JÜLICH
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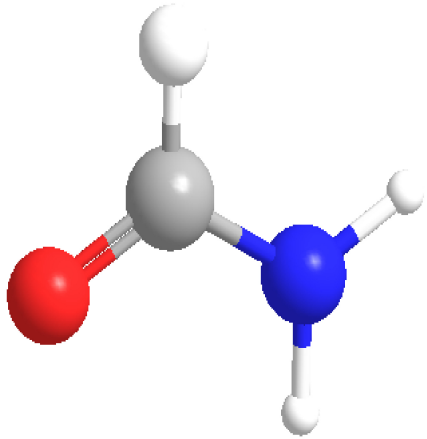
Thermophoresis and the 'Origin-of-Life

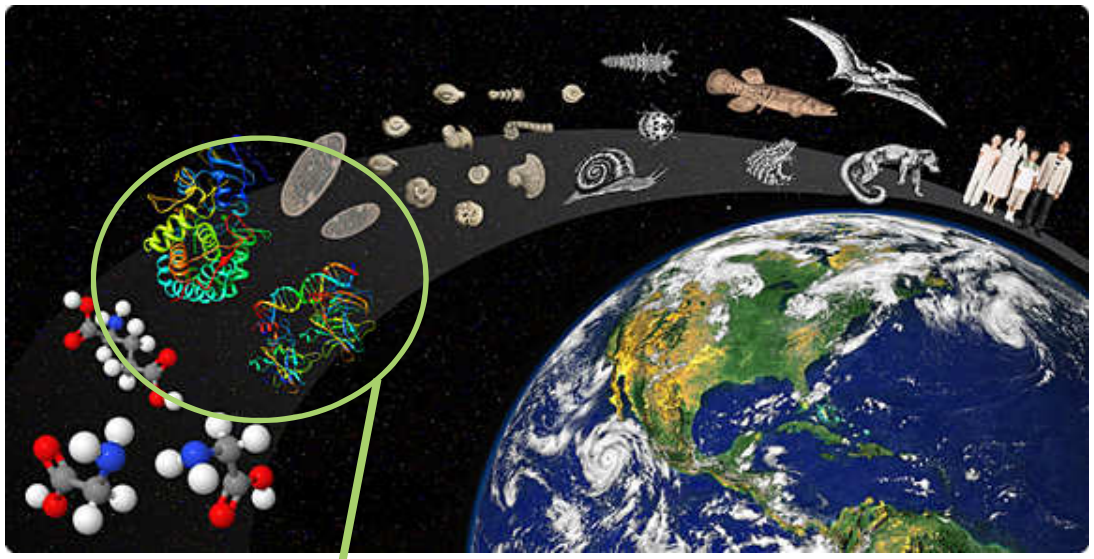


116th General Assembly
German Bunsen Society

26.05.2017 | Doreen Niether, D. Afanasenkau, J.K.G. Dhont and S. Wiegand

Looking for the Origin of Life

- Biological evolution: development of complex life forms from simple organisms
- Chemical evolution: formation of organic molecules and proto-biomolecules
- Current research: transition from chemical to biological evolution



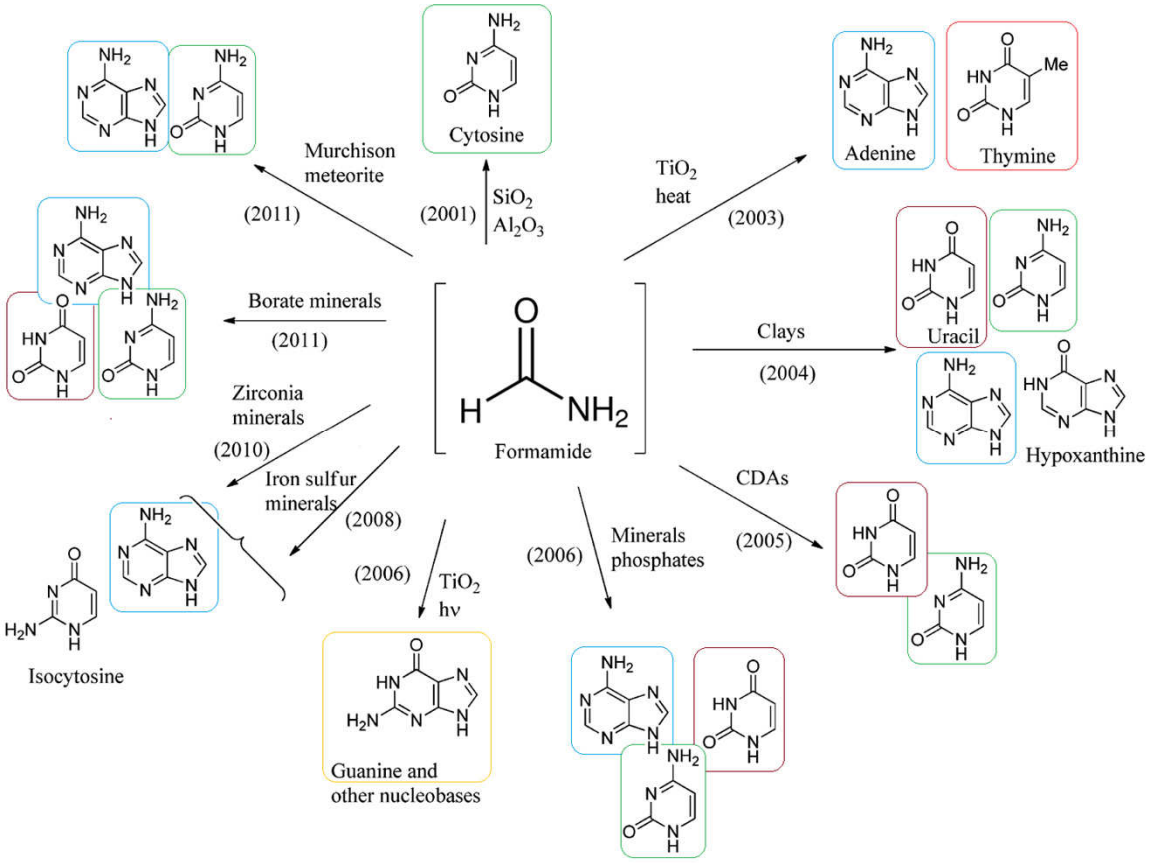
Chemical mechanisms
(How can biotic/prebiotic molecules form?)

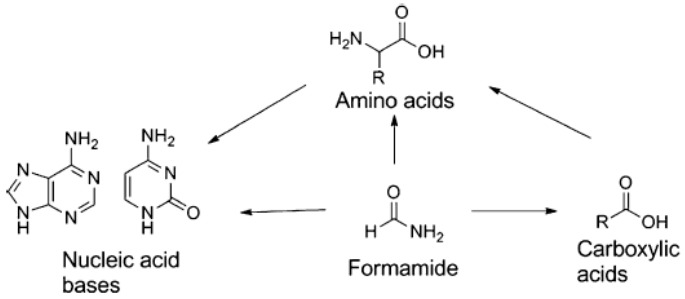
Physical mechanisms
(What were possible reaction conditions?)

