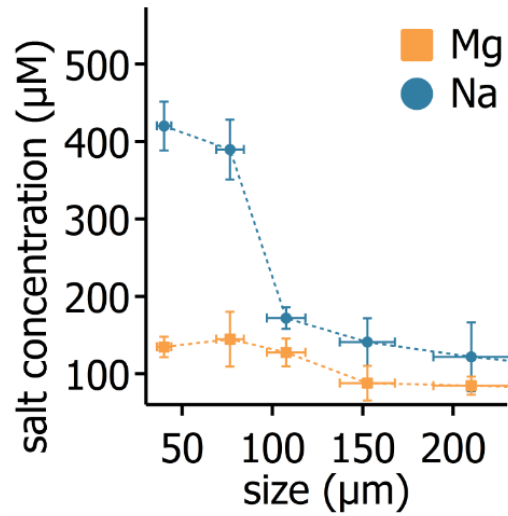
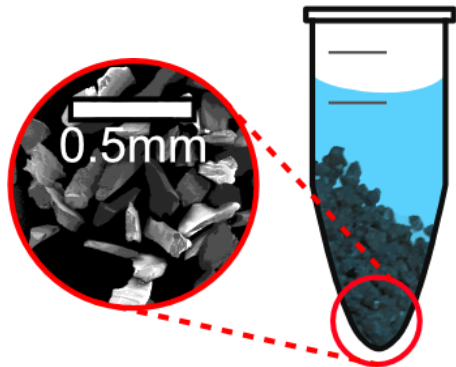


Setup



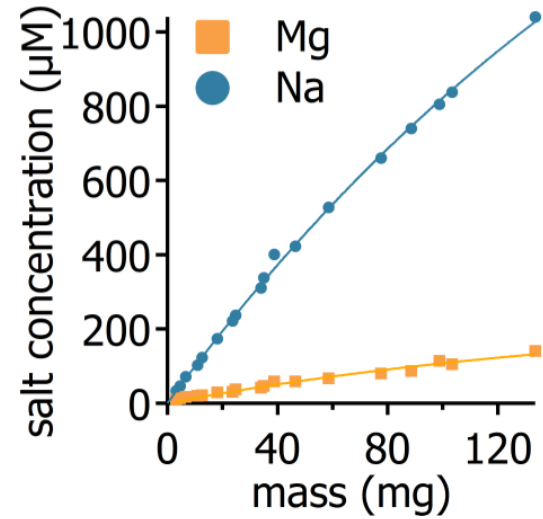
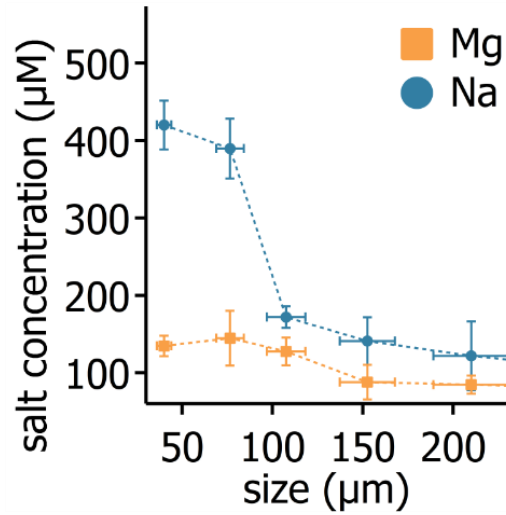
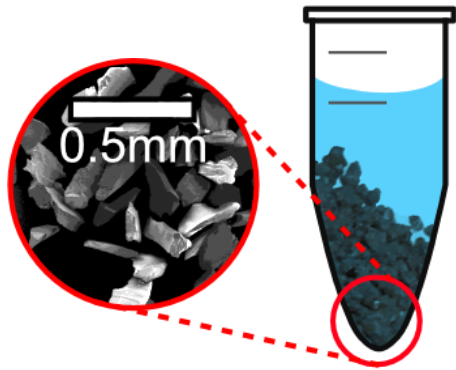
Results: Heat flows boost **Mg/Na**

Leaching only:

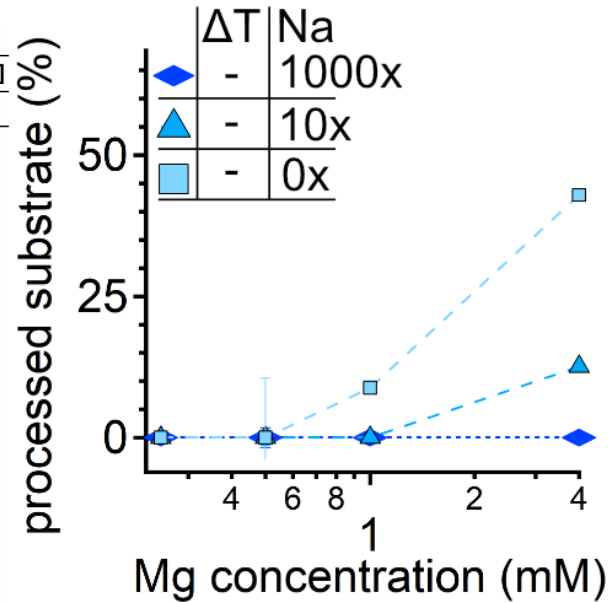
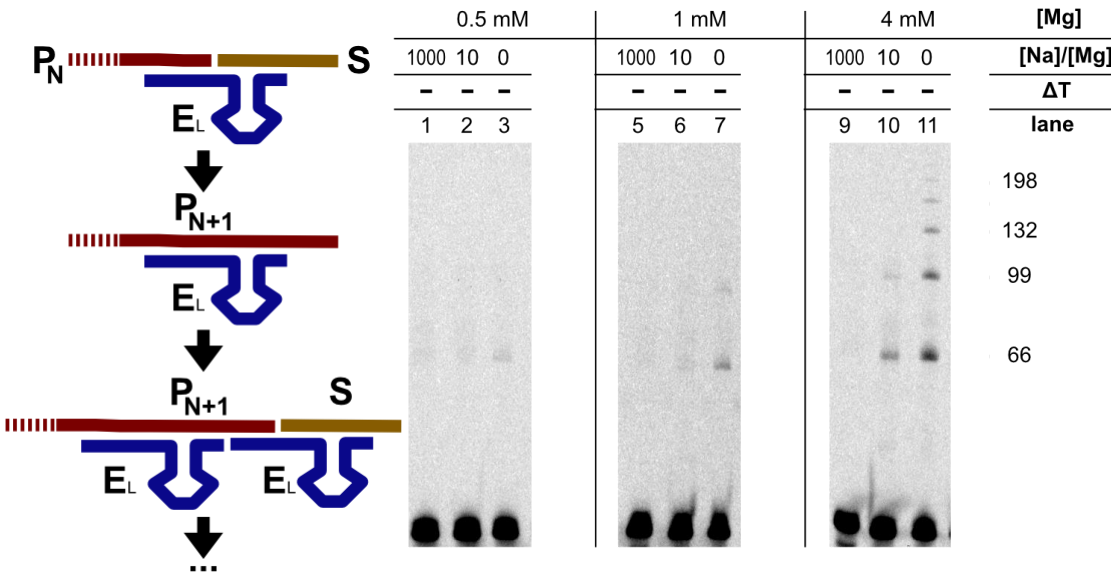


Results: Heat flows boost Mg/Na

Leaching only:

