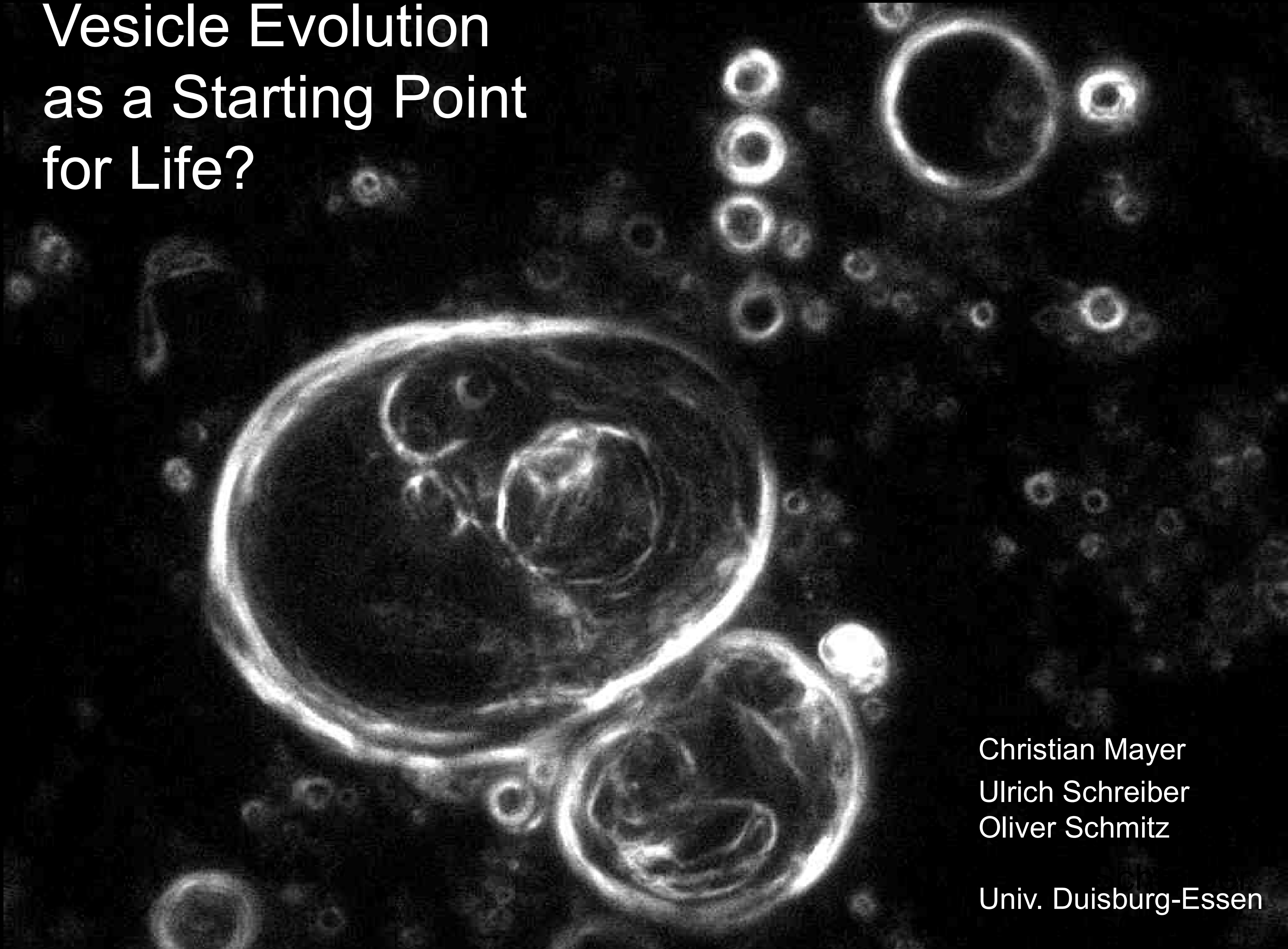
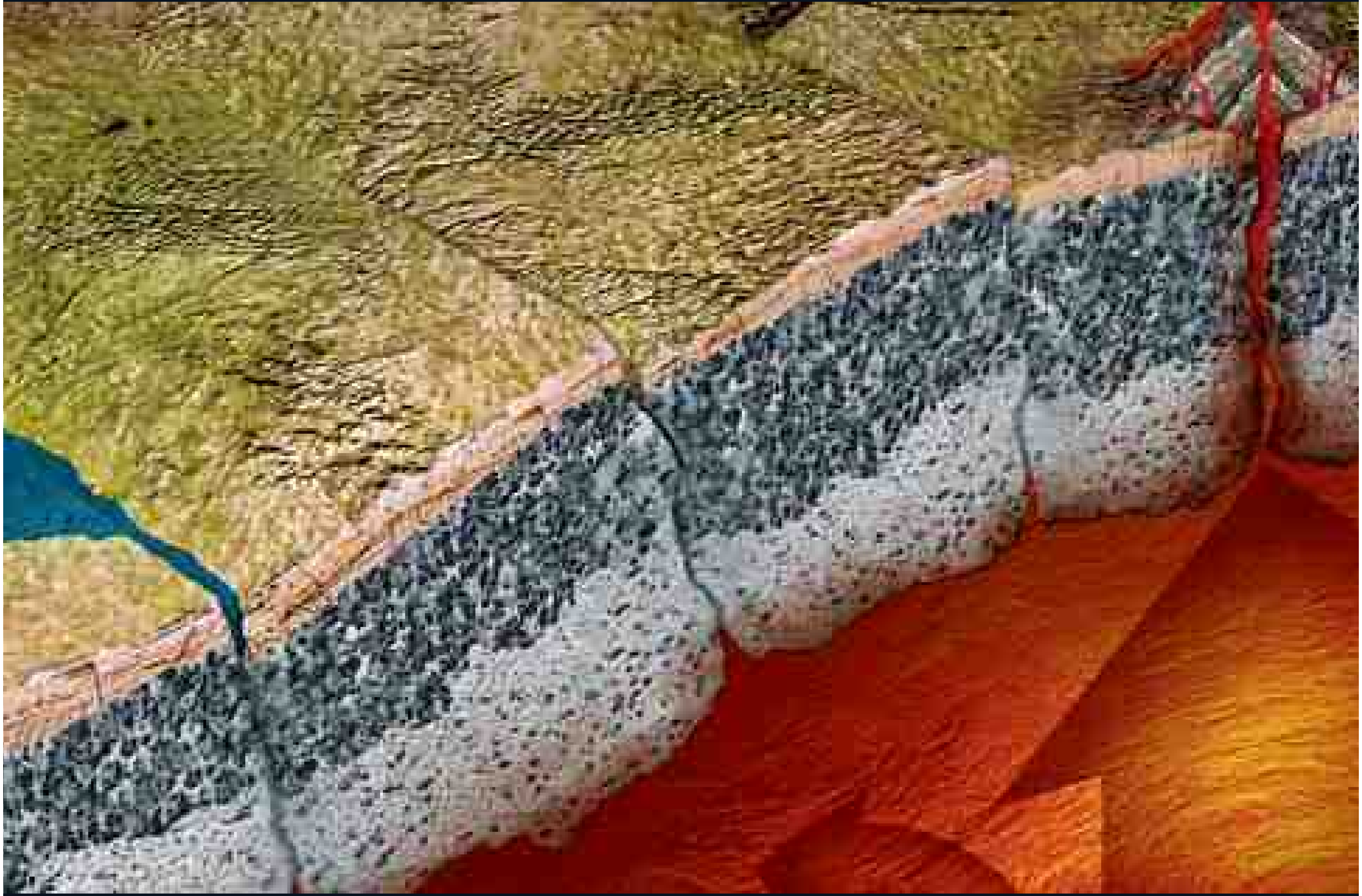
Vesicle Evolution as a Starting Point for Life?