Formamide - a precurser of life

Starting material for abiotic synthesis of

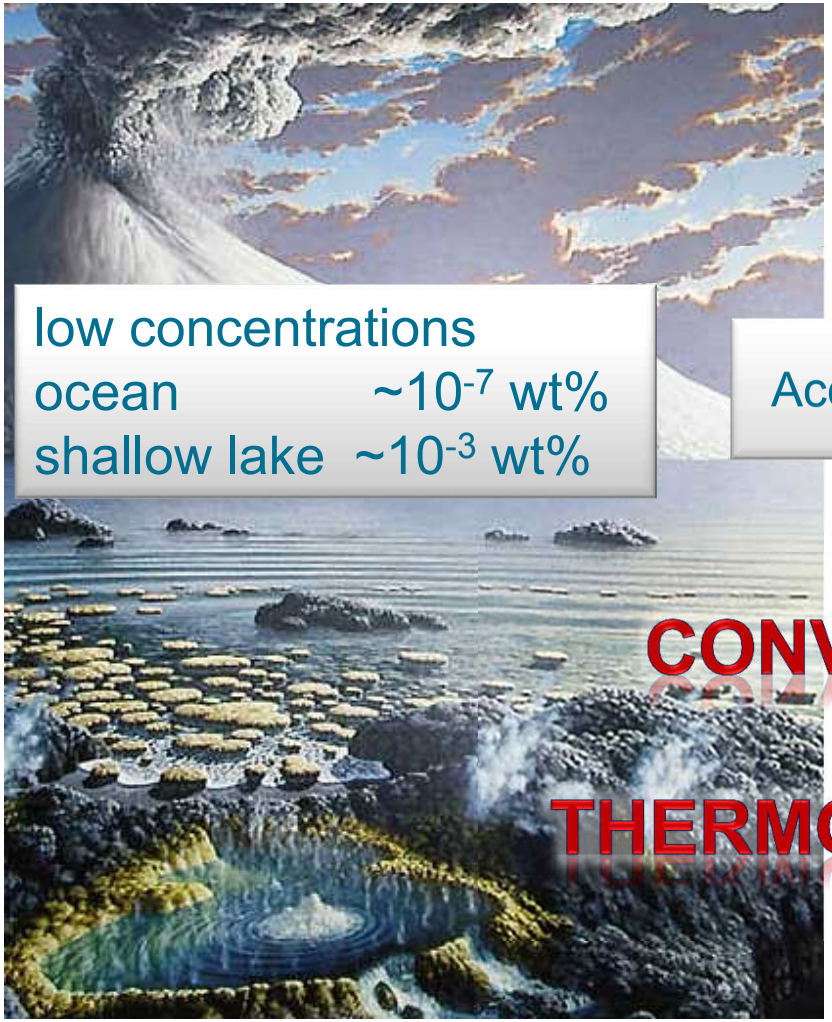
- Prebiotic nucleobases
- Carboxylic acids
- Amino acids





R. Saladino et al./ Physics of Life Reviews 9 (2012) 84-104

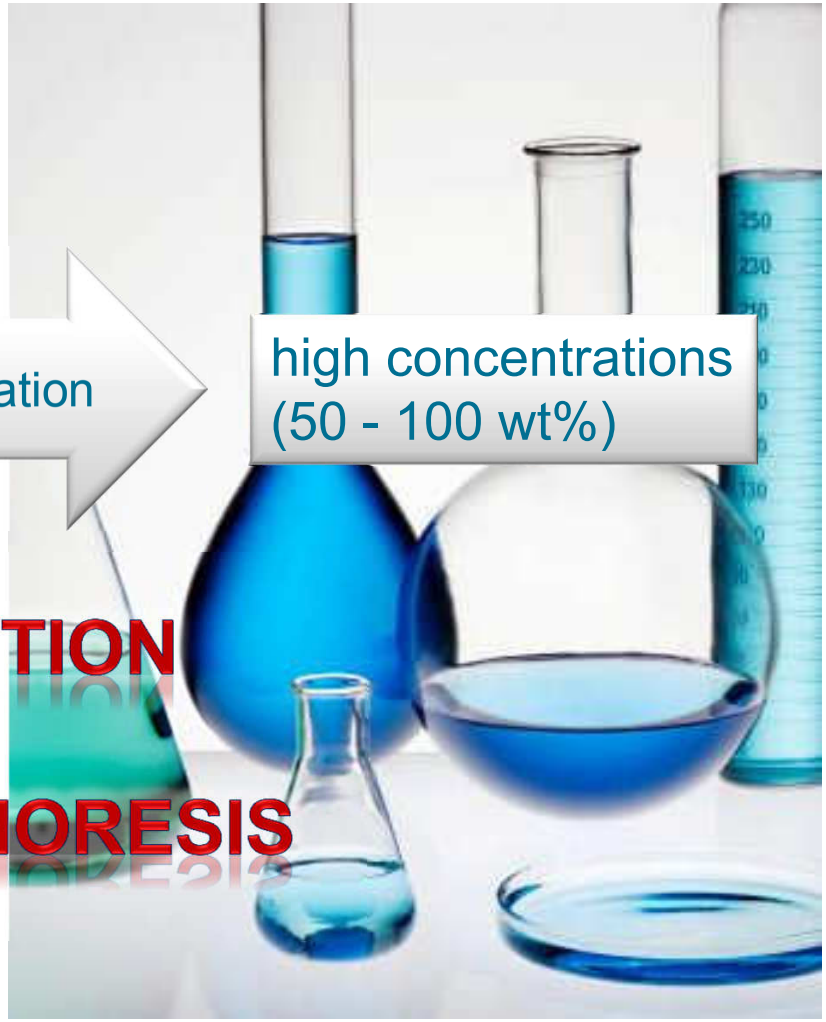
The concentration problem



low concentrations
ocean ~10^{-7} wt%
shallow lake ~10^{-3} wt%

Accumulation

high concentrations
(50 - 100 wt%)