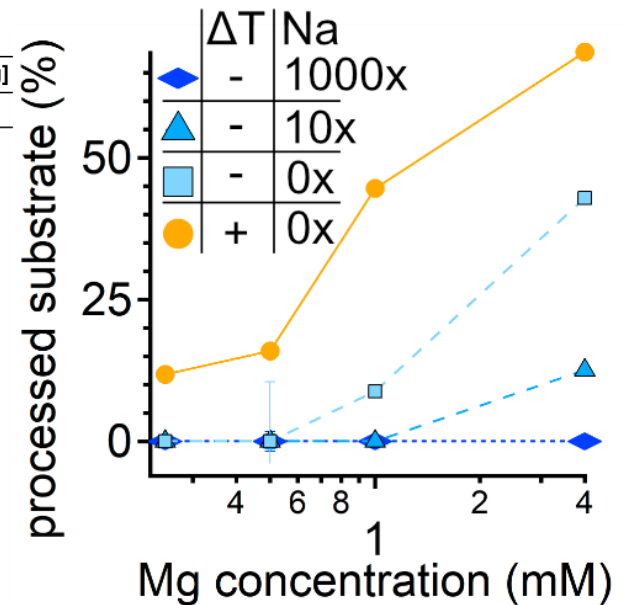
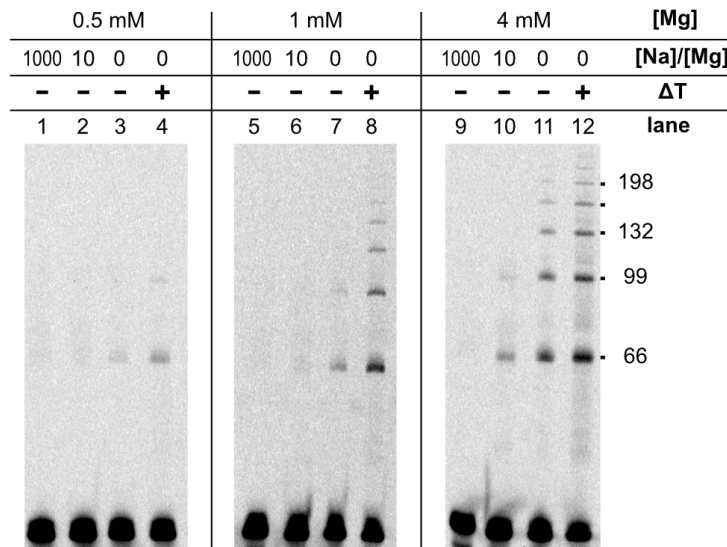
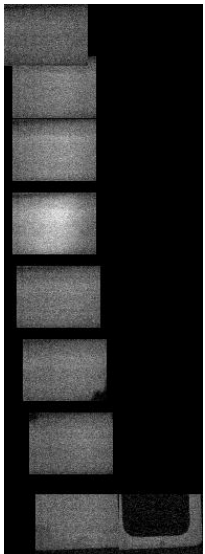


Ribozyme function:



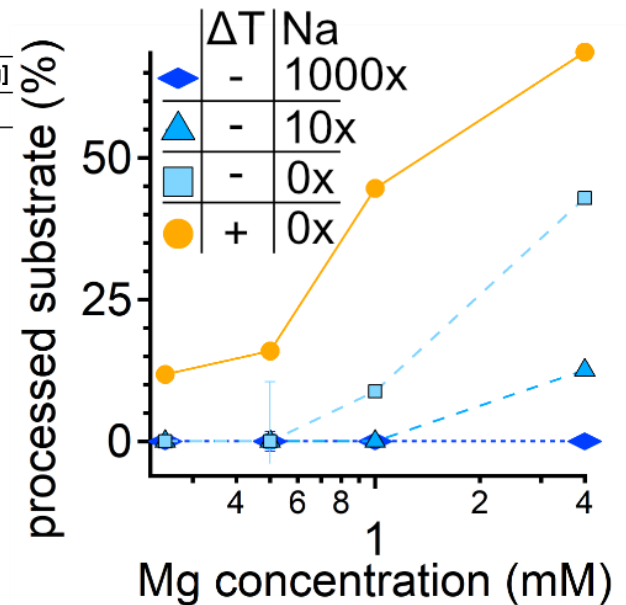
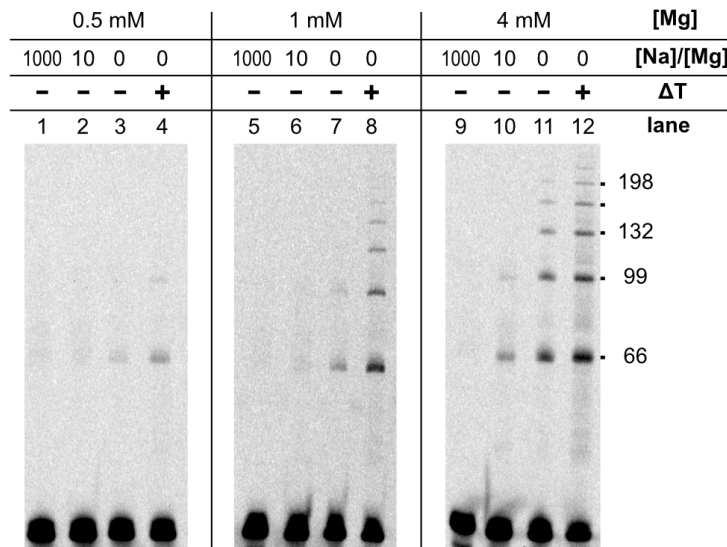
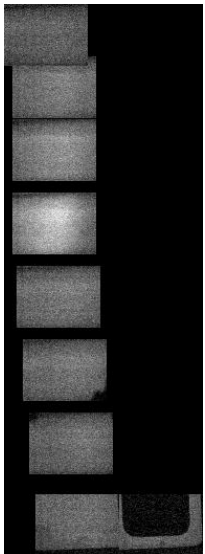
Results: Heat flows boost Mg/Na

Ribozyme function in the trap:



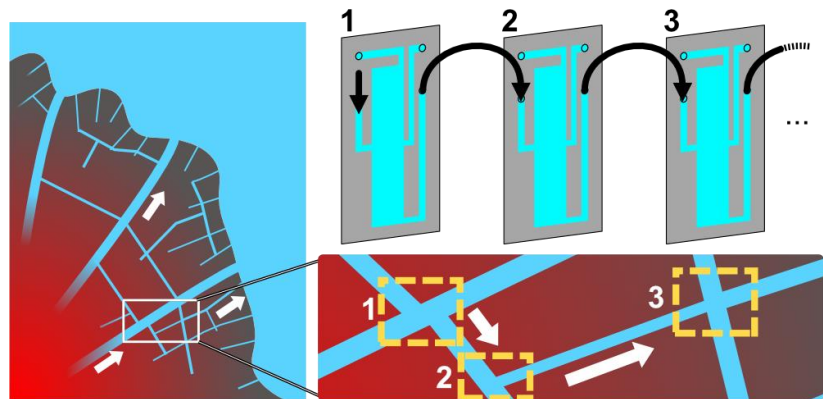
Results: Heat flows boost Mg/Na

Ribozyme function in the trap:

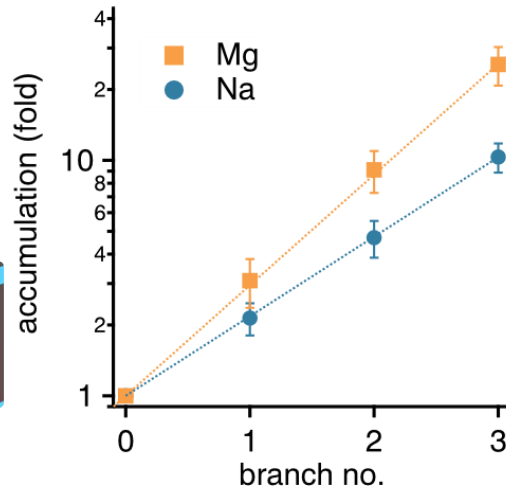


Results: Heat flows boost Mg/Na

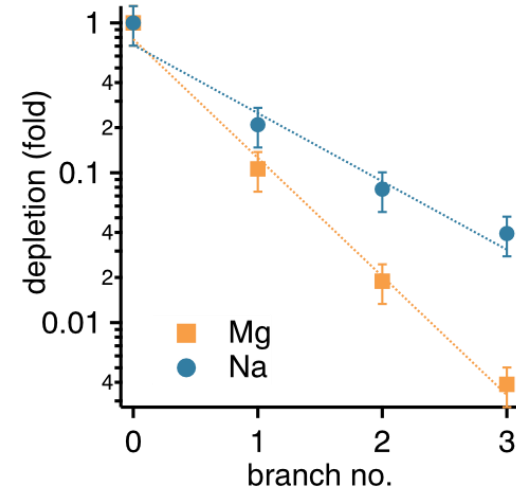
Cascade of thermal traps:



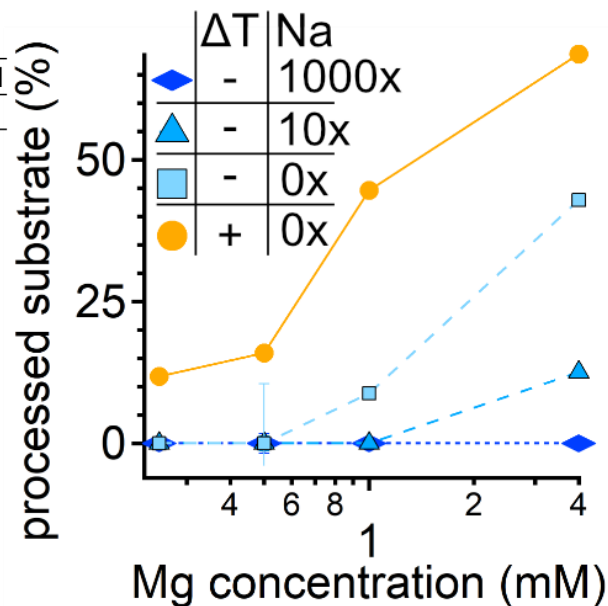
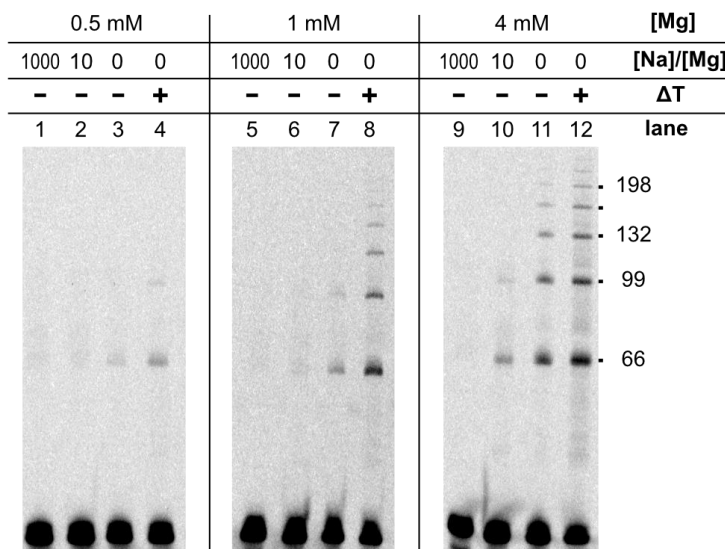
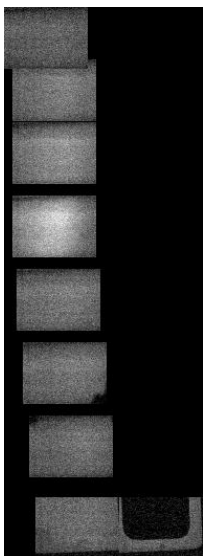
experiment: bottom out



experiment: top out

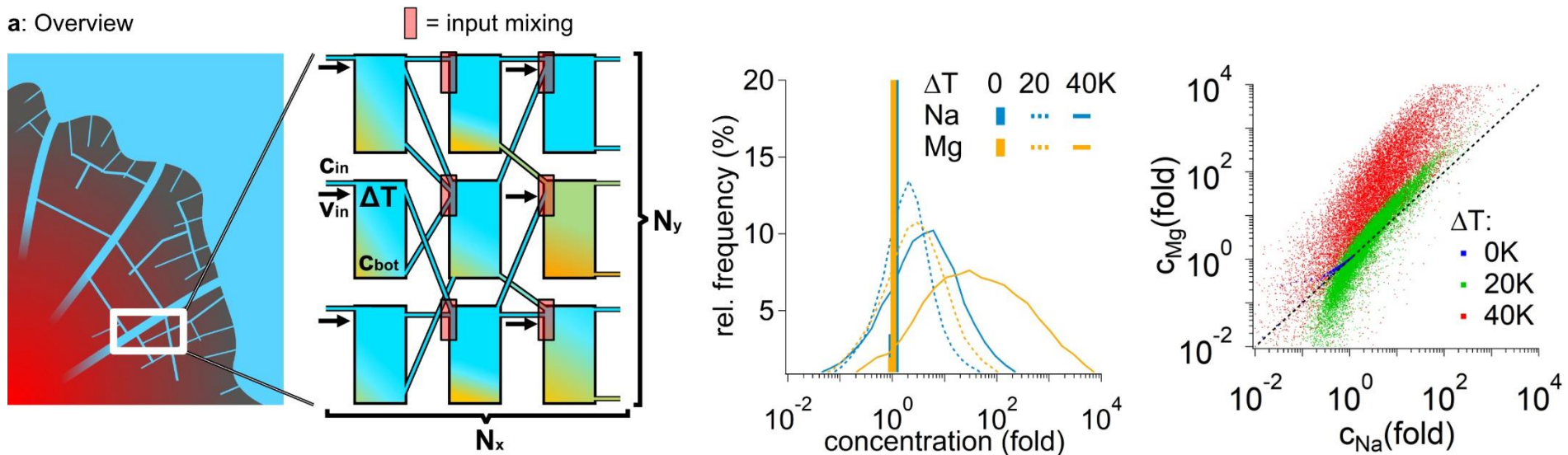


Ribozyme function in the trap:

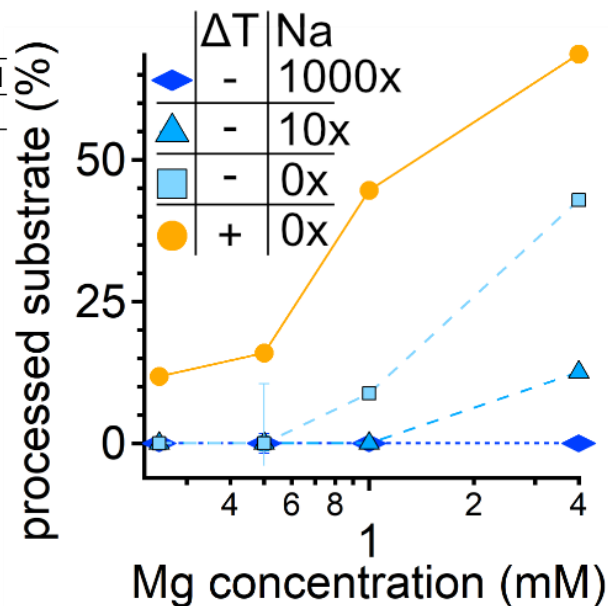
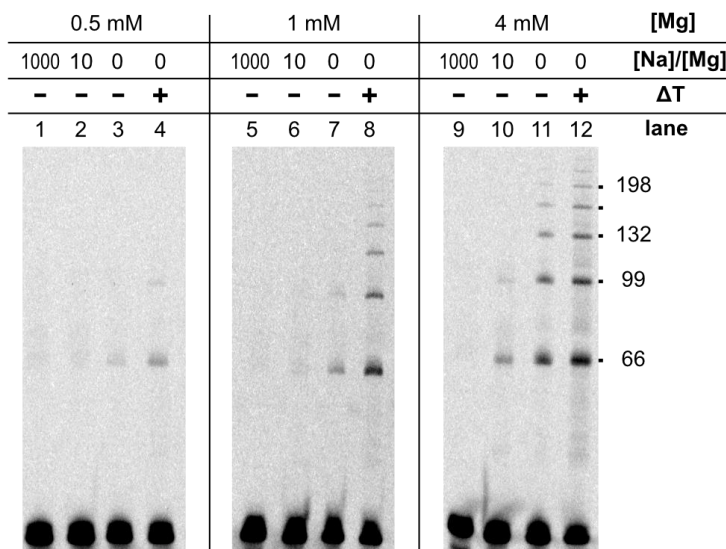
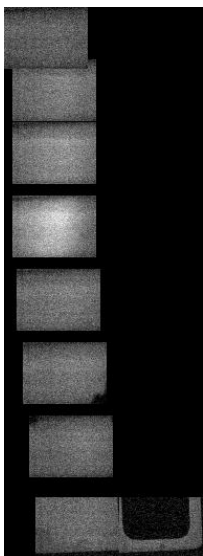


Results: Heat flows boost Mg/Na

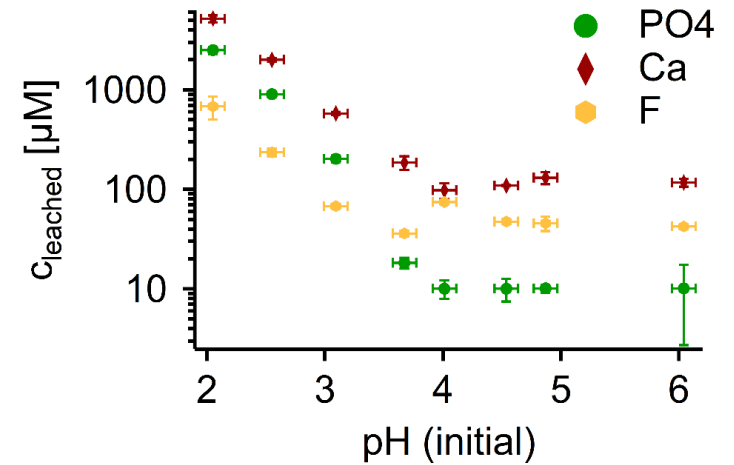
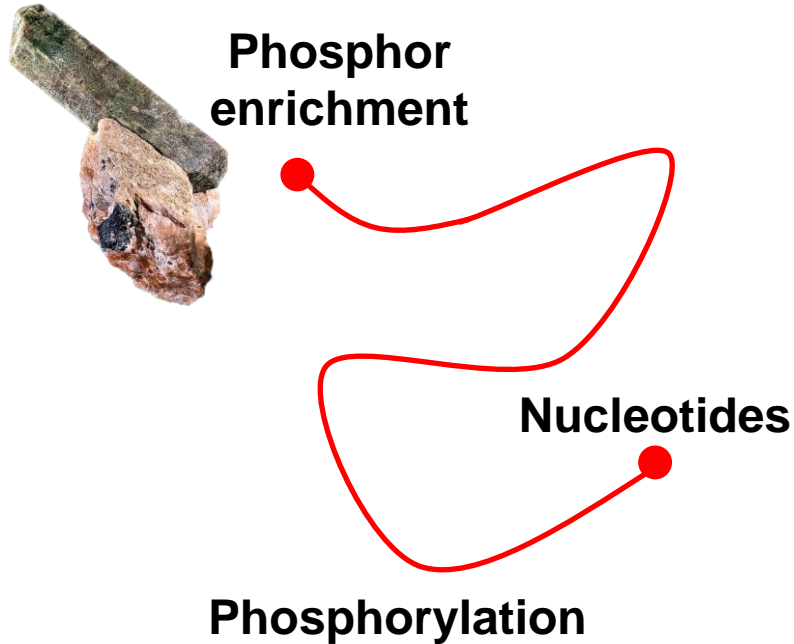
a: Overview



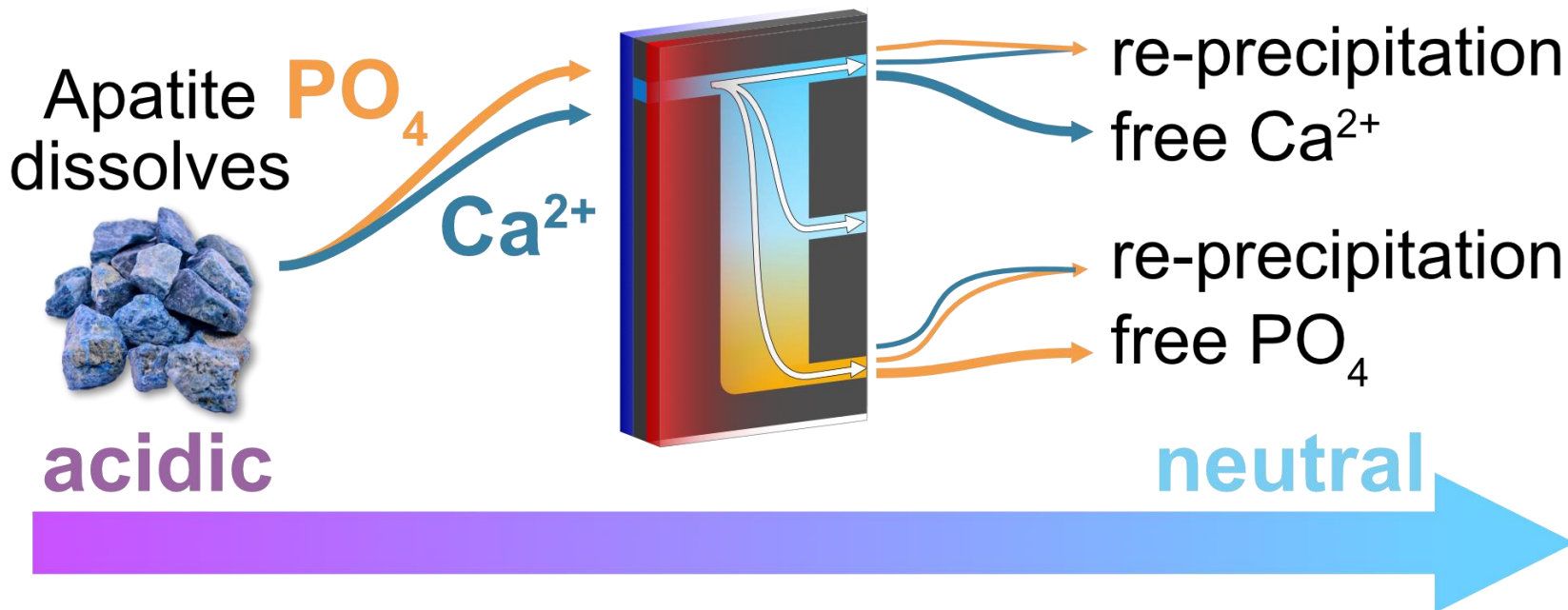
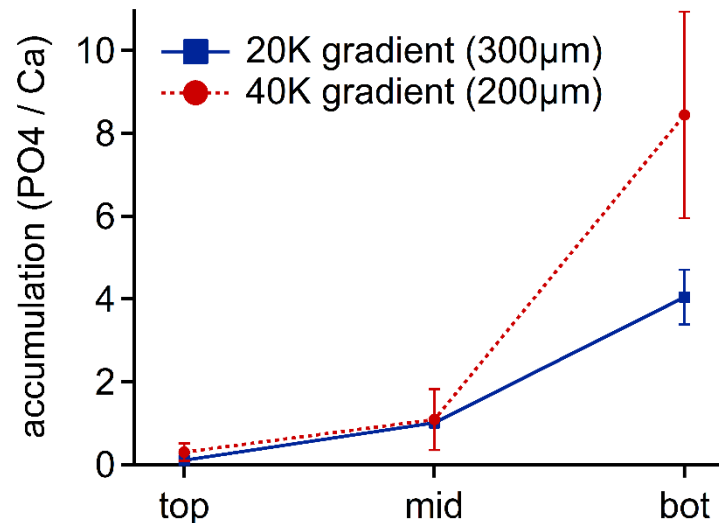
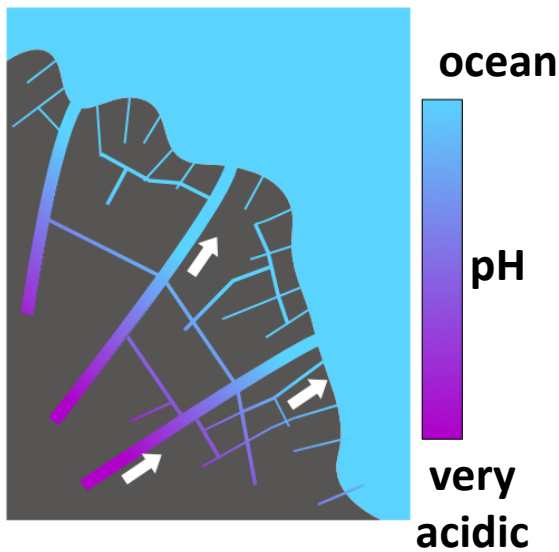
Ribozyme function in the trap:



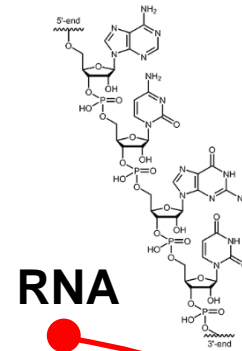
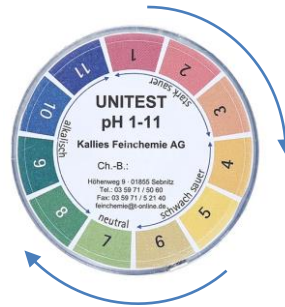
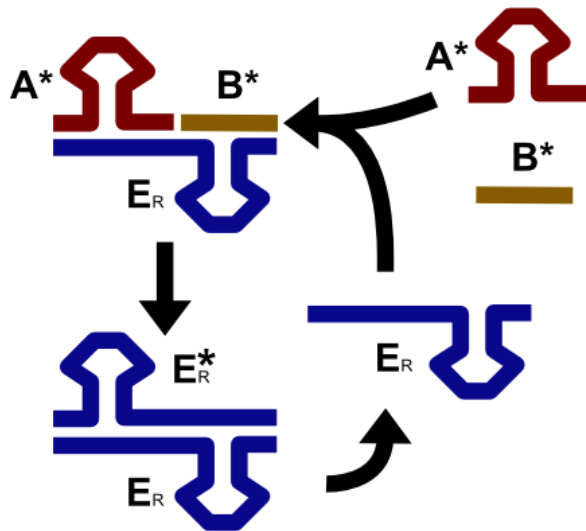
Ionic boundary conditions