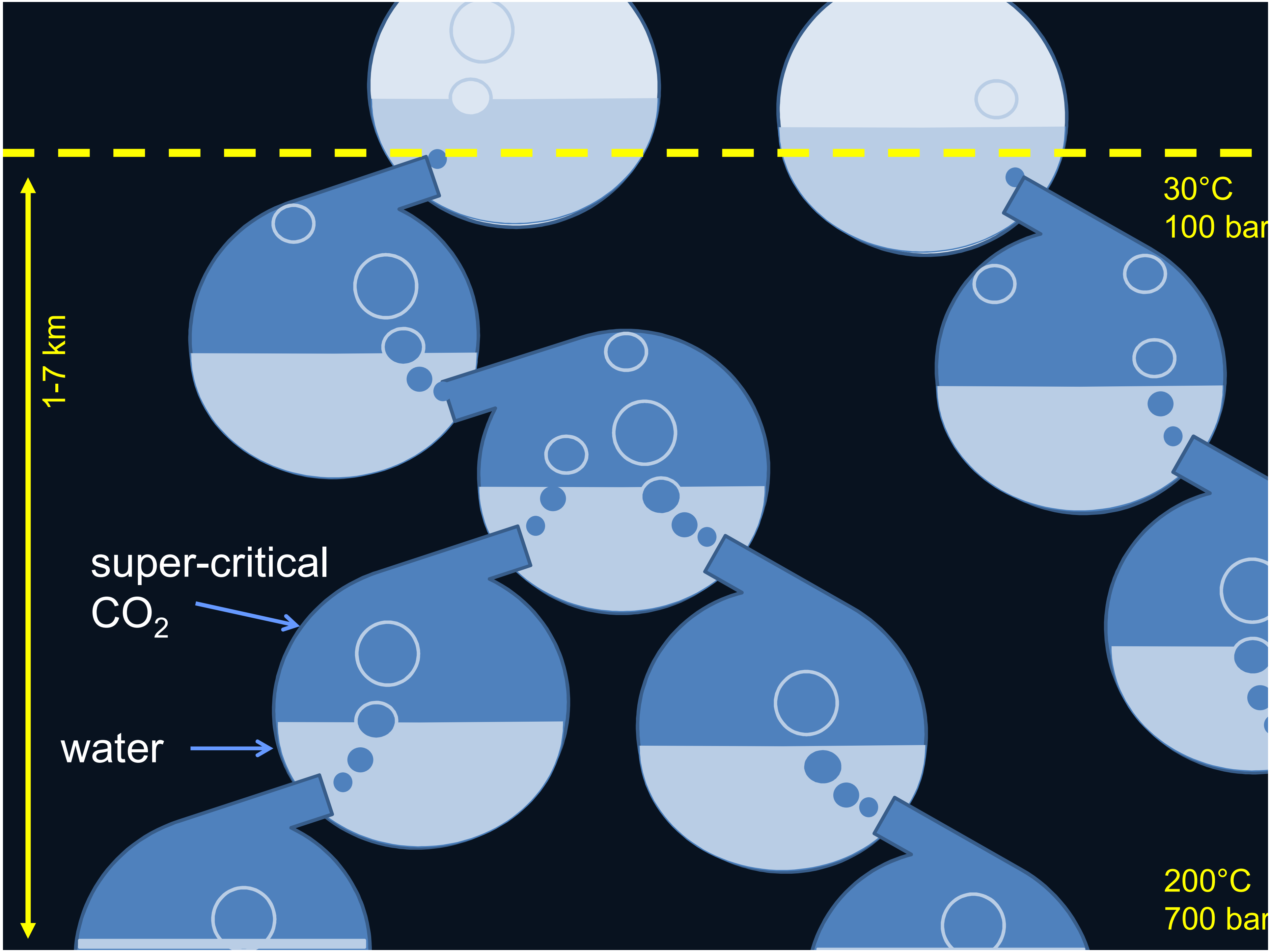


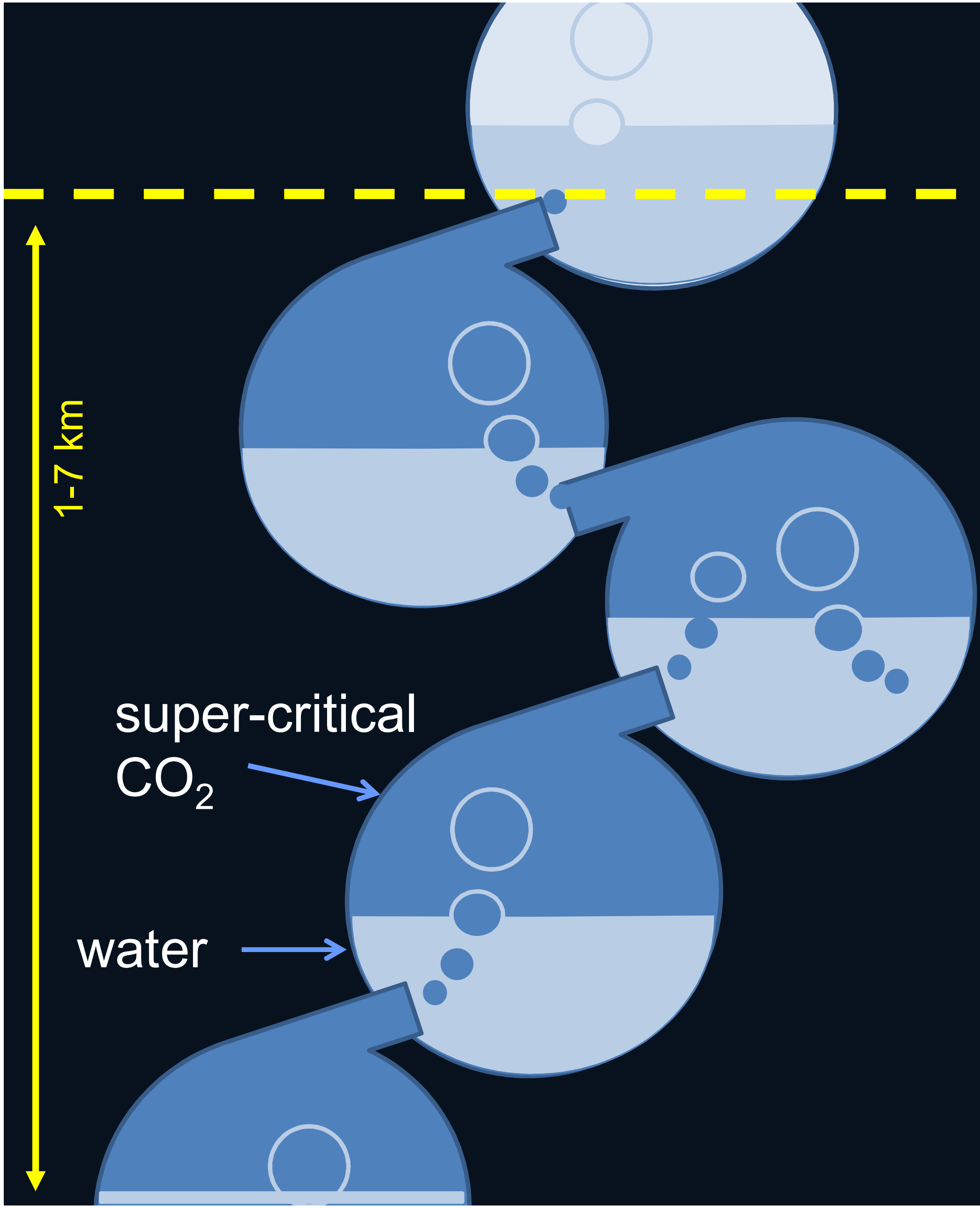
Christian Mayer
Ulrich Schreiber
Oliver Schmitz

Univ. Duisburg-Essen

tectonic fault zones in the planetary crust




30°C
100 bar
1-7 km
super-critical
CO_2
water
200°C
700 bar

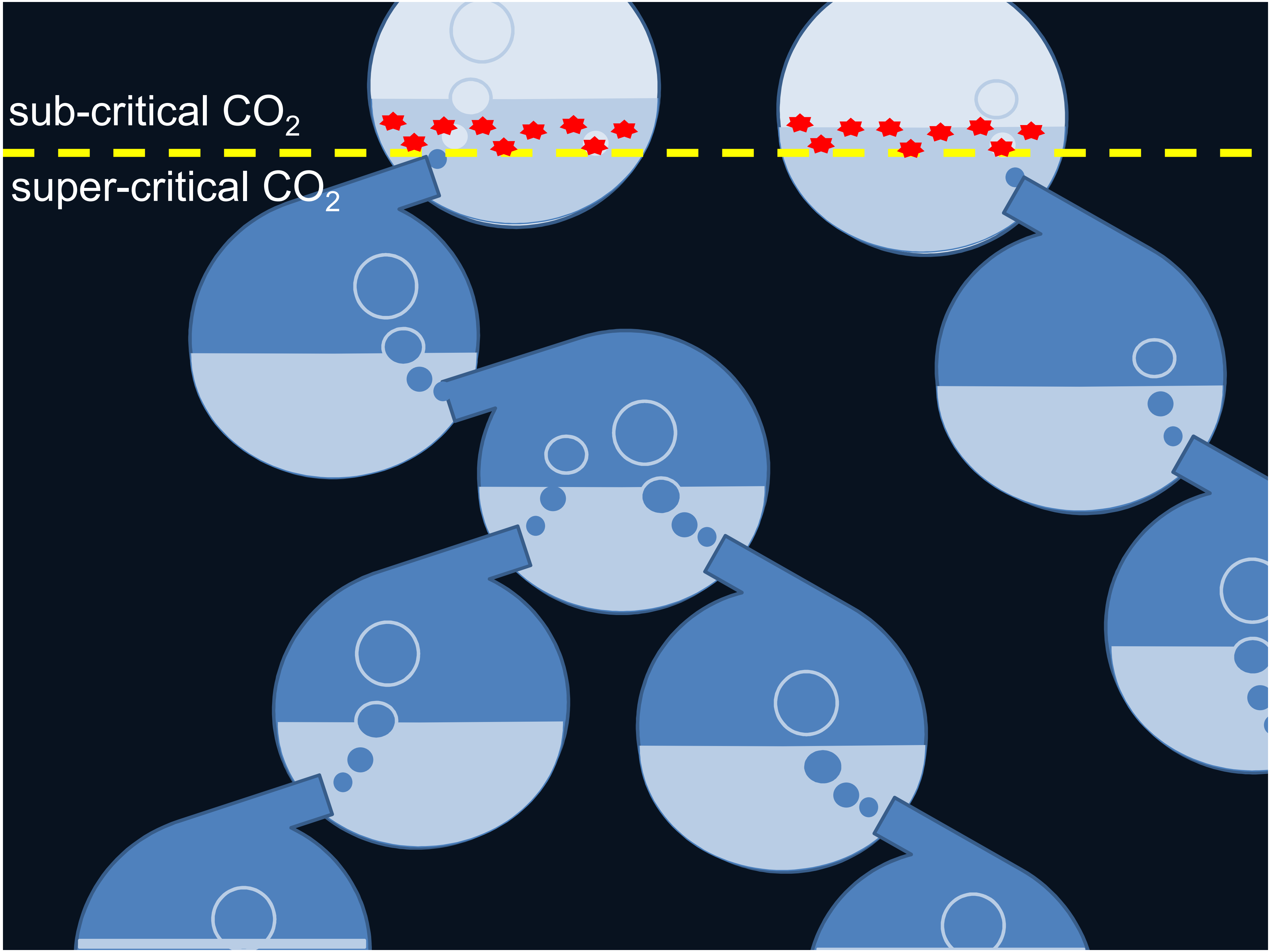


formation of:

- amphiphilic compounds

- peptides

- nucleotides


sub-critical CO_2
super-critical CO_2

fluid inclusions in
quartz crystals

U. Schreiber, C. Mayer, O.J. Schmitz et al.
„Organic compounds in fluid inclusions of Archean quartz – prebiotic chemistry on early Earth",
PLOS-ONE 12(6): e0177570

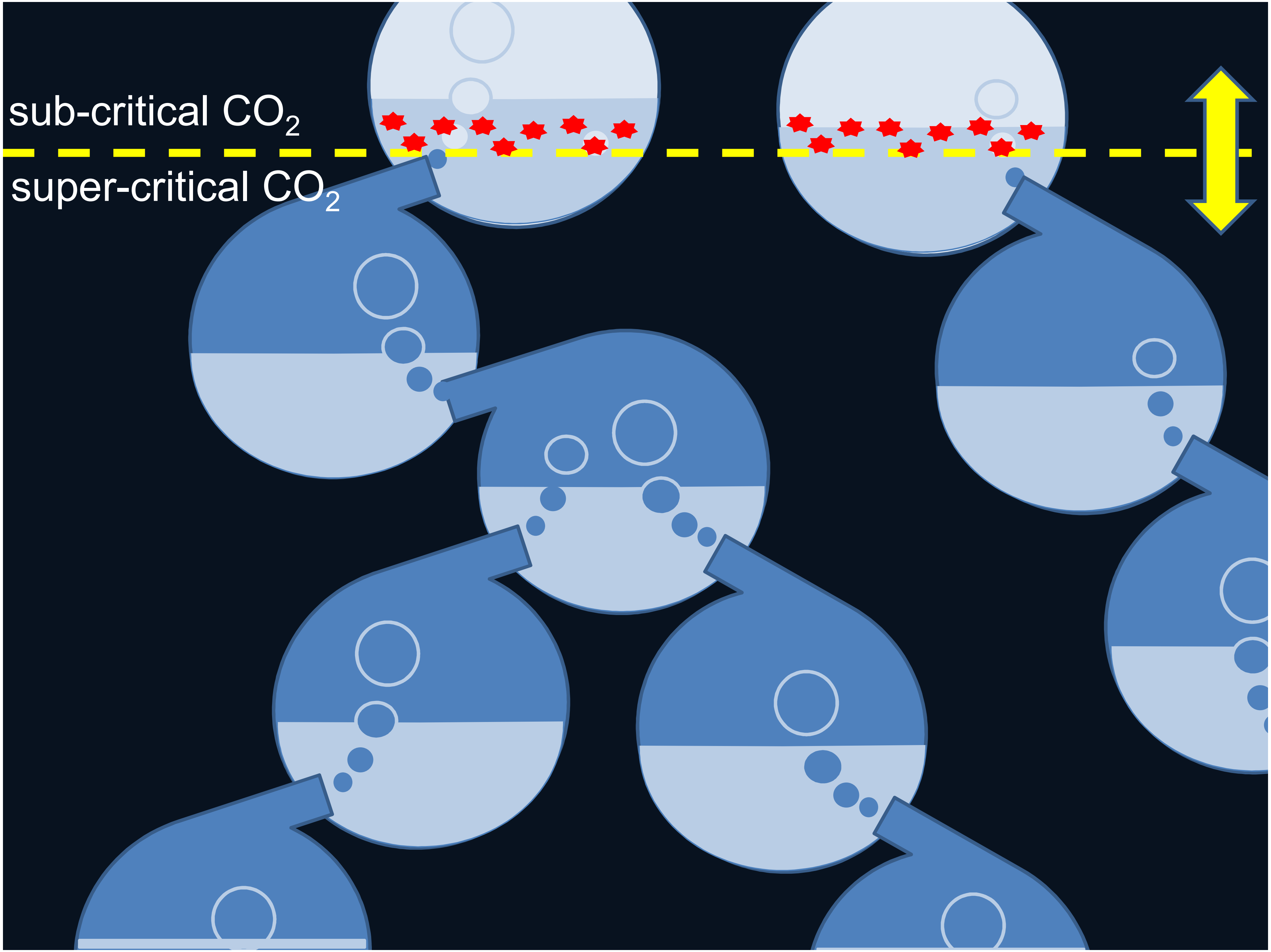
Ulrich Schreiber

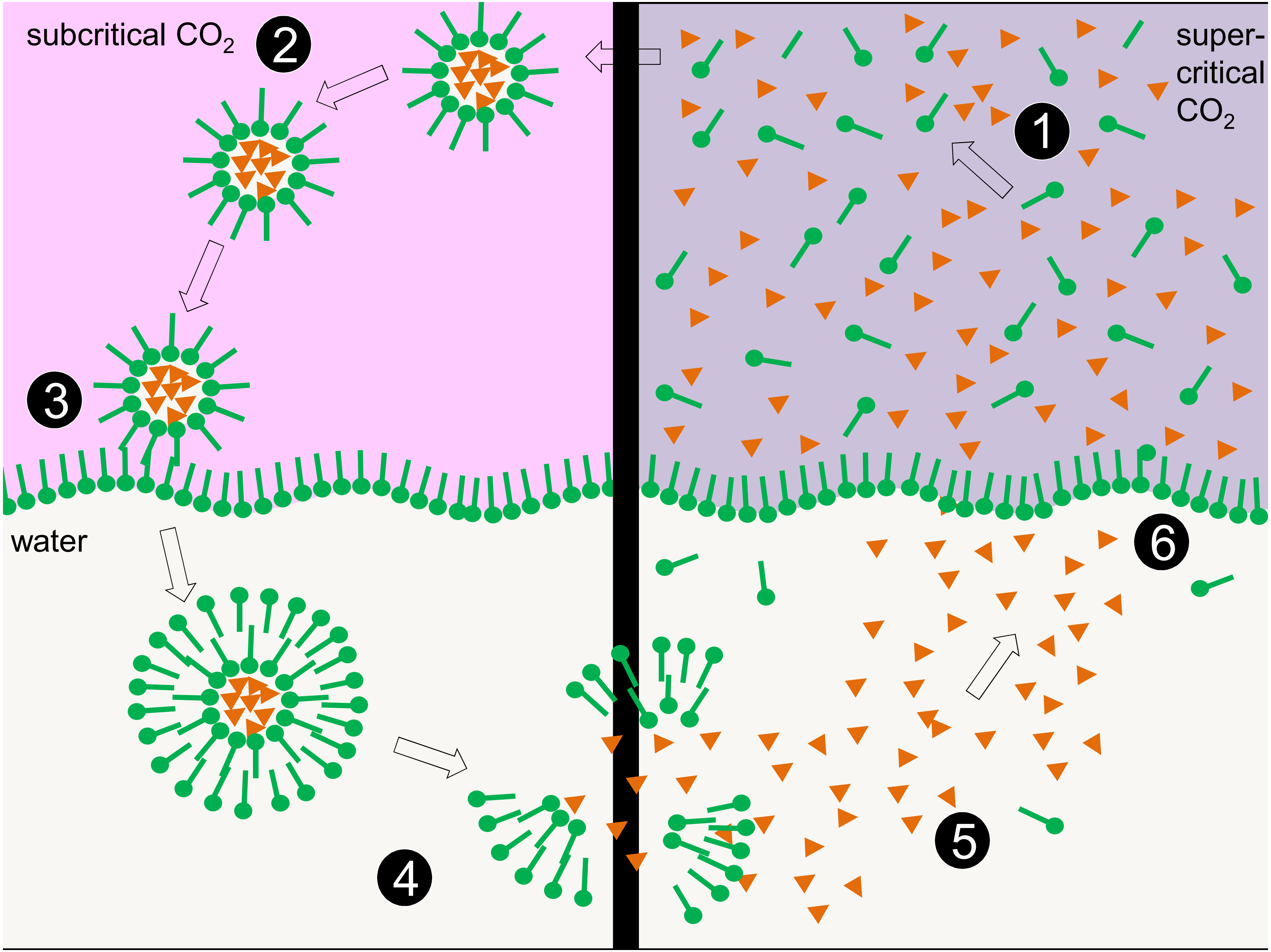
Table 1. Organic compounds identified in hydrothermally grown quartz crystals near Jack Hills in Western Australia. The index letter "a" refers to the technical approach used for the analysis: a = 1 for one-dimensional gas chromatography with flame ionization detector[8], a = 2 for comprehensive two-dimensional gas chromatography coupled to a quadrupole MS and a = 3 for liquid chromatography with a high-resolution TOF-MS.