CONVECTION
+
THERMOPHORESIS

Convection

Transport mechanism in gases or liquids

Dependent on density,
viscosity,
heat capacity,
thermal conductivity

temperature difference

↓

different densities

↓

cold (denser) fluid moves down, hot fluid moves up

↓

circular flow

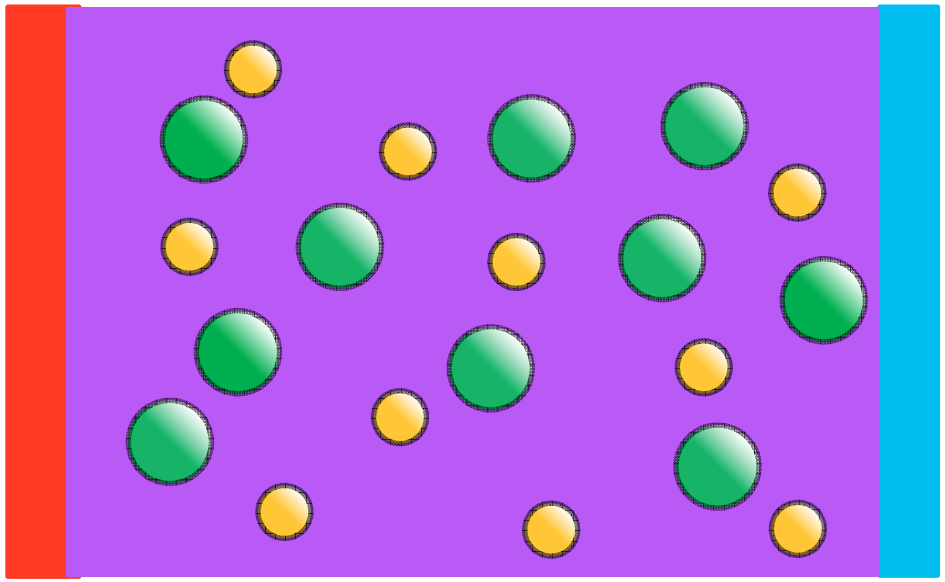
Thermodiffusion

Movement of particles driven by temperature gradient

$$\vec{j} = -D\vec{\nabla}\omega - \omega(1-\omega)D_T\vec{\nabla}T$$

Steady state $\vec{j}=0$

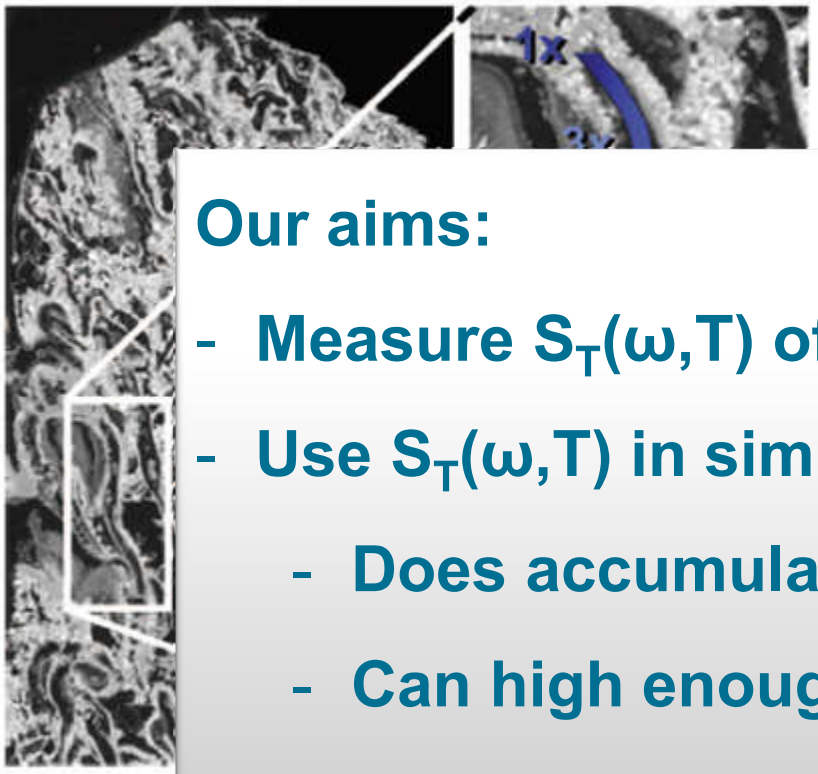
$$\frac{D_T}{D} = -\frac{\vec{\nabla}\omega}{\omega(1-\omega)\vec{\nabla}T}$$



$$S_T = \frac{D_T}{D} \propto \frac{\Delta\omega}{\Delta T}$$

D - diffusion coefficient,
ω - concentration,
D_T - thermodiffusion coefficient,
$\vec{j}$ - flux,
T – temperature
S_T –Soret coefficient

Thermophoretic Accumulation



Our aims:

- **Measure $S_T(\omega,T)$ of formamide/water**
- **Use $S_T(\omega,T)$ in simulations to find out**
  - **Does accumulation work for formamide?**
  - **Can high enough concentrations be reached?**

- Setting: porous minerals near hydrothermal vents
- Nucleotides and RNA accumulate in pores
- same principle as thermogravitational column, but open (influx of matter)

Baaske et al., PNAS vol. 104, no. 22, 9349 (2007)