Results: Heat flows boost PO_4/Ca



Ionic boundary conditions: pH

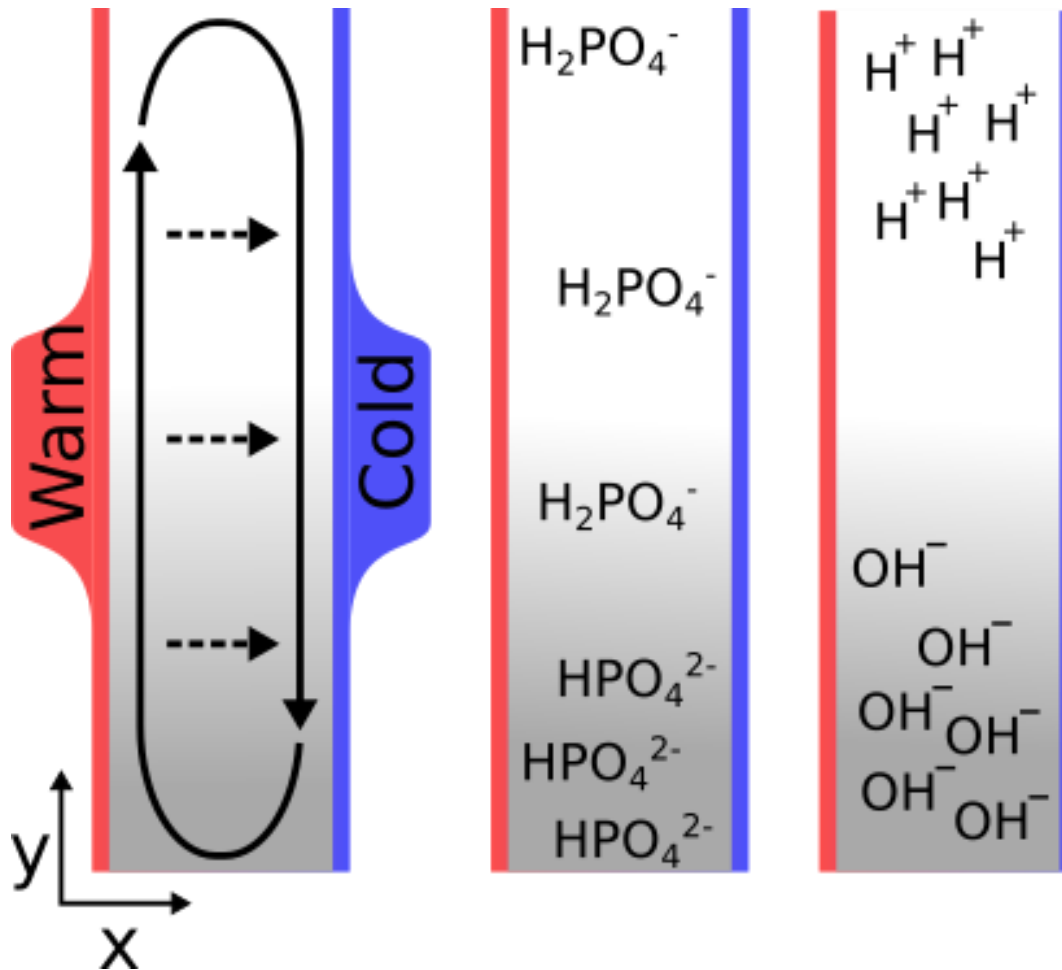


Molecular evolution

Ribozymes



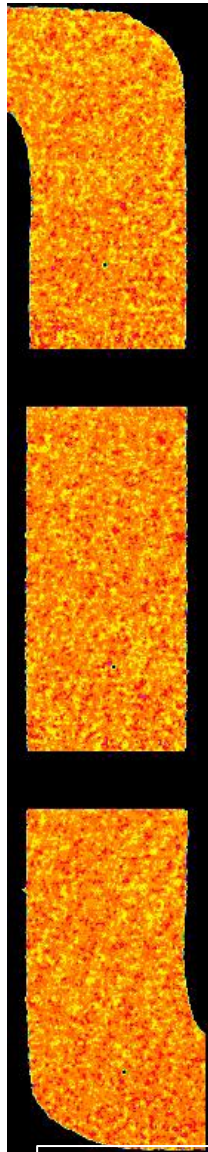
Separation of oxonium/hydroxid



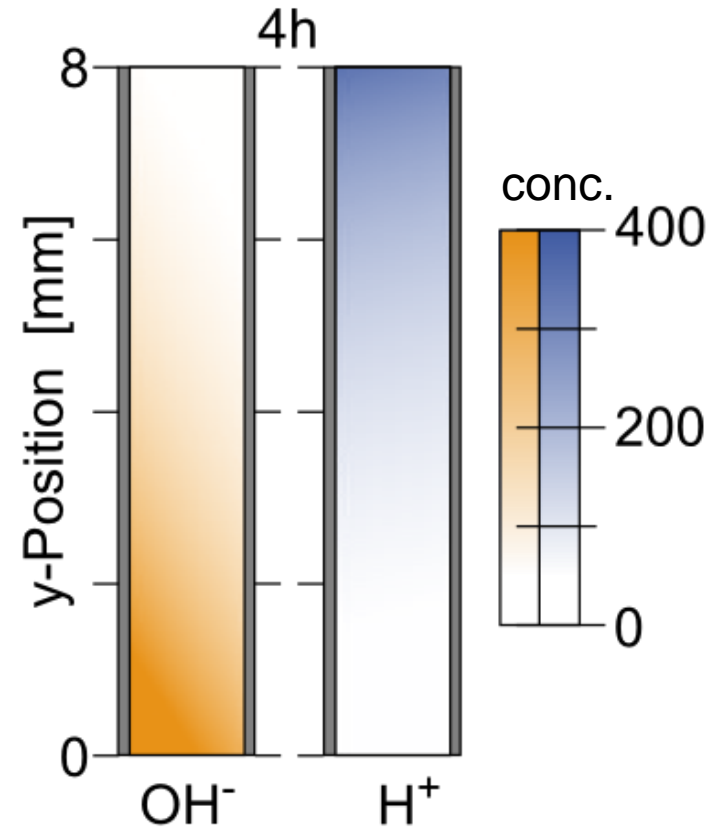
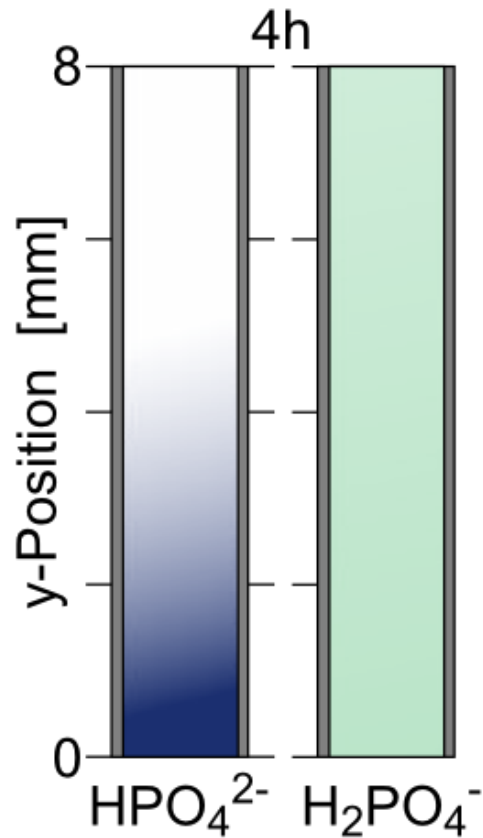
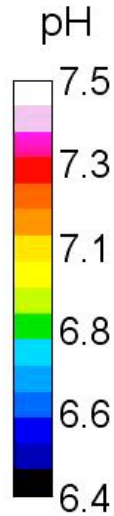
Proton Gradient and pH oscillations emerge from heat flow at the microscale

L. Keil, F. Möller, M. Kieß, P. Kudella and C. B. Mast, *Nature Communication* 8, 1897 (2017)

Separation of oxonium/hydroxid



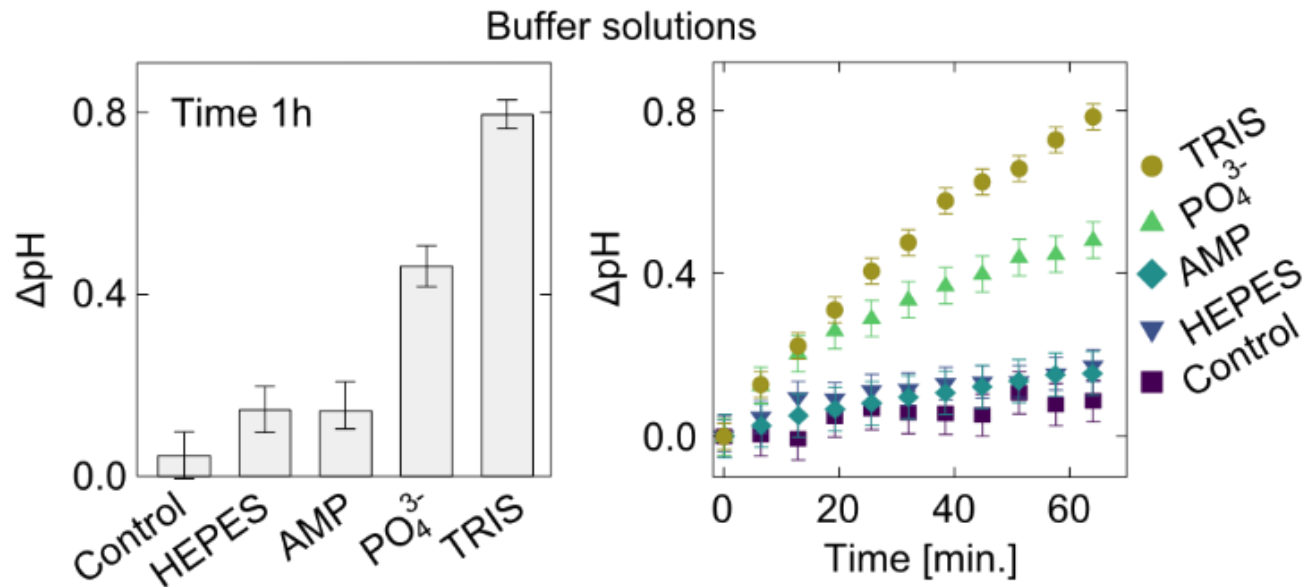
0.0 hours



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L. Keil, F. Möller, M. Kieß, P. Kudella and C. B. Mast, **Nature Communication** 8, 1897 (2017)