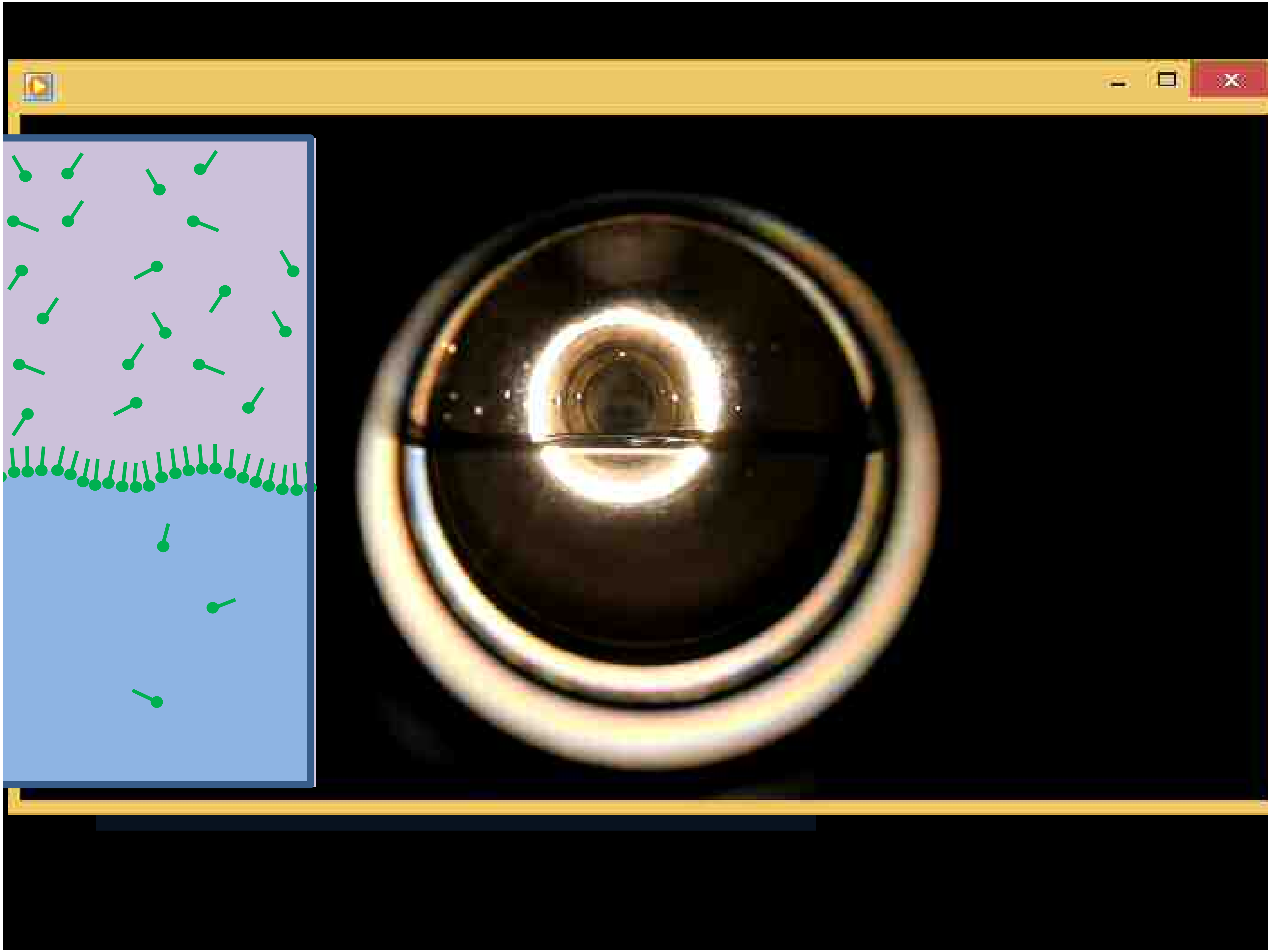
compound class	compound	structure	a
Hydrocarbons	Methane	CH_4	1
	Ethane	CH_3-CH_3	1
	Ethene	$CH_2 = CH_2$	1
	Ethyne	$CH \equiv CH$	1
	Propane	CH_3-CH_2-CH_3	1
	Propene	CH_3-$CH = CH_2$	1
	n-Butane	CH_3-CH_2-CH_2-CH_3	1
	1-Butene	CH_3-CH_2-$CH = CH_2$	1
	3-Methylpropene	$(CH_3)_2CH = CH_2$	1
Halocarbons	2,2-Dichloroethanol	$CHCl_2$-CH_2OH	2
	1,1,2,2-Tetrachloroethane	$CHCl_2$-$CHCl_2$	2
	1,1,2,3-Tetrachloropropane	$CHCl_2$-CHCl-CH_2Cl	2
	3-Chloro-1-propanol	CH_2Cl-CH_2-CH_2OH	2
	1,1-Dimethyl-3-chloropropanol	CH_2Cl-CH_2-$C(CH_3)_2OH$	2
	3,3-Dichloro-1-propanol	$CHCl_2$-CH_2-CH_2OH	2
	1,3-Dichloro-2-propanone	CH_2Cl-(CO)-CH_2Cl	2
	2,2,3-Trichloropropional	CH_2Cl-CCl_2-CHO	2
	1,2,3-Trichloro-1-propene	CH_2Cl-CCl = CHCl	2
Alcohols	4-Methyl-2-pentanol	CH_3-$CH(CH_3)$-CH_2-CHOH-CH_3	2
	3-Methyl-4-penten-1-ol	CH_2 = CH-$CH(CH_3)$-CH_2-CH_2OH	2
	3-Hexen-1-ol	CH_3-CH_2-CH = CH-CH_2-CH_2OH	2
	Tetramethyl-2-hexadecen-1-ol	$(C_{19}H_{37})$-CH_2OH	2
Aldehydes	Heptanal	C_6H_{13}-CHO	2
	Octanal	C_7H_{15}-CHO	2
	Nonanal	C_8H_{17}-CHO	2
	Decanal	C_9H_{19}-CHO	2
	Undecanal	$C_{10}H_{21}$-CHO	2
	Dodecanal	$C_{11}H_{23}$-CHO	2
	[illegible]	[illegible]	[illegible]

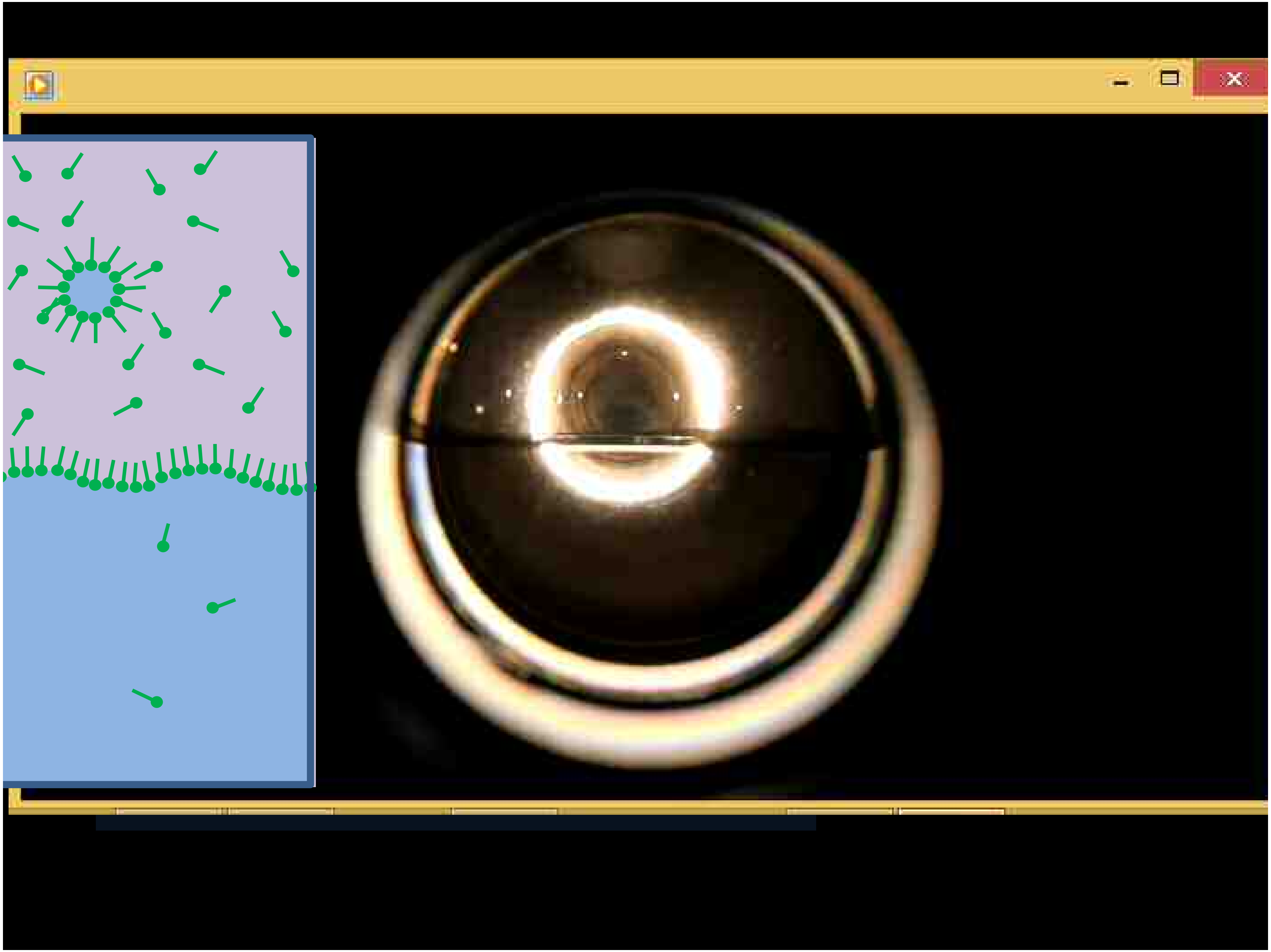
	Propene	CH_3-CH = CH_2	1
	n-Butane	CH_3-CH_2-CH_2-CH_3	1
	1-Butene	CH_3-CH_2-CH = CH_2	1
	3-Methylpropene	$(CH_3)_2$CH = CH_2	1
Halocarbons	2,2-Dichloroethanol	$CHCl_2$-CH_2OH	2
	1,1,2,2-Tetrachloroethane	$CHCl_2$-$CHCl_2$	2
	1,1,2,3-Tetrachloropropane	$CHCl_2$-CHCl-CH_2Cl	2
	3-Chloro-1-propanol	CH_2Cl-CH_2-CH_2OH	2
	1,1-Dimethyl-3-chloropropanol	CH_2Cl-CH_2-$C(CH_3)_2$OH	2
	3,3-Dichloro-1-propanol	$CHCl_2$-CH_2-CH_2OH	2
	1,3-Dichloro-2-propanone	CH_2Cl-(CO)-CH_2Cl	2
	2,2,3-Trichloropropional	CH_2Cl-CCl_2-CHO	2
	1,2,3-Trichloro-1-propene	CH_2Cl-CCl = CHCl	2
Alcohols	4-Methyl-2-pentanol	CH_3-CH(CH_3)-CH_2-CHOH-CH_3	2
	3-Methyl-4-penten-1-ol	CH_2 = CH-CH(CH_3)-CH_2-CH_2OH	2
	3-Hexen-1-ol	CH_3-CH_2-CH = CH-CH_2-CH_2OH	2
	Tetramethyl-2-hexadecen-1-ol	($C_{19}H_{37}$)-CH_2OH	2
Aldehydes	Heptanal	C_6H_{13}-CHO	2
	Octanal	C_7H_{15}-CHO	2
	Nonanal	C_8H_{17}-CHO	2
	Decanal	C_9H_{19}-CHO	2
	Undecanal	$C_{10}H_{21}$-CHO	2
	Dodecanal	$C_{11}H_{23}$-CHO	2
	Tridecanal	$C_{12}H_{25}$-CHO	2
	Tetradecanal	$C_{13}H_{27}$-CHO	2
	Pentadecanal	$C_{14}H_{29}$-CHO	2
	Hexadecanal	$C_{15}H_{31}$-CHO	2
	Heptadecanal	$C_{16}H_{33}$-CHO	2
	3-Methoxybutyral	CH_3-CH(OCH_3)-CH_2-CHO	2
Unknown		$C_7H_9N_5$	3
		$C_5H_6N_6O_3$	3
		$C_7H_{12}N_6O_4$	3
		$C_9H_{16}N_6O_5$	3
		$C_{15}H_{18}N_6O_4$	3