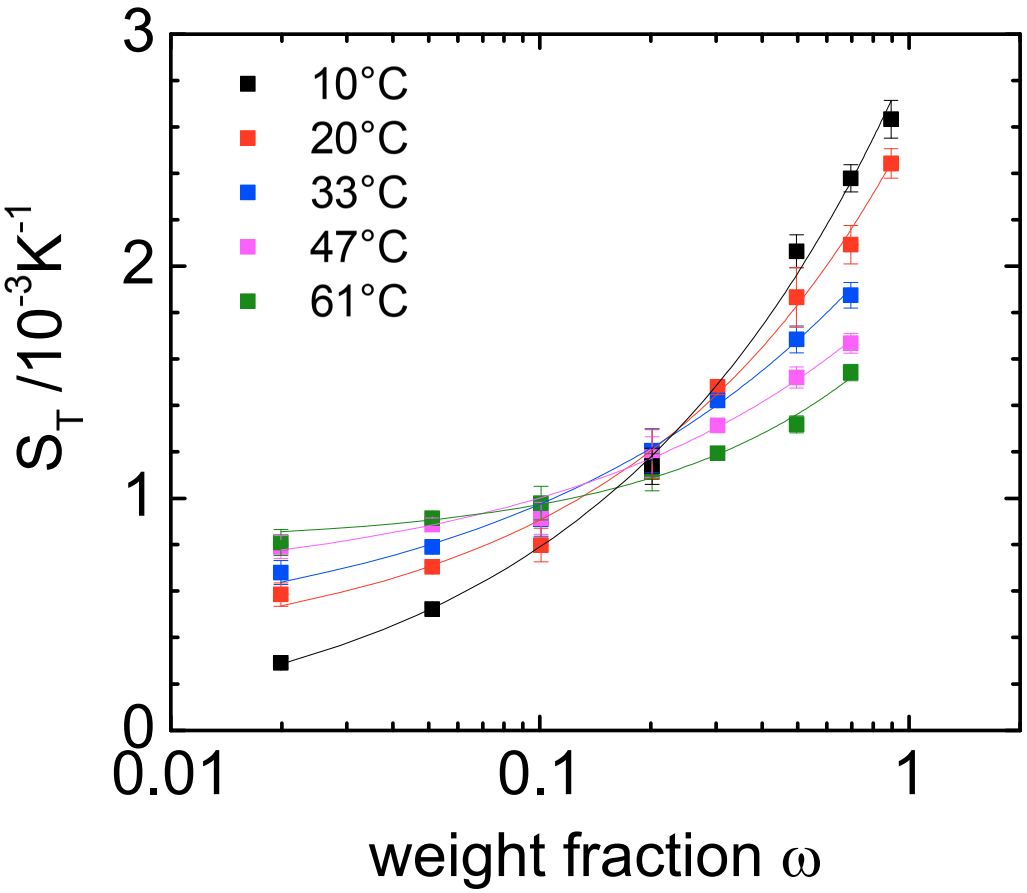
Thermodiffusion of Formamide in Water

Experimental results

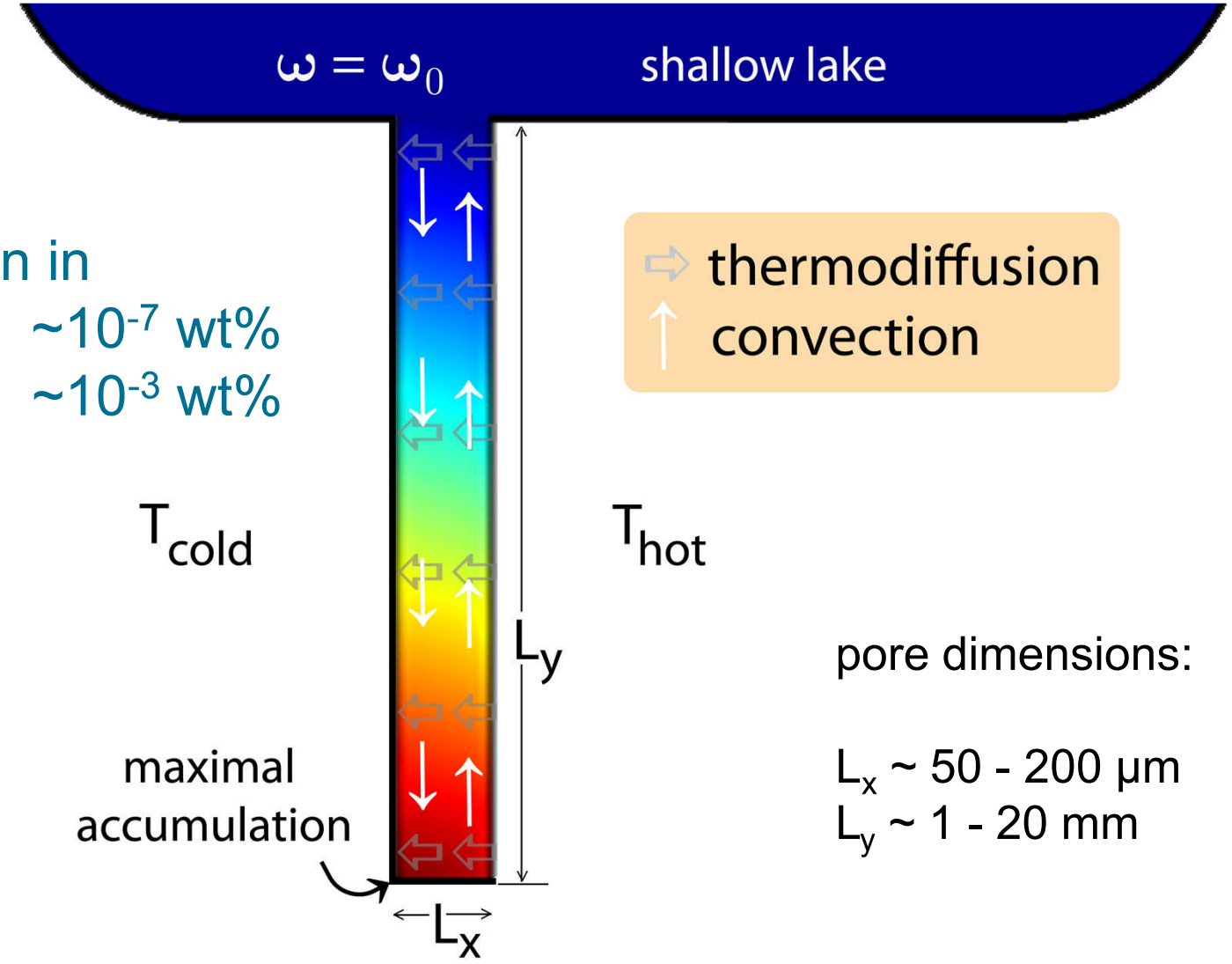
- Fit with Hill equation:

$$S_T(\omega) = \frac{\omega^a}{K + \omega^a} + S_T^0$$

- Approaches constant value for small concentrations
- becomes more thermophobic with increasing concentration



Simulation with COMSOL



concentration in
ocean ~10^{-7} wt%
shallow lake ~10^{-3} wt%

pore dimensions:

L_x ~ 50 - 200 µm
L_y ~ 1 - 20 mm

[D. Niether, D. Afanasenkau, J.K.G. Dhont, SW, P*NAS* **113** (2016) 4272]

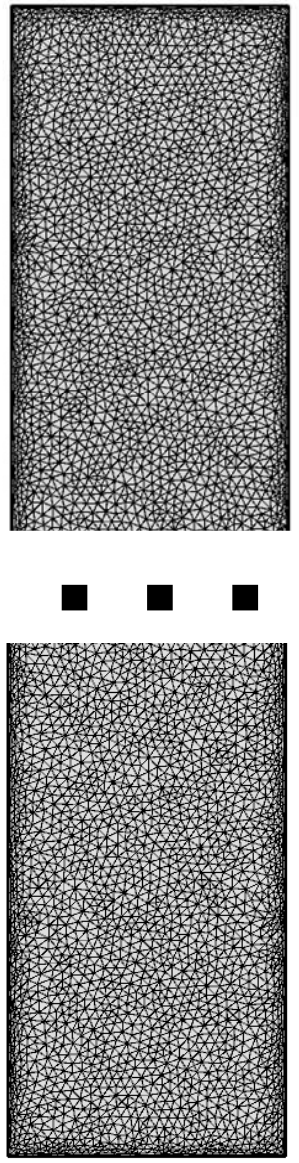
Simulation with COMSOL

temperature and concentration dependant parameters of formamide/water:

- Soret coefficient
- density
- viscosity
- heat capacity
- thermal conductivity

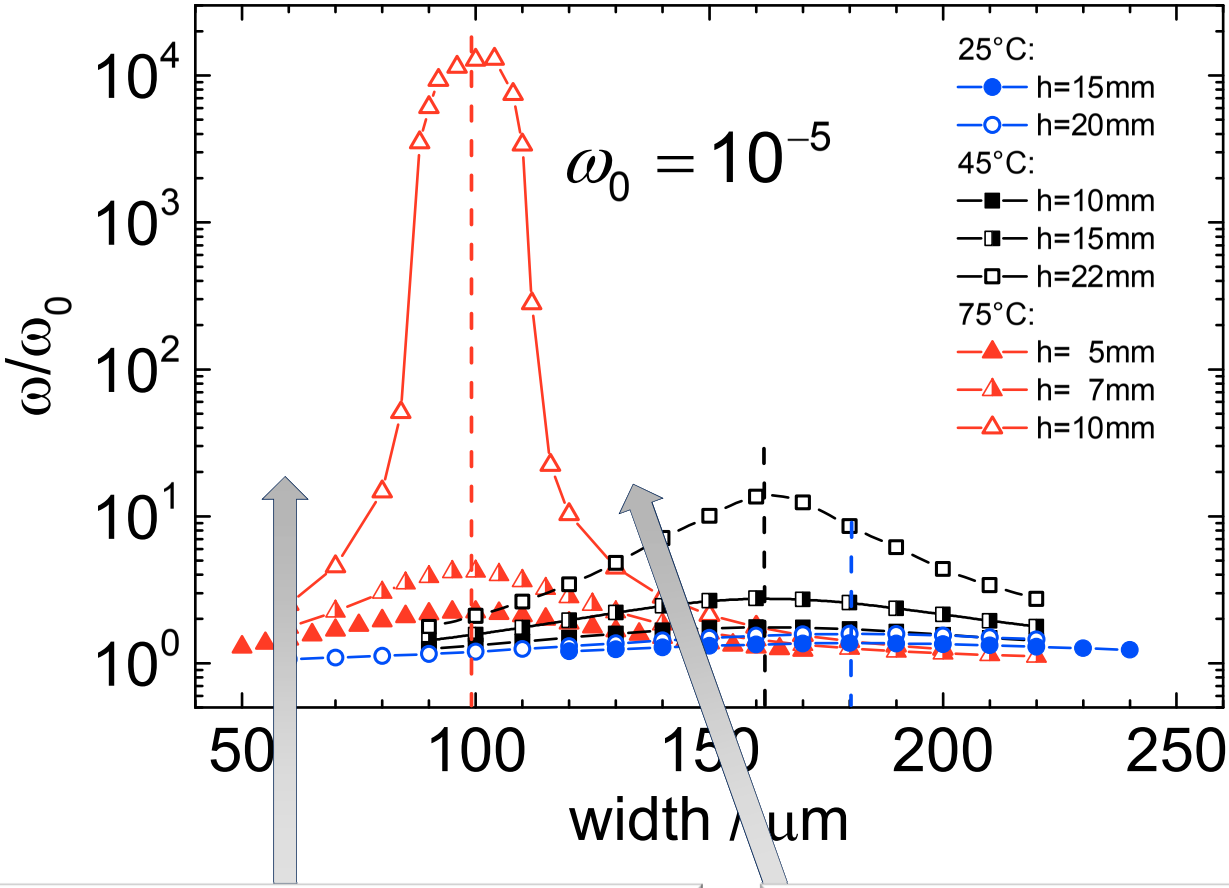
Finite elements simulation:

- Navier-Stokes equations
- Heat transfer equations
- Thermal diffusion/convection



[D. Niether, D. Afanasenkau, J.K.G. Dhont, SW, P*NAS* **113** (2016) 4272]

Geometry and temperature influence

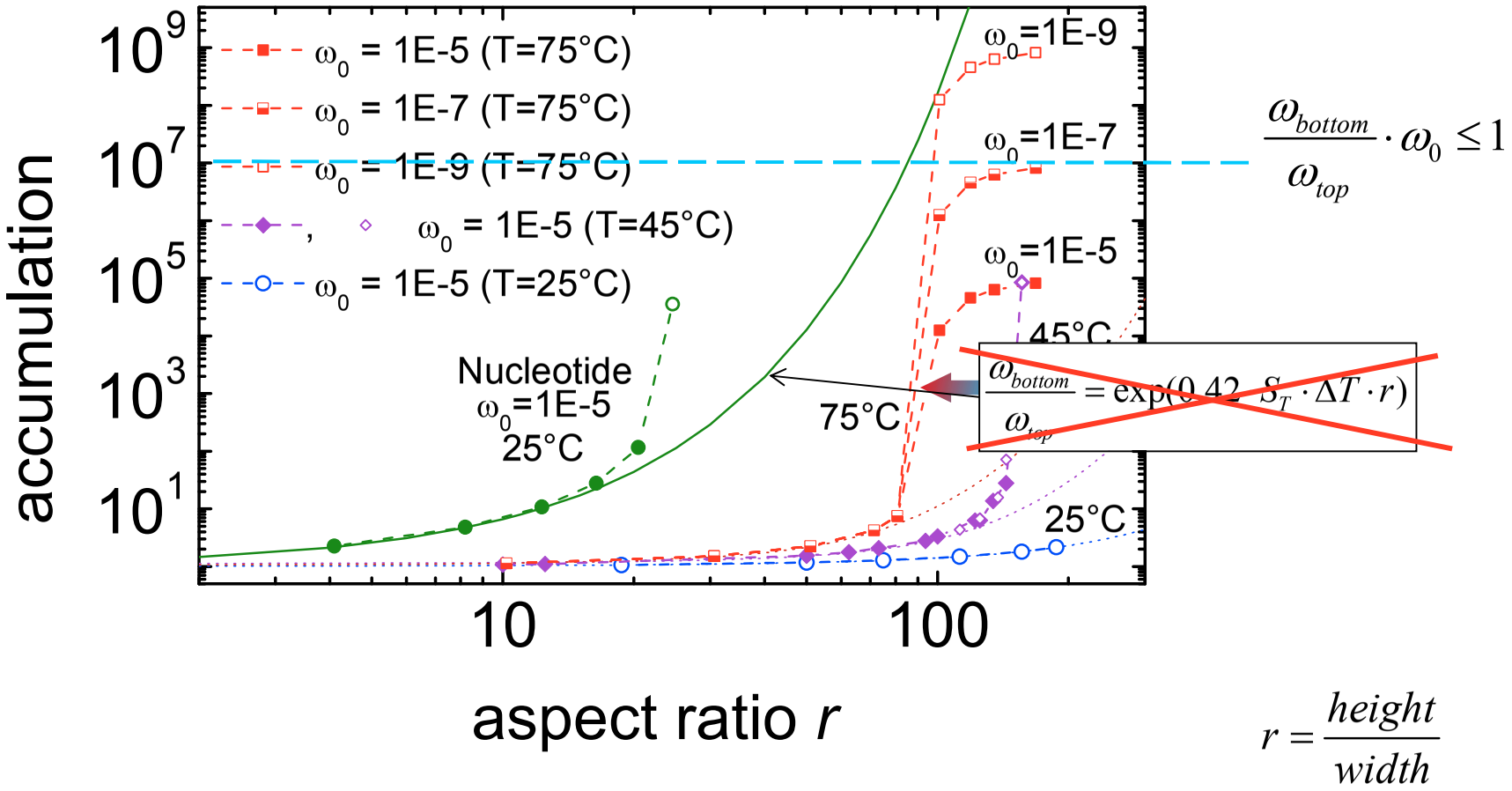


reduced convection

(only effective for larger w_0)