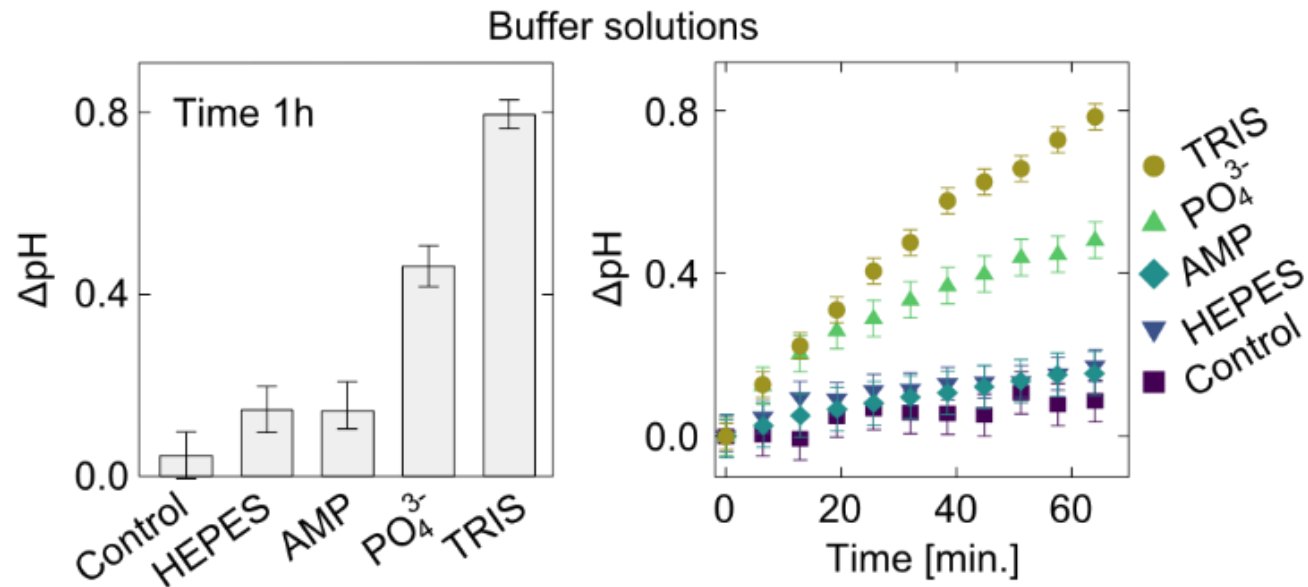
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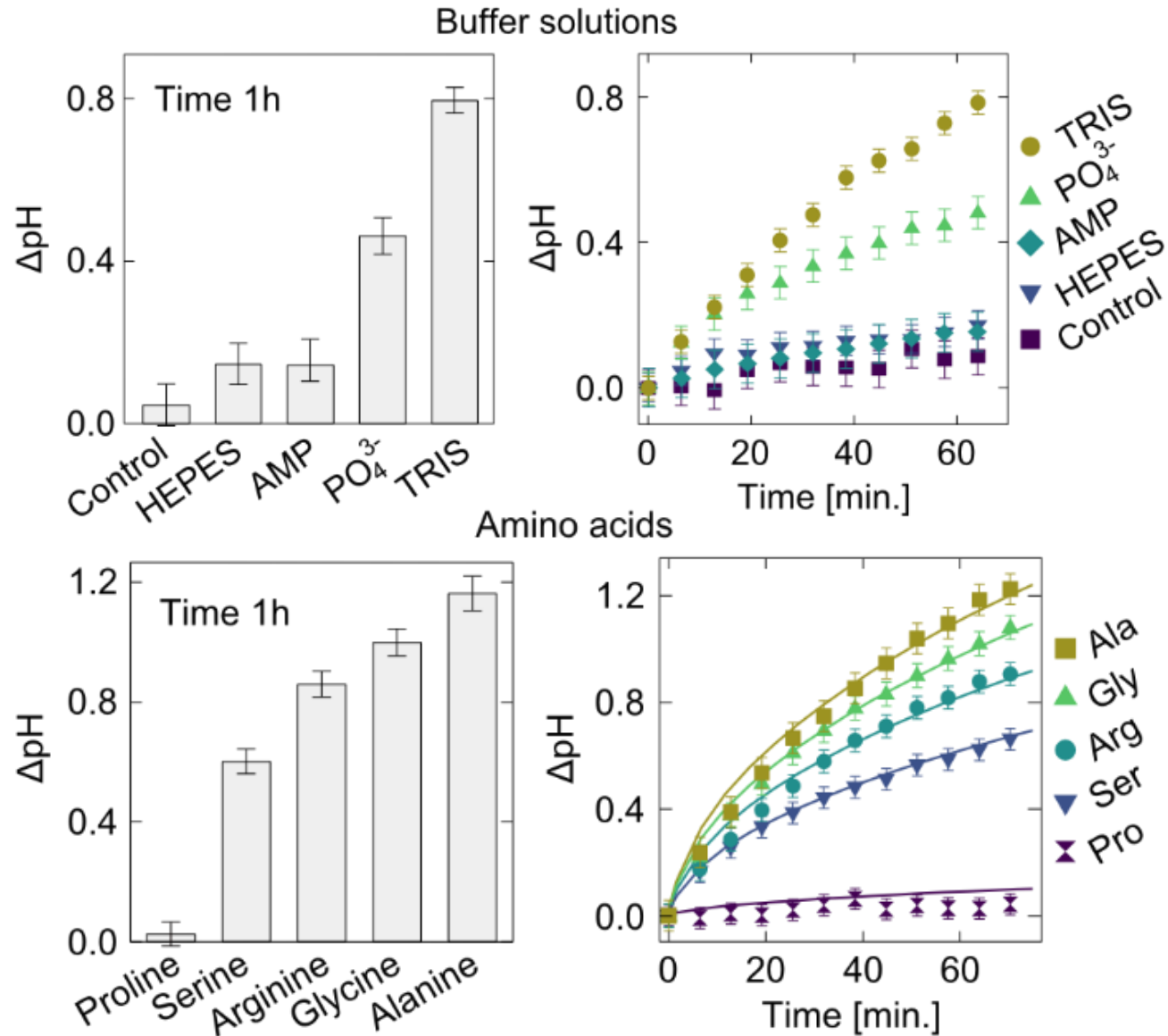
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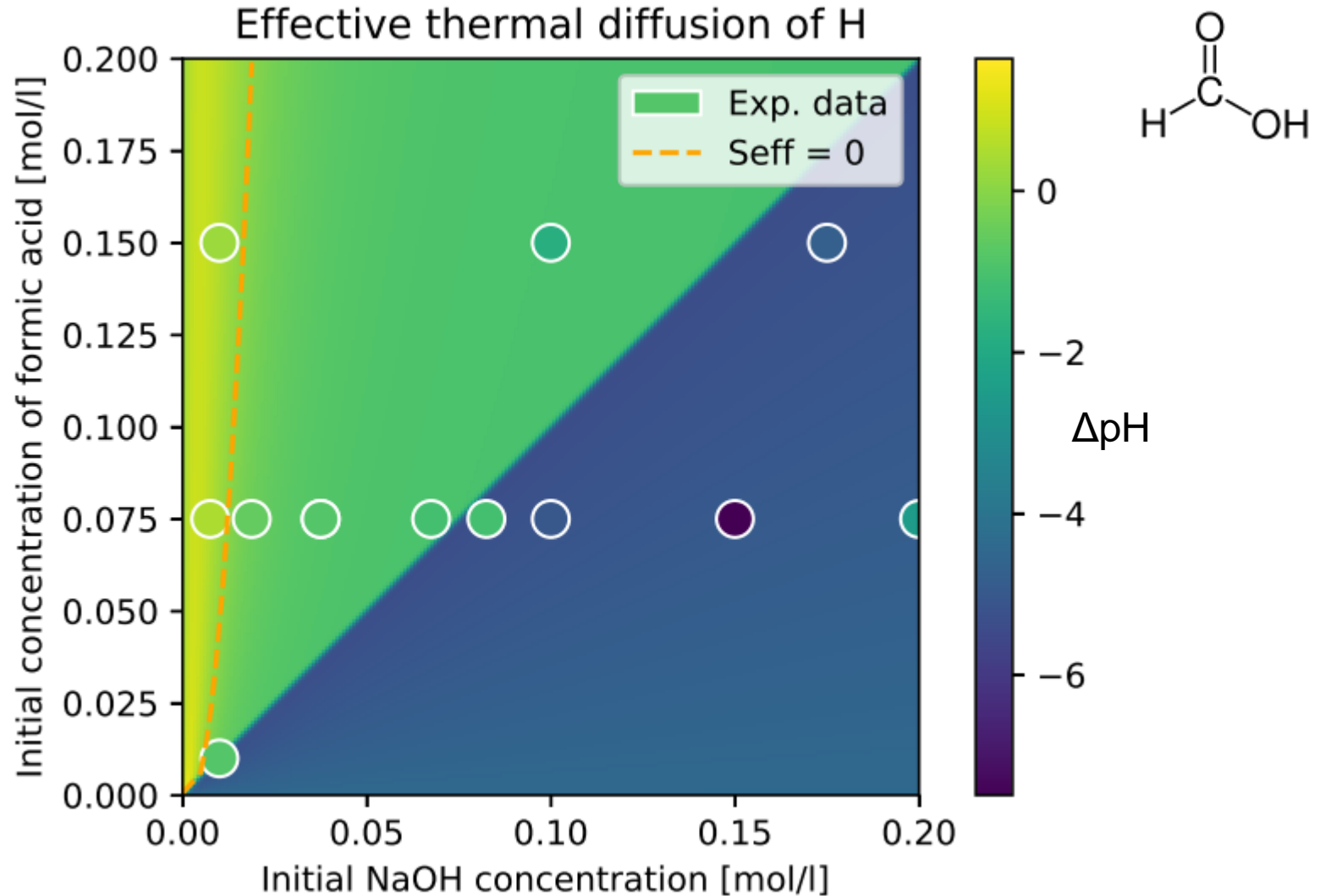
Separation of oxonium/hydroxid