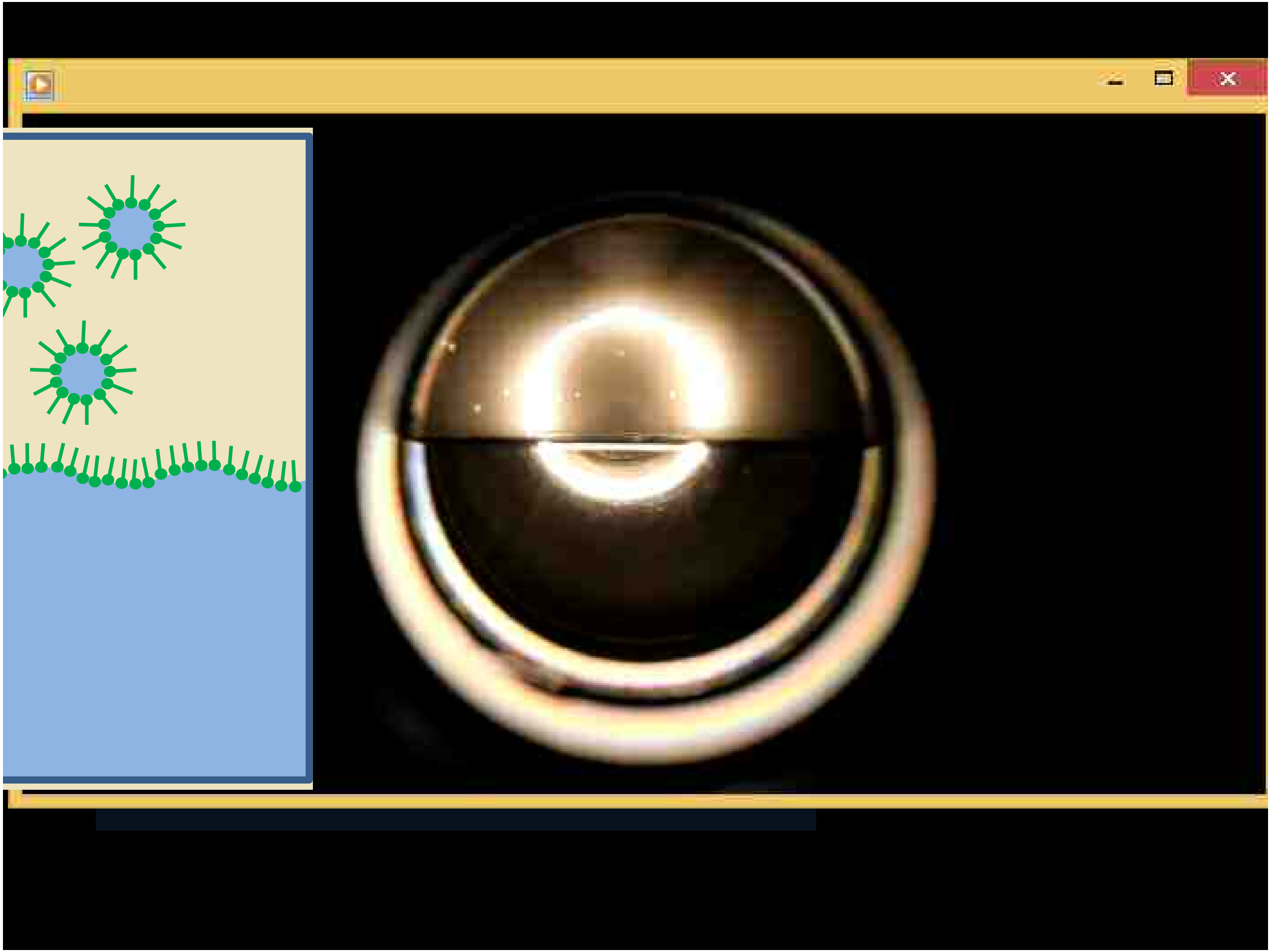
https://doi.org/10.1371/journal.pone.0177570.t001