convection too fast

Accumulation of Formamide

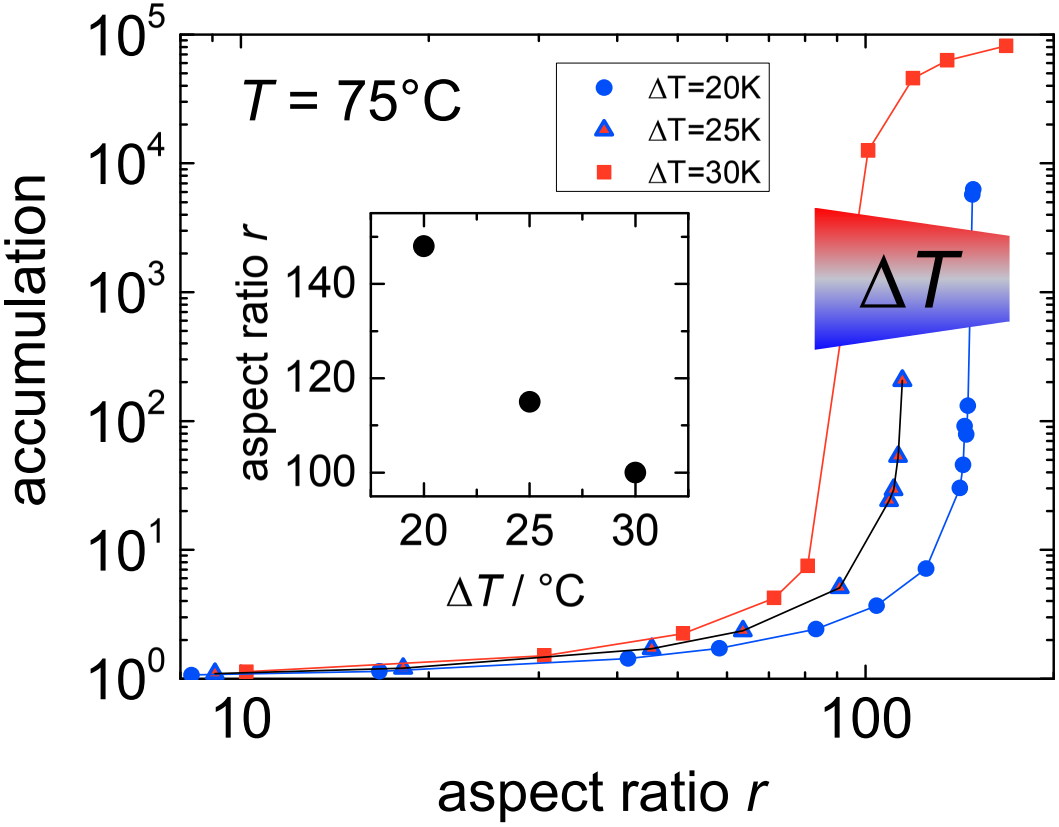


pore needs a certain height for effective accumulation

- depends on Soret coefficient and ambient temperature

Accumulation of Formamide

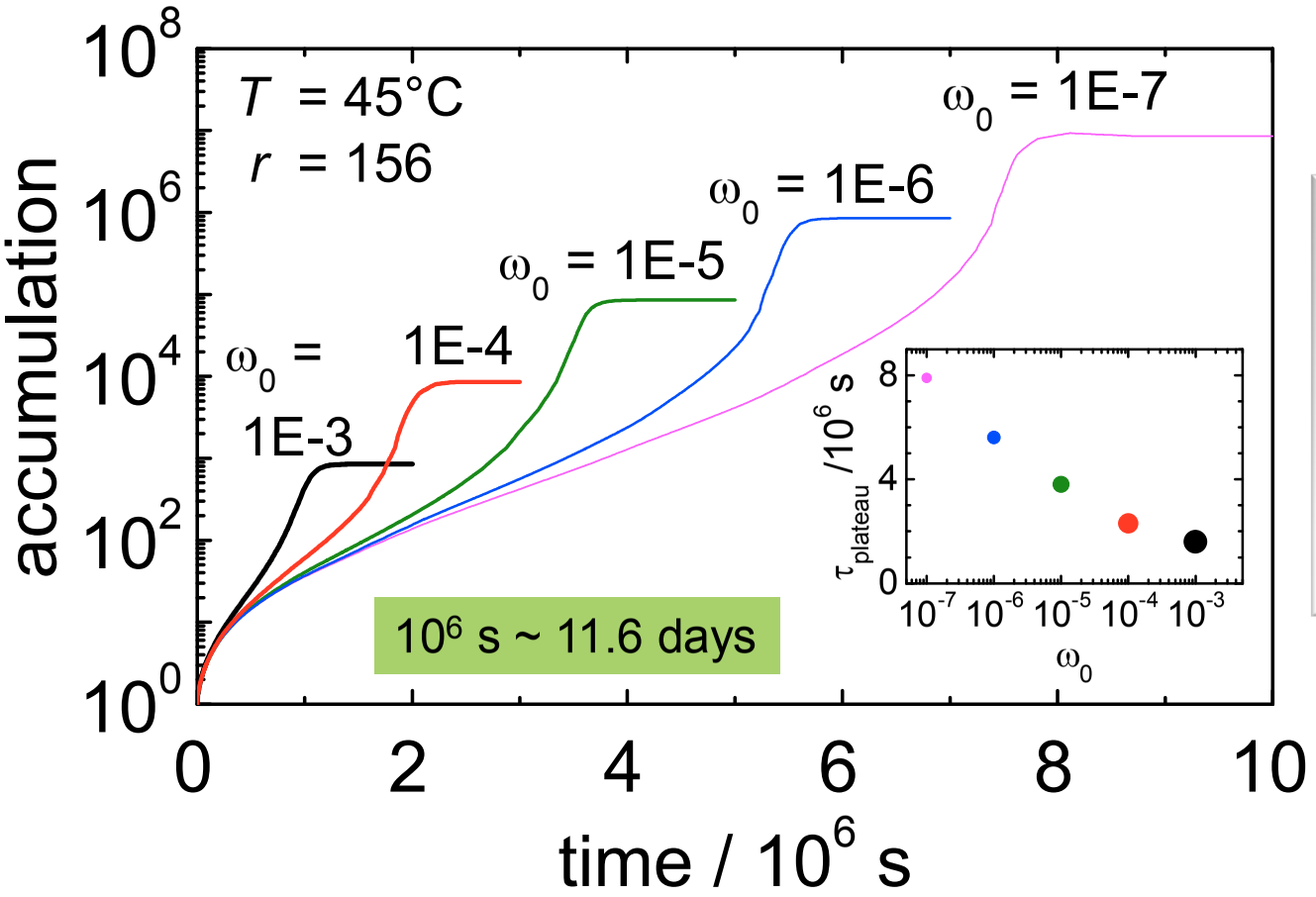
Dependence on the temperature difference