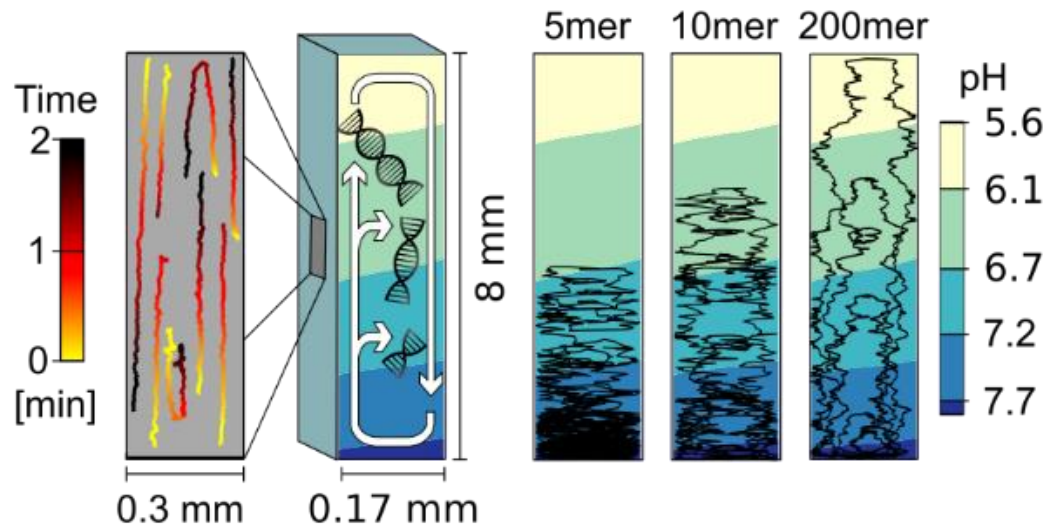
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Inversion of pH gradient: formic acid



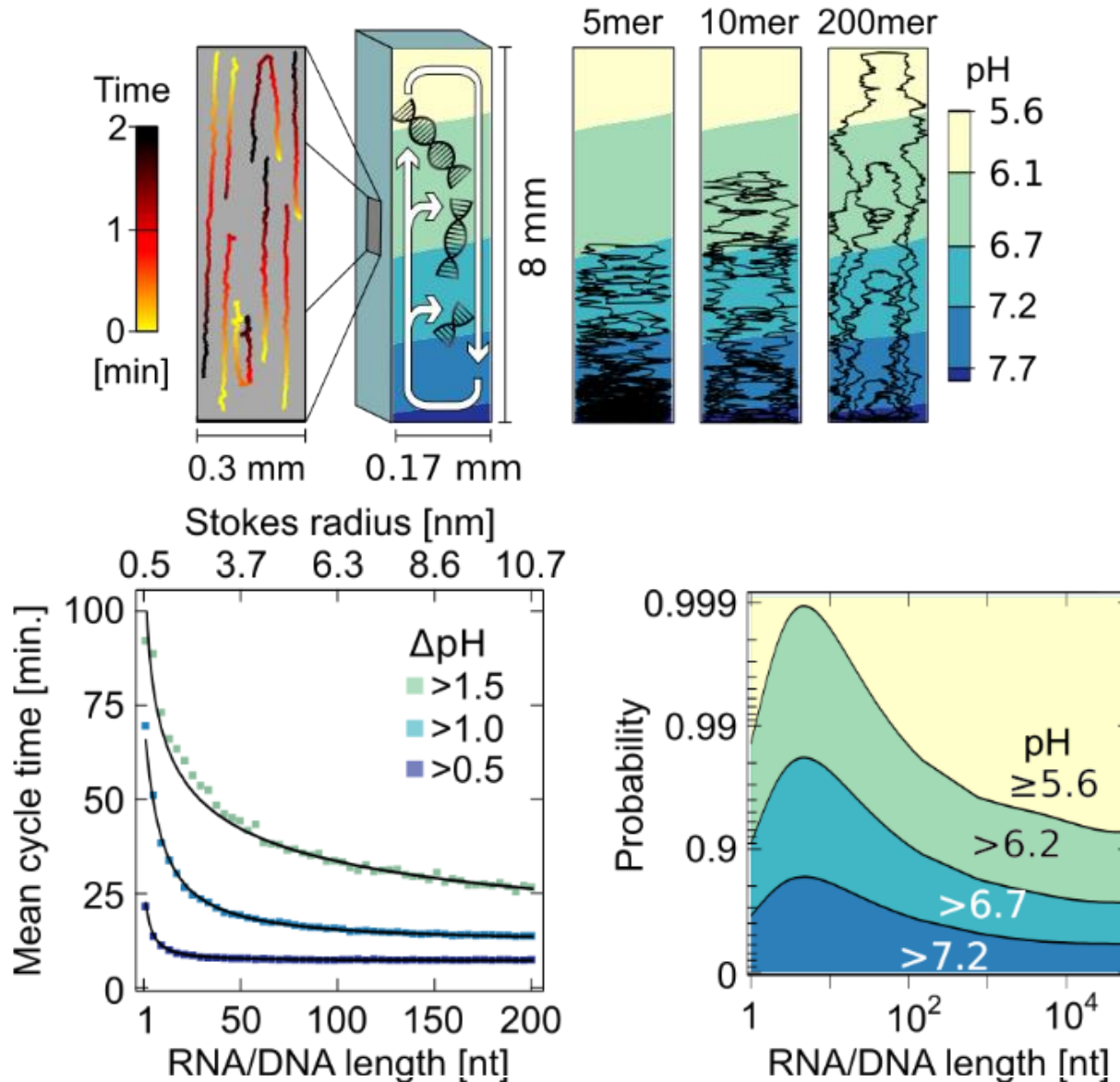
Combination with DNA/RNA



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

L. Keil, F. Möller, M. Kieß, P. Kudella and C. B. Mast, *Nature Communication* 8, 1897 (2017)

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Dänekamp, **D. Braun**

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B. Altaner, J. Raith, **U. Gerland**

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