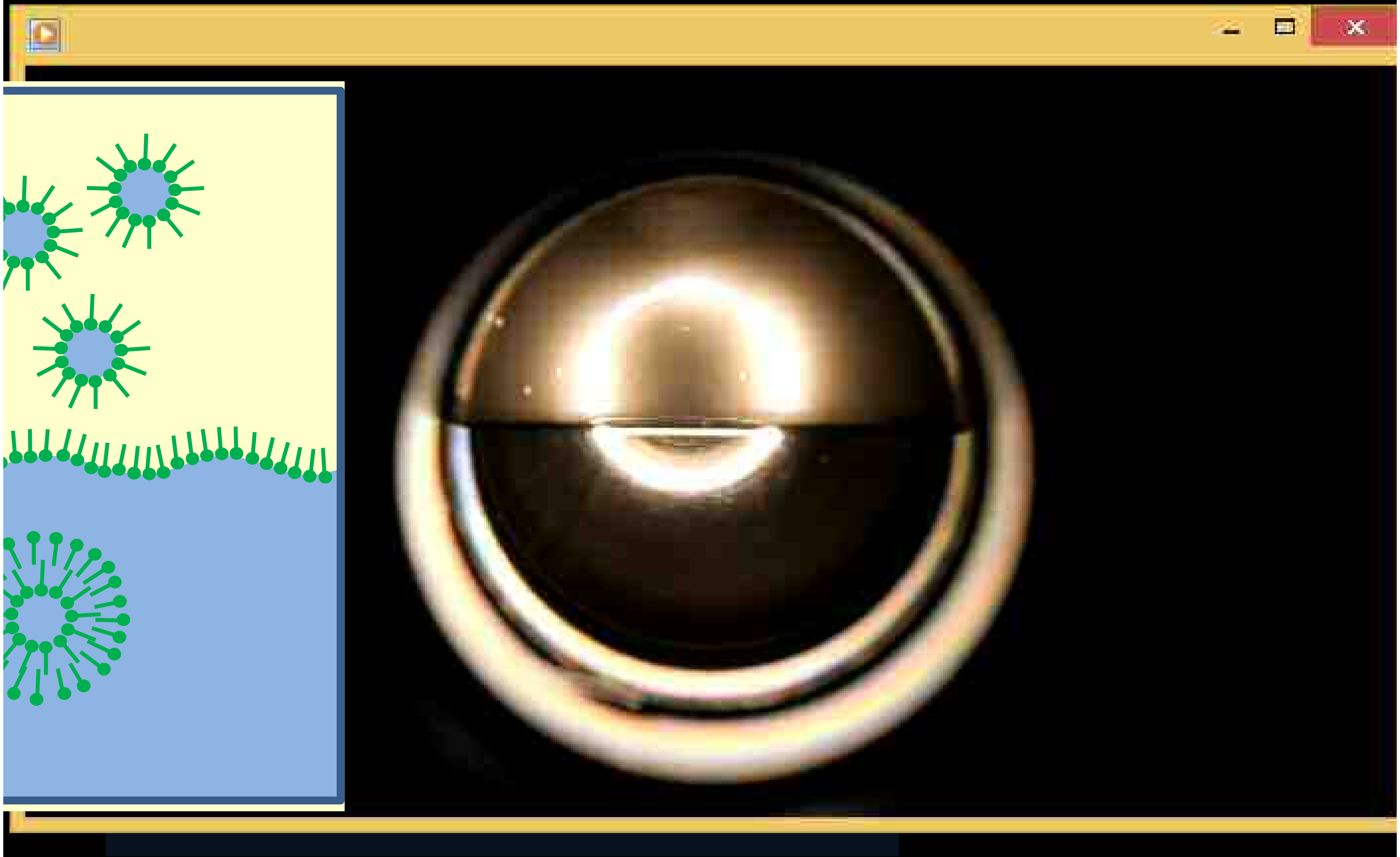

sub-critical CO_2
super-critical CO_2

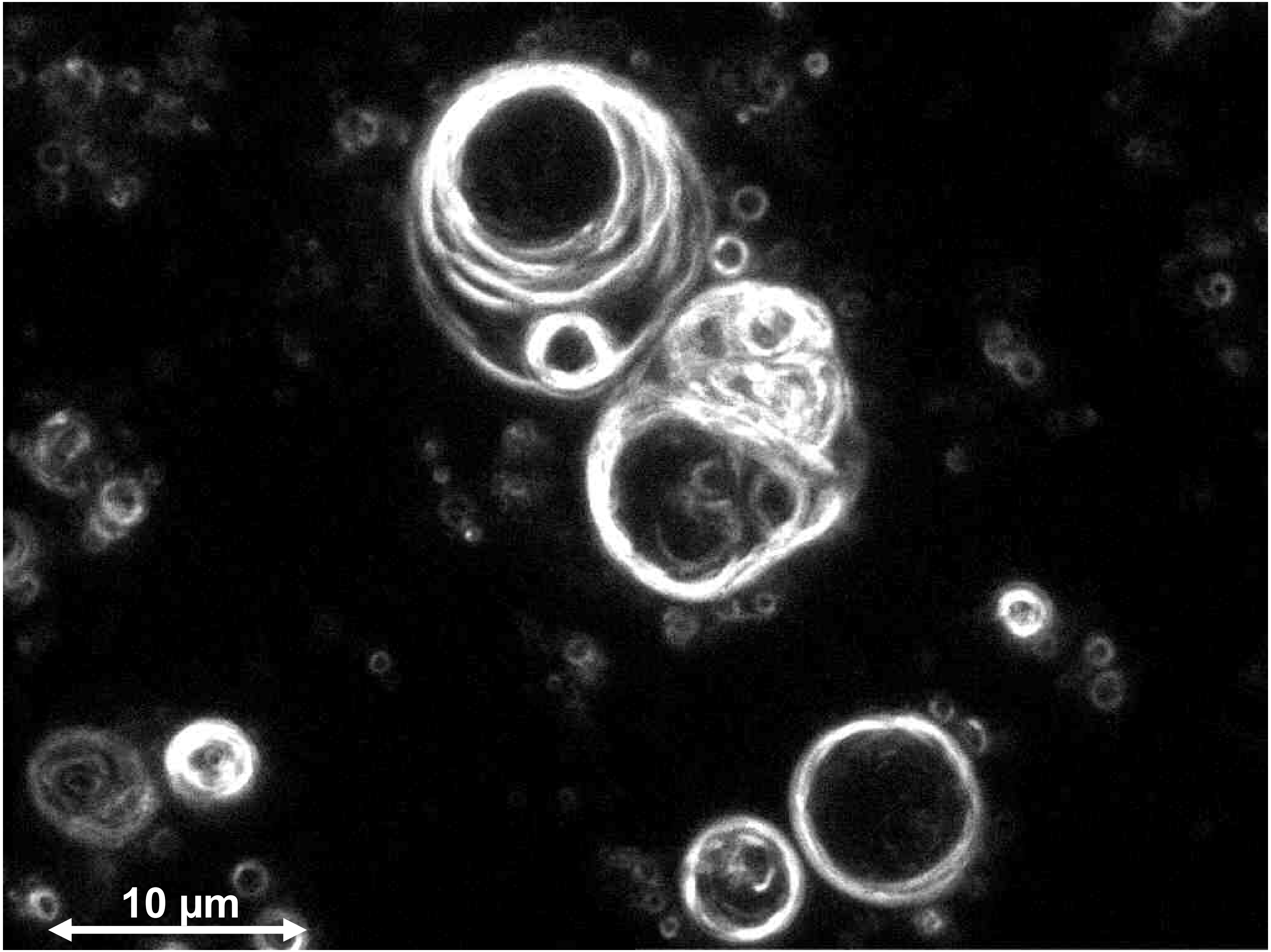

subcritical CO_2
2
super-
critical
CO_2
1
3
water
4
5
6

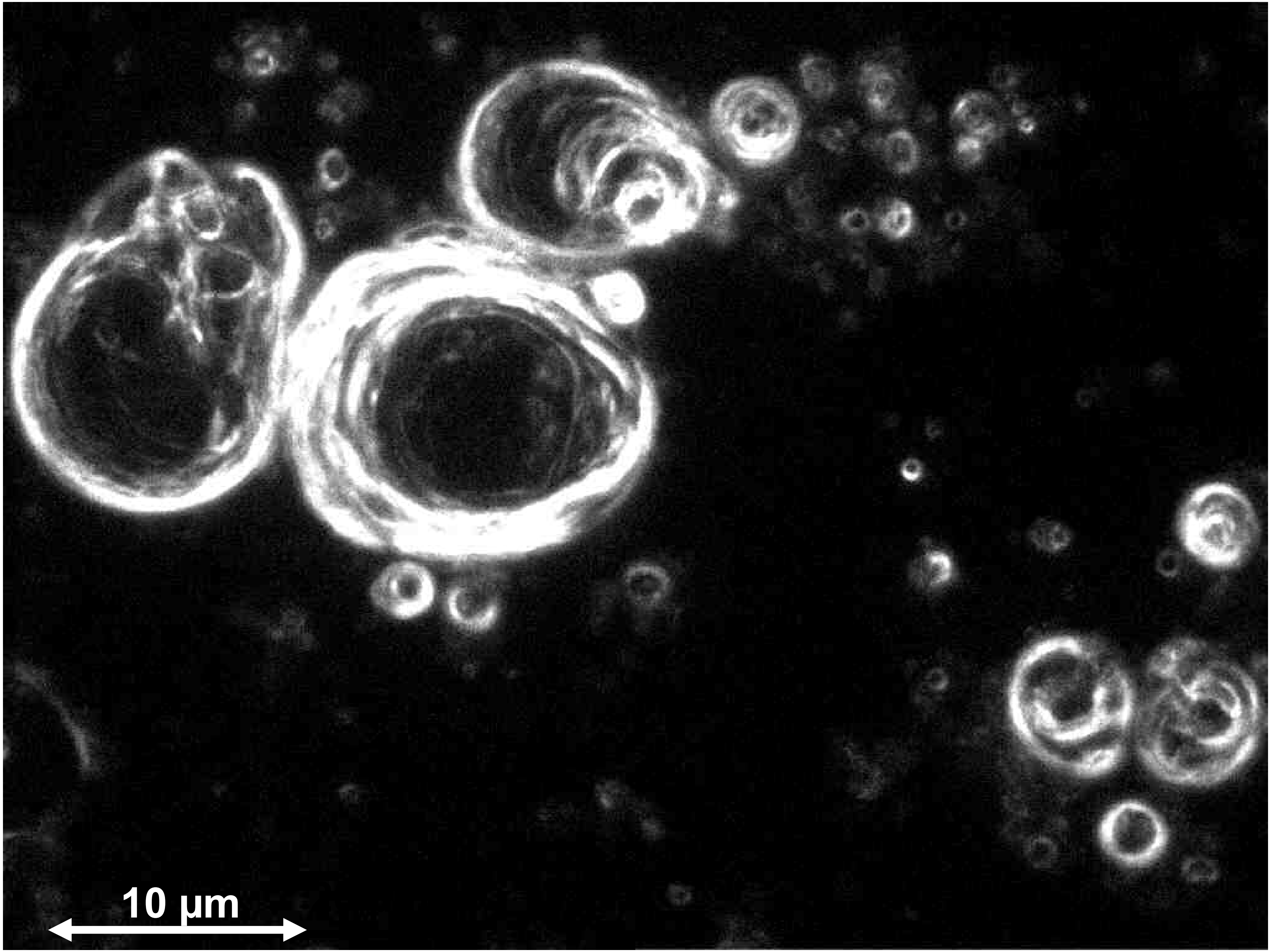


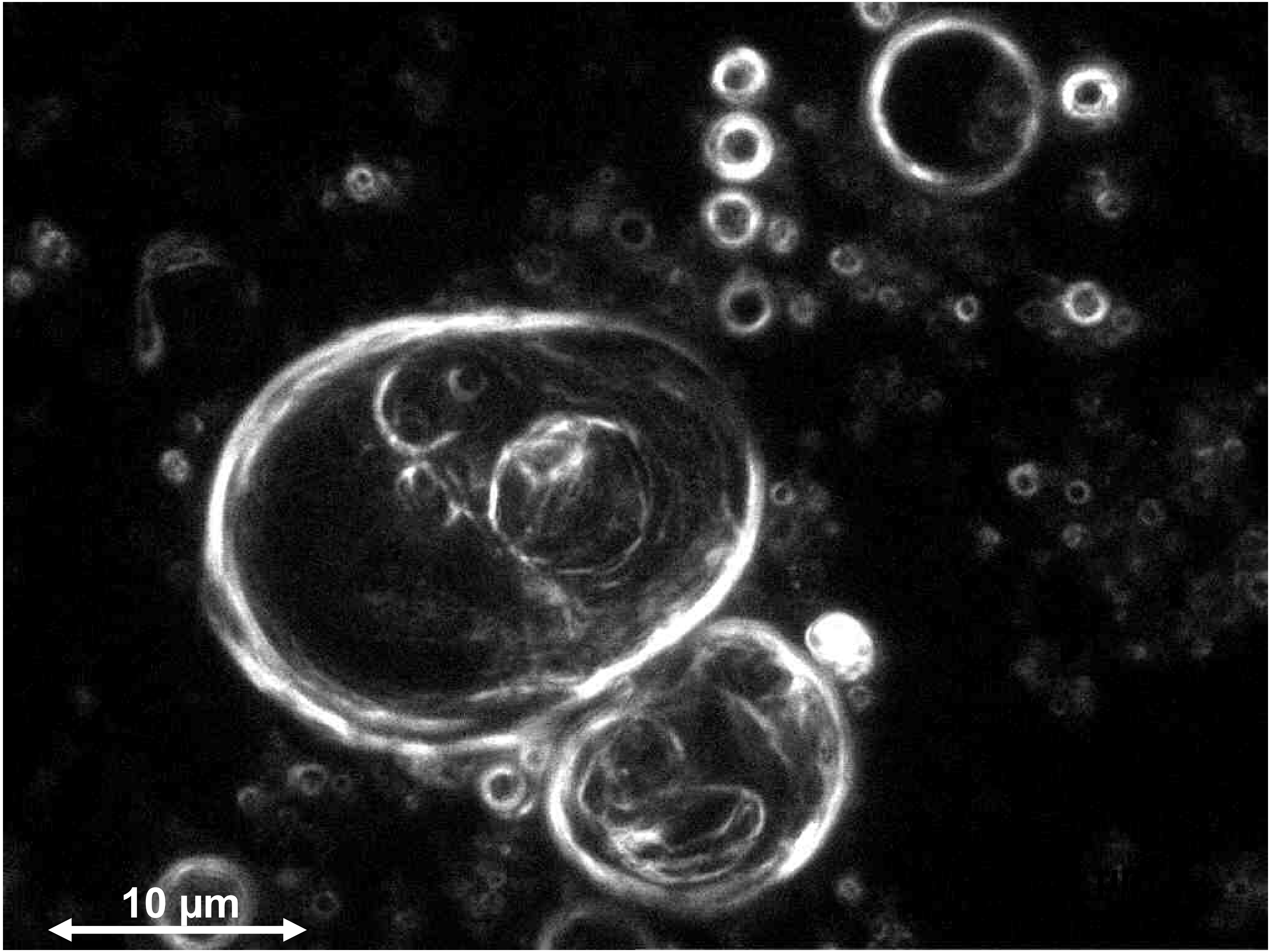


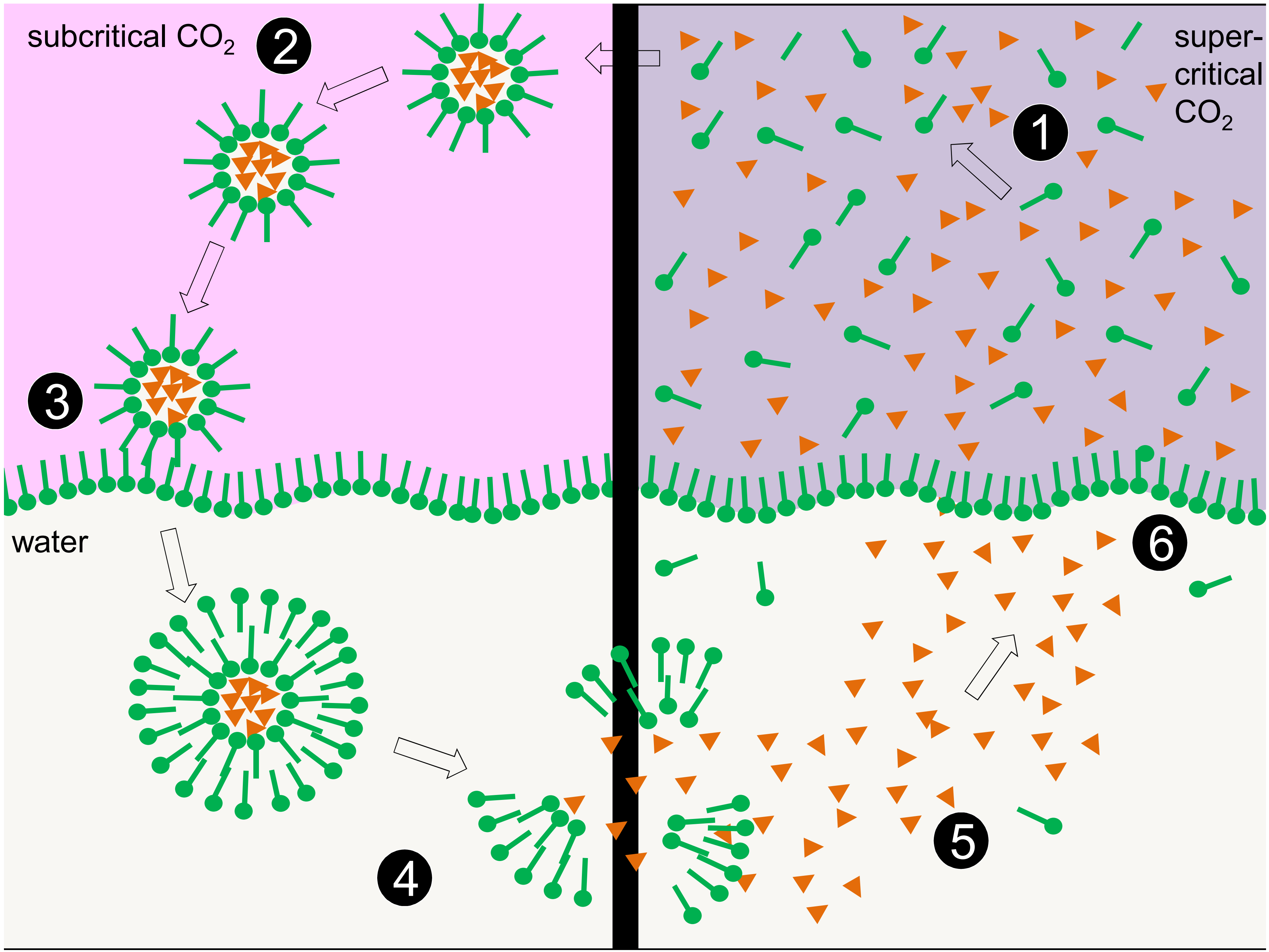





10 µm


10 µm


10 µm



subcritical CO_2
2
super-
critical
CO_2
1
3
water
6
5
4

hydrothermal formation of peptides

12 proteinogenic amino acids occur in hydrothermal environments:

6 non-polar

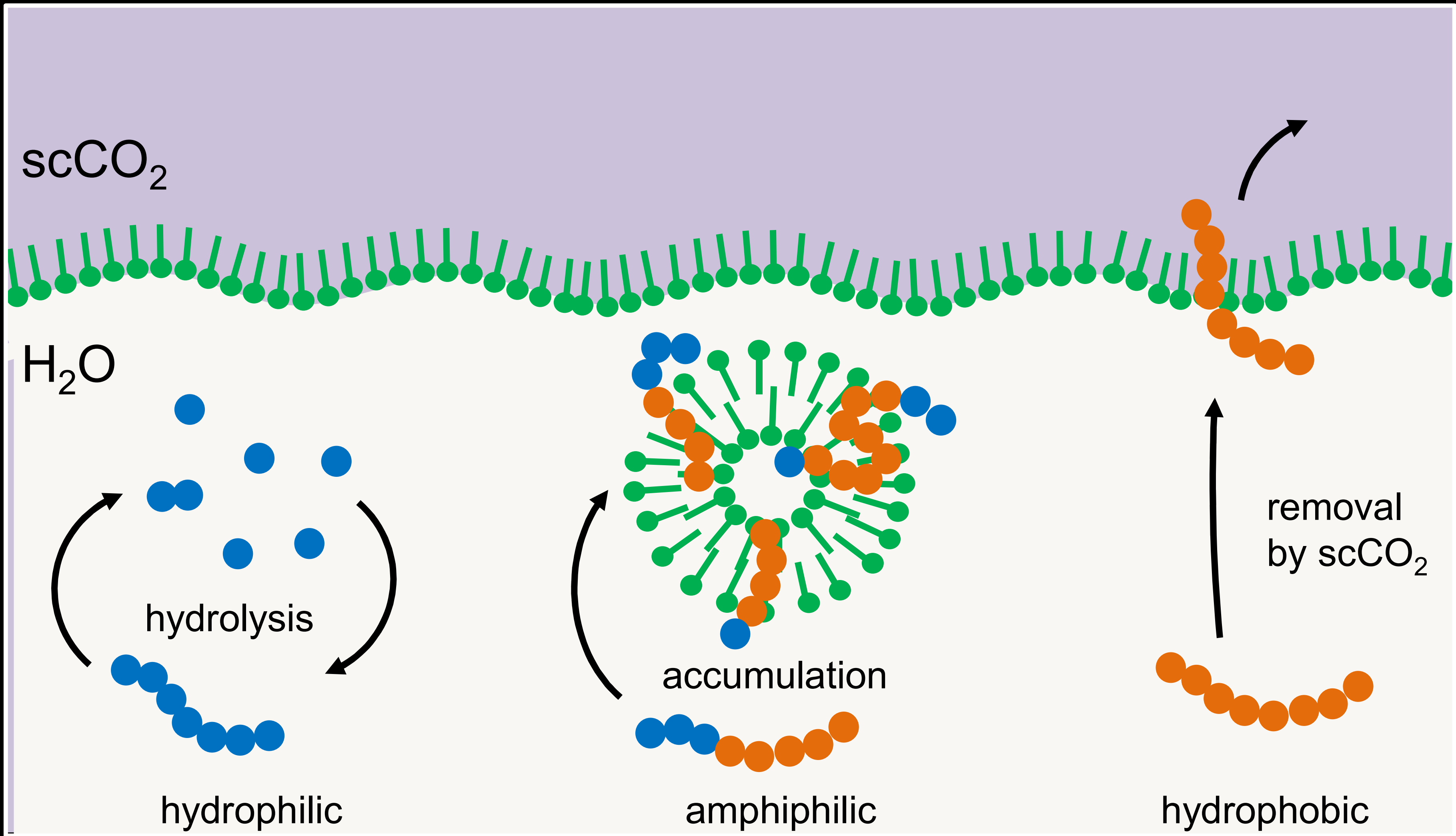
6 polar

non-polar:

Alanine
Proline
Valine
Leucine
Isoleucine
Phenylalanine

polar:

Glycine
Serine
Threonine
Aspartic acid
Glutamic acid
Lysine



peptide formation: amino acids and peptides with growing chain lengths

$$R\text{-}COOH + R'\text{-}NH_2 \underset{\text{hydrolysis } k_h}{\overset{\text{condensation } k_c}{\rightleftharpoons}} R\text{-}CO\text{-}NH\text{-}R' + H_2O$$

$$\frac{dc_1}{dt} = 2\,k_h\,(c_2 + c_3 + c_4 + c_5 + c_6) - 2\,k_c c_1(2c_1 + c_2 + c_3 + c_4 + c_5) \quad [1]$$

$$\frac{dc_2}{dt} = 2\,k_c c_1^2 + 2\,k_h\,(c_3 + c_4 + c_5 + c_6) - 2\,k_c c_2(c_1 + 2c_2 + c_3 + c_4) - k_h c_2 \quad [2]$$

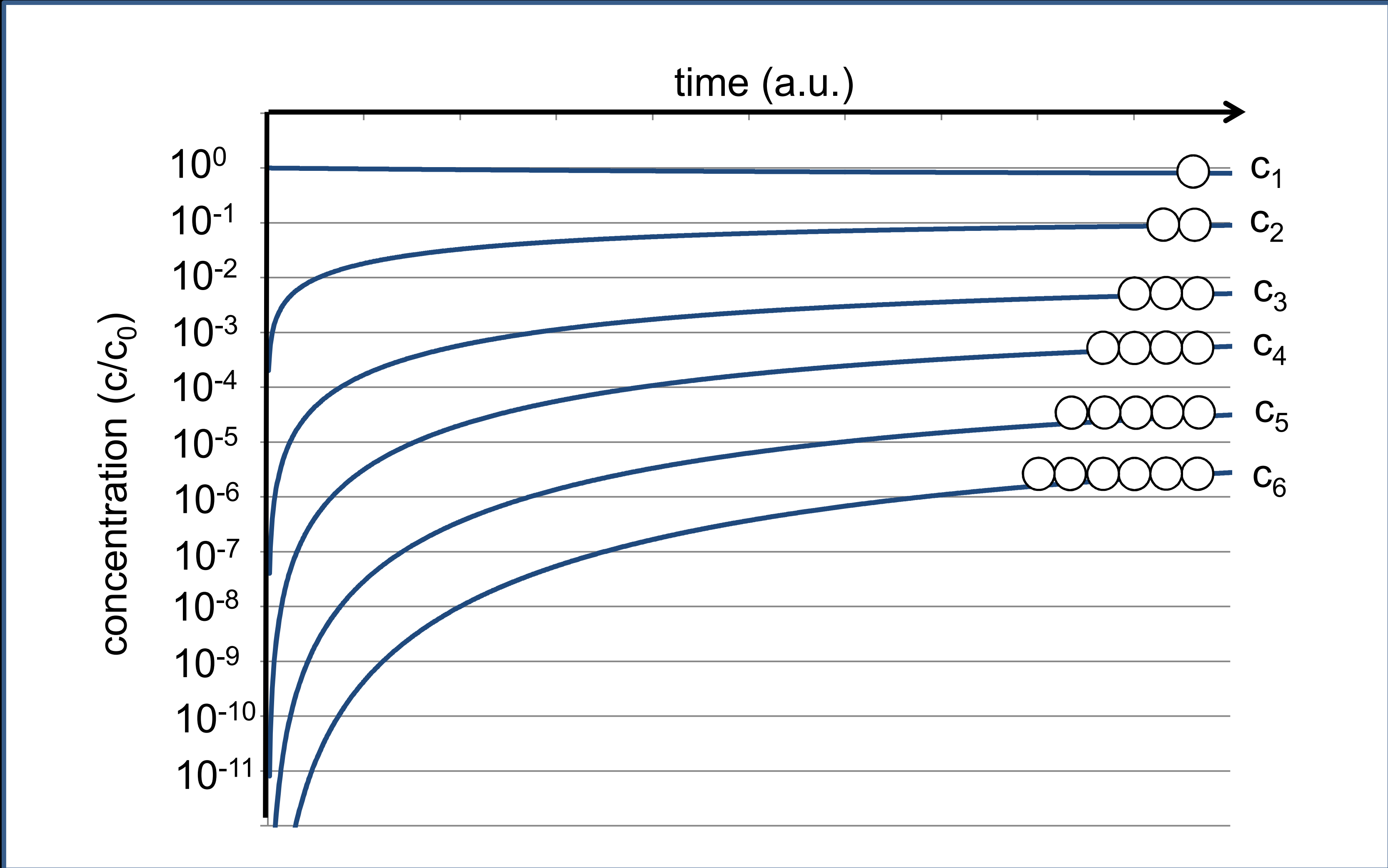
$$\frac{dc_3}{dt} = 2\,k_c c_1 c_2 + 2\,k_h\,(c_4 + c_5 + c_6) - 2\,k_c c_3(c_1 + c_2 + 2c_3) - 2k_h c_3 \quad [3]$$

$$\frac{dc_4}{dt} = 2\,k_c c_1 c_3 + 2\,k_c c_2^2 + 2\,k_h\,(c_5 + c_6) - 2\,k_c c_4(c_1 + c_2) - 3k_h c_4 \quad [4]$$

$$\frac{dc_5}{dt} = 2\,k_c c_1 c_4 + 2\,k_c c_2 c_3 + 2\,k_h c_6 - 2\,k_c c_5 c_1 - 4k_h c_5 \quad [5]$$

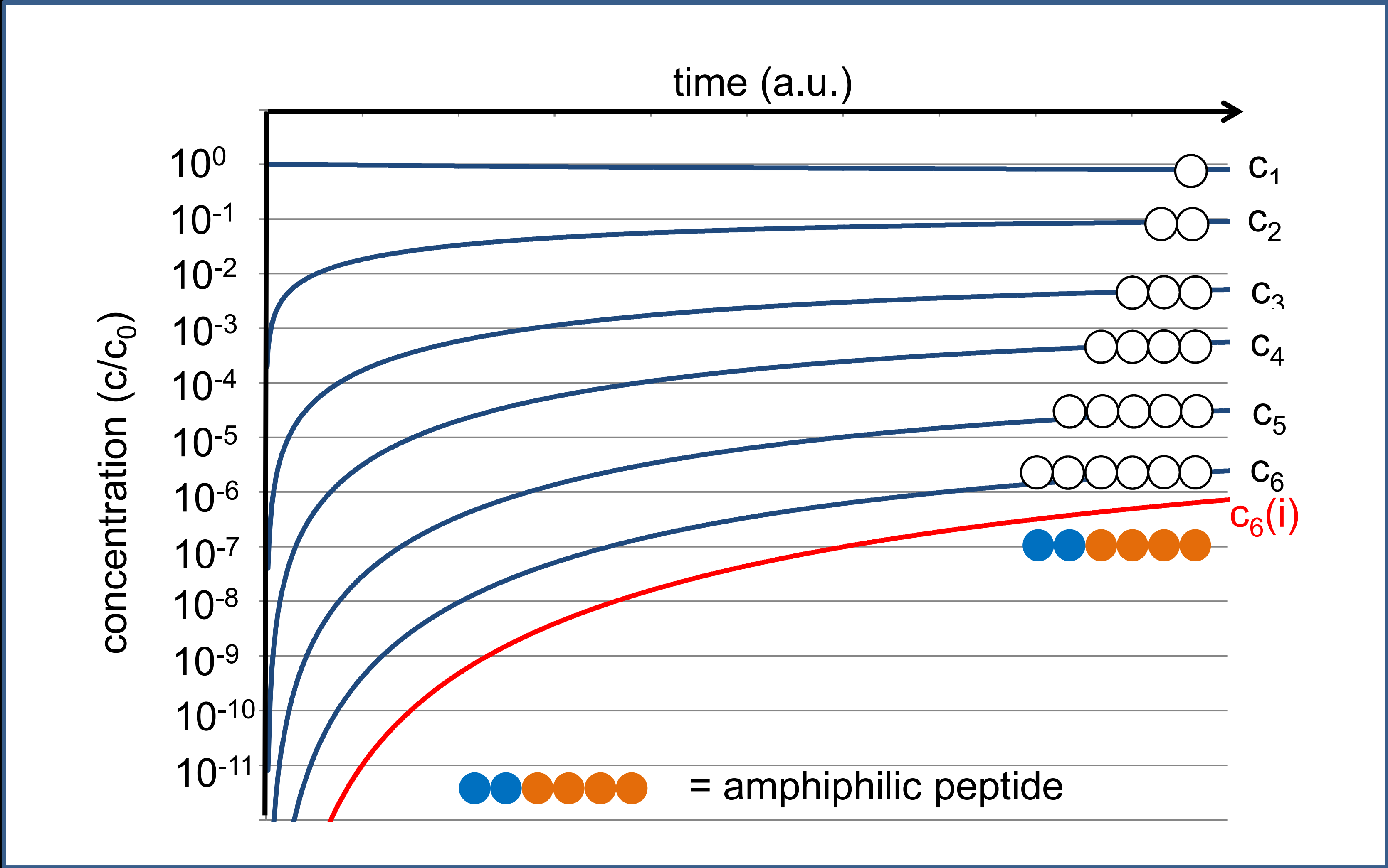
$$\frac{dc_6}{dt} = 2\,k_c c_1 c_5 + 2\,k_c c_2 c_4 + 2\,k_c c_3^2 - 5k_h c_6 \quad [6]$$

peptide formation: amino acids and peptides with growing chain lengths