larger temperature difference → accumulation at smaller heights

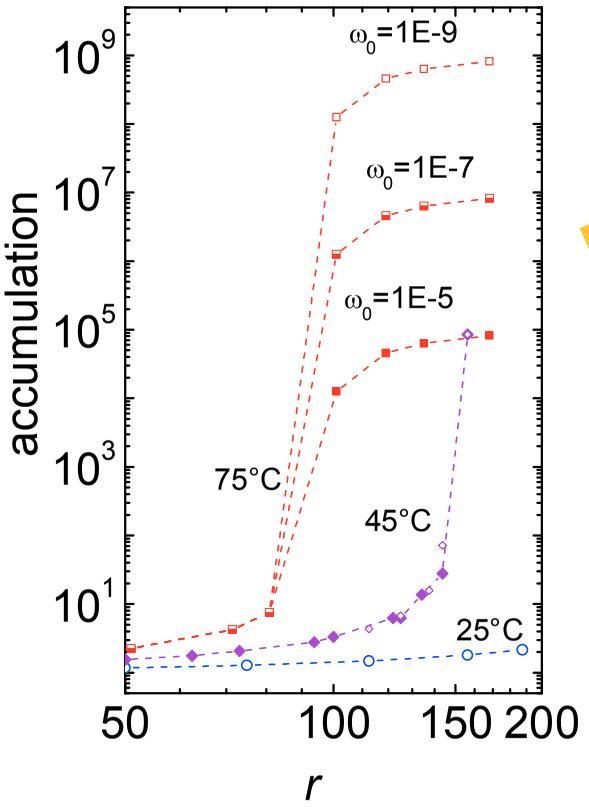
Accumulation of Formamide

Dependence on the starting concentration

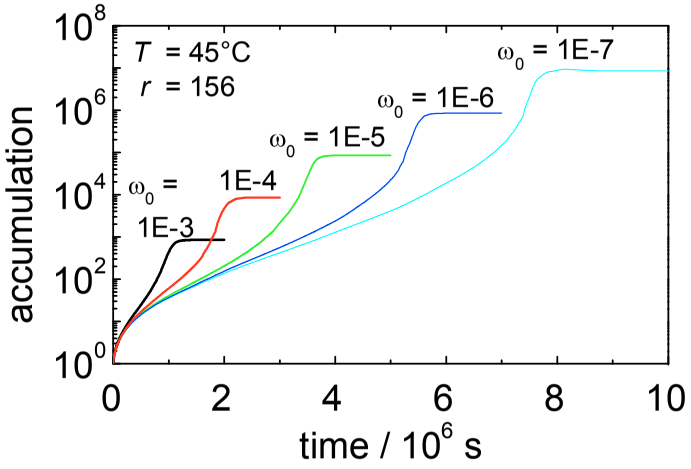


concentration rise to ~85%, independent of starting concentration

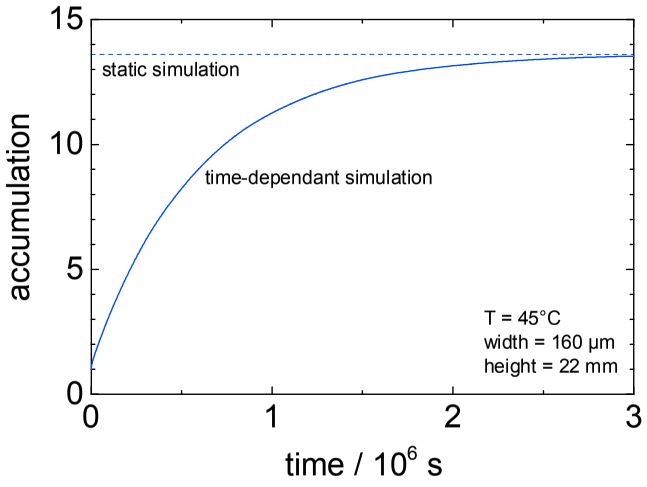
Accumulation of Formamide
Dependence on pore height

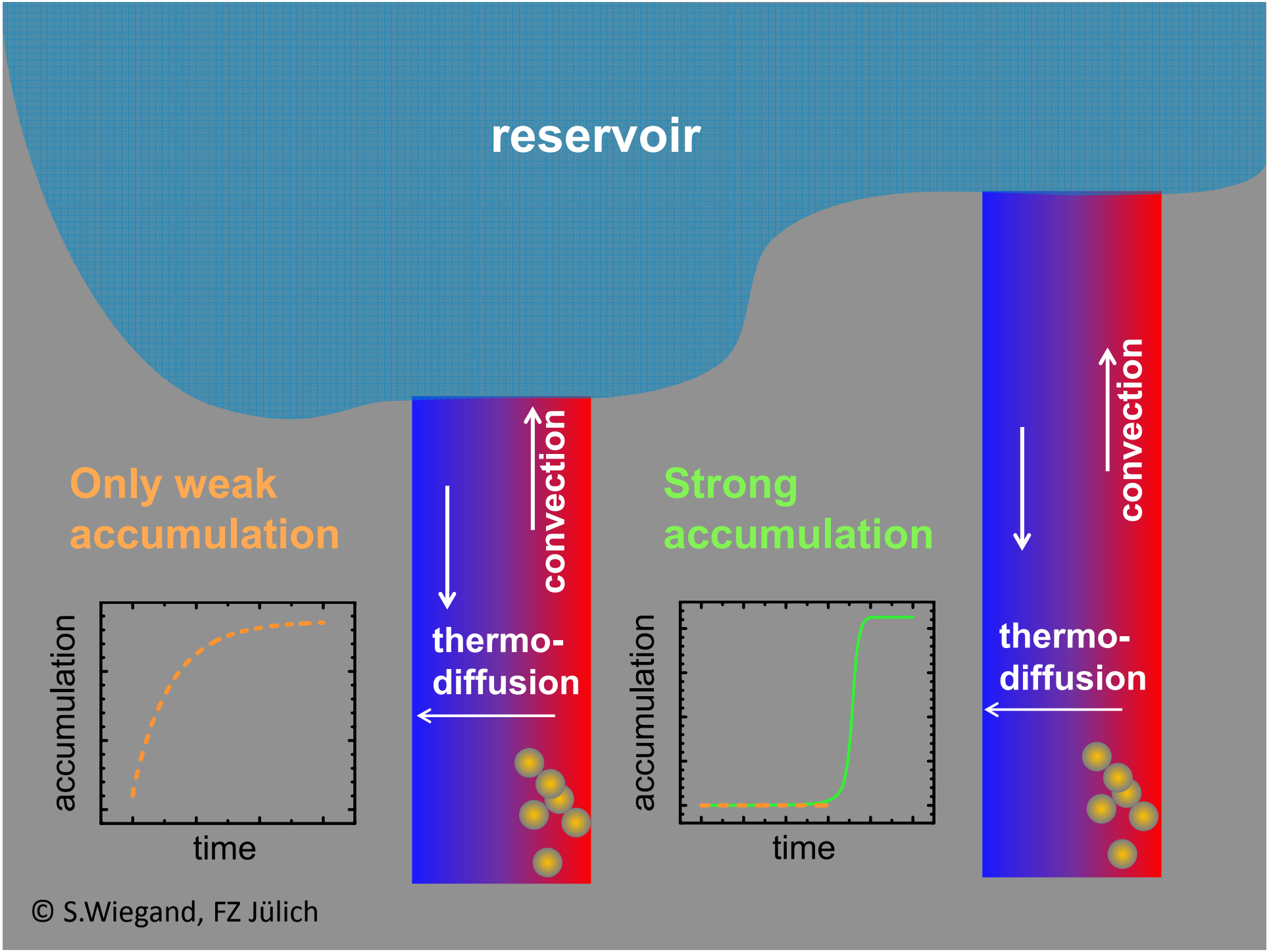


high ratios



low ratios




reservoir
Only weak accumulation
accumulation
time
convection
thermo-diffusion
Strong accumulation
accumulation
time
convection
thermo-diffusion
© S.Wiegand, FZ Jülich

Can we understand the steep increase?
simple heuristic approach

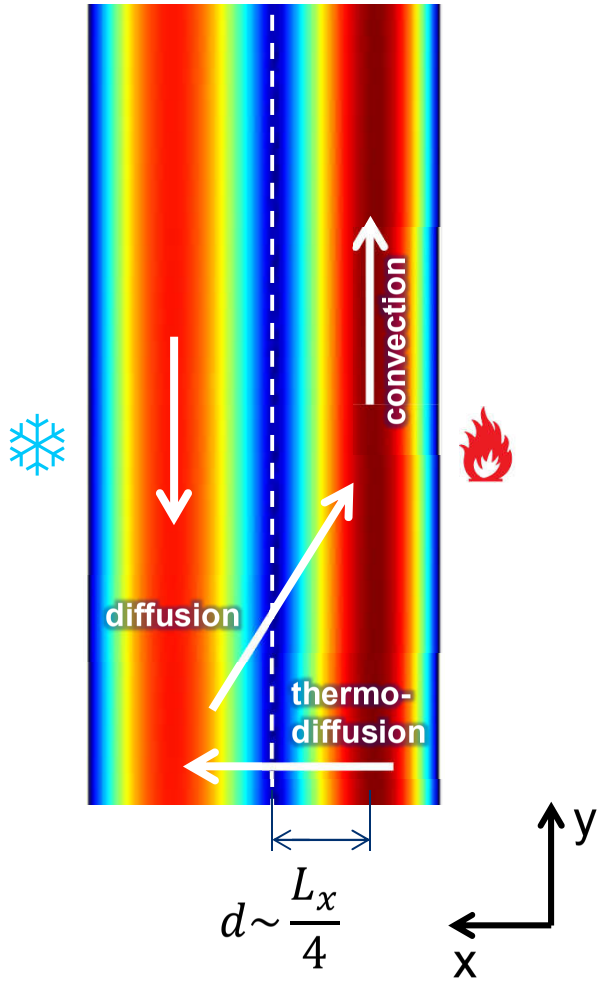
$$v_y = v_{convection} + D\frac{\Delta_y w}{L_y}$$

$$v_x = -D\frac{\Delta_x w}{L_x} + w(1-w)D_T\frac{\Delta T}{L_x}$$

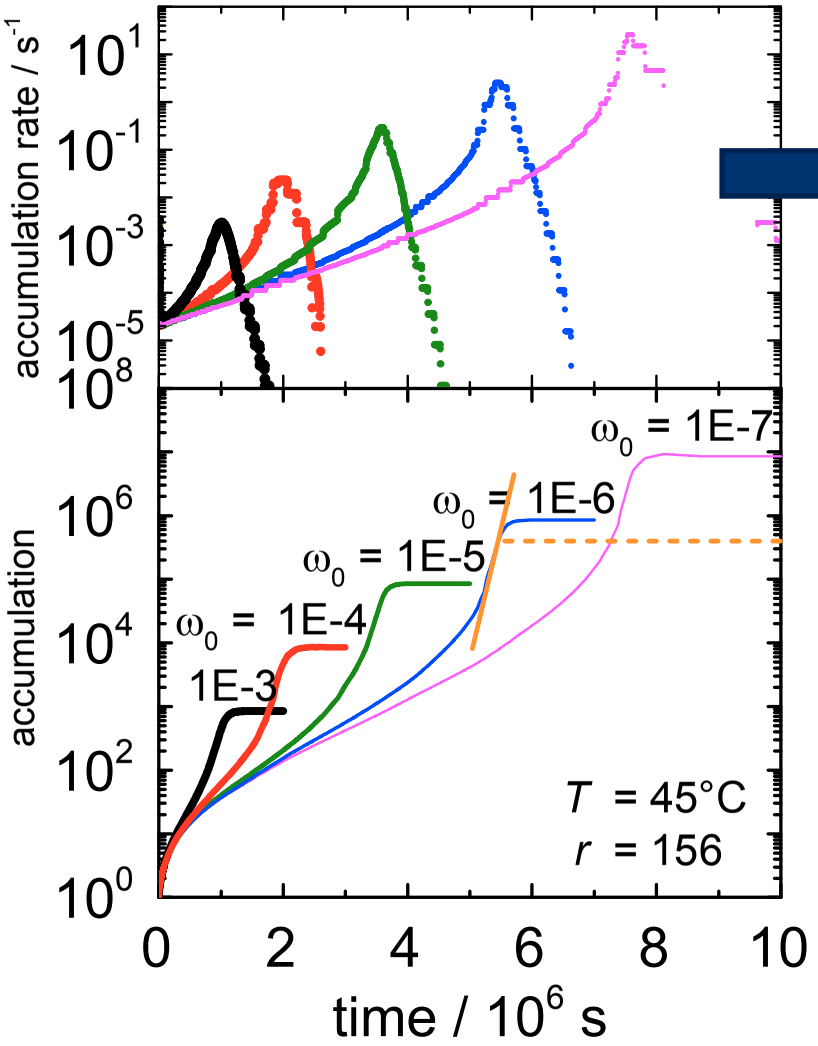
time to reach the top of the column **>** time to cross the middle of the column

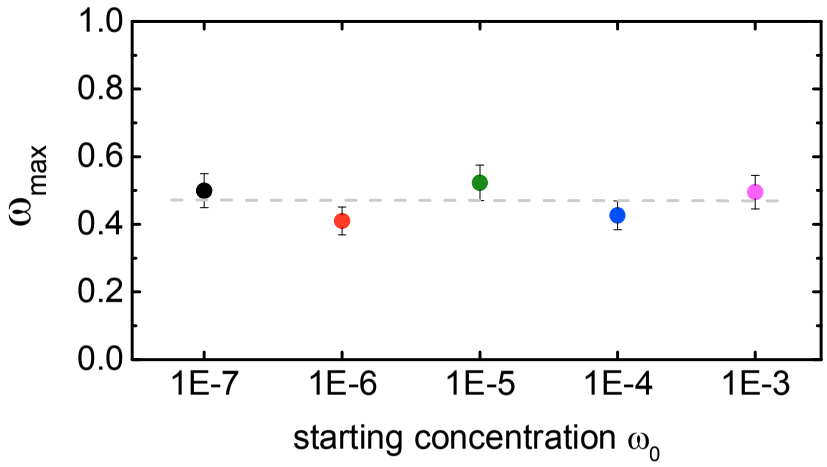
$$\frac{L_y}{v_y} > \frac{L_x}{4v_x} \Rightarrow \frac{L_y}{L_x} > \frac{v_y}{4v_x}$$

$$(r^*)^2 = \left(\frac{L_y}{L_x}\right)^2 > \frac{\left(L_y \cdot v_{convection} + D \cdot \Delta_y w\right)}{4 \cdot (-D\Delta_x w + w(1-w)D_T\Delta T)}$$



Simple heuristic approach





r^* has a minimum at $\omega = 0.5$

$$\left(r^*\right)^2 \propto \frac{1}{\omega(1-\omega)D_T\Delta T}$$

Conclusion

- Experimental determination of S_T and D_T
- Simulation of accumulation in pores with regard to the temperature and concentration dependence of substance parameters
  - accumulation possible at different temperatures, temperature differences and starting concentrations
  - very effective at large pore ratios (up to 85 wt%)
  - time varies for different starting parameters (~45-90d)
- Simulations for ideal system (stable conditions, pure formamide/water mixture) – accumulation in real system probably less effective

Publications:

- "Accumulation of formamide in hydrothermal pores to form prebiotic nucleobases", D. Niether, D. Afanasenkau, J. K. G. Dhont, S. Wiegand, *Proc. Natl. Acad. Sci. USA* 113(16), 4272 - 4277 (2016)
- "Heuristic Approach to Understanding the Accumulation Process in Hydrothermal Pores", D.Niether, S.Wiegand, *Entropy* 19, 33 (2017)

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Thank you for your attention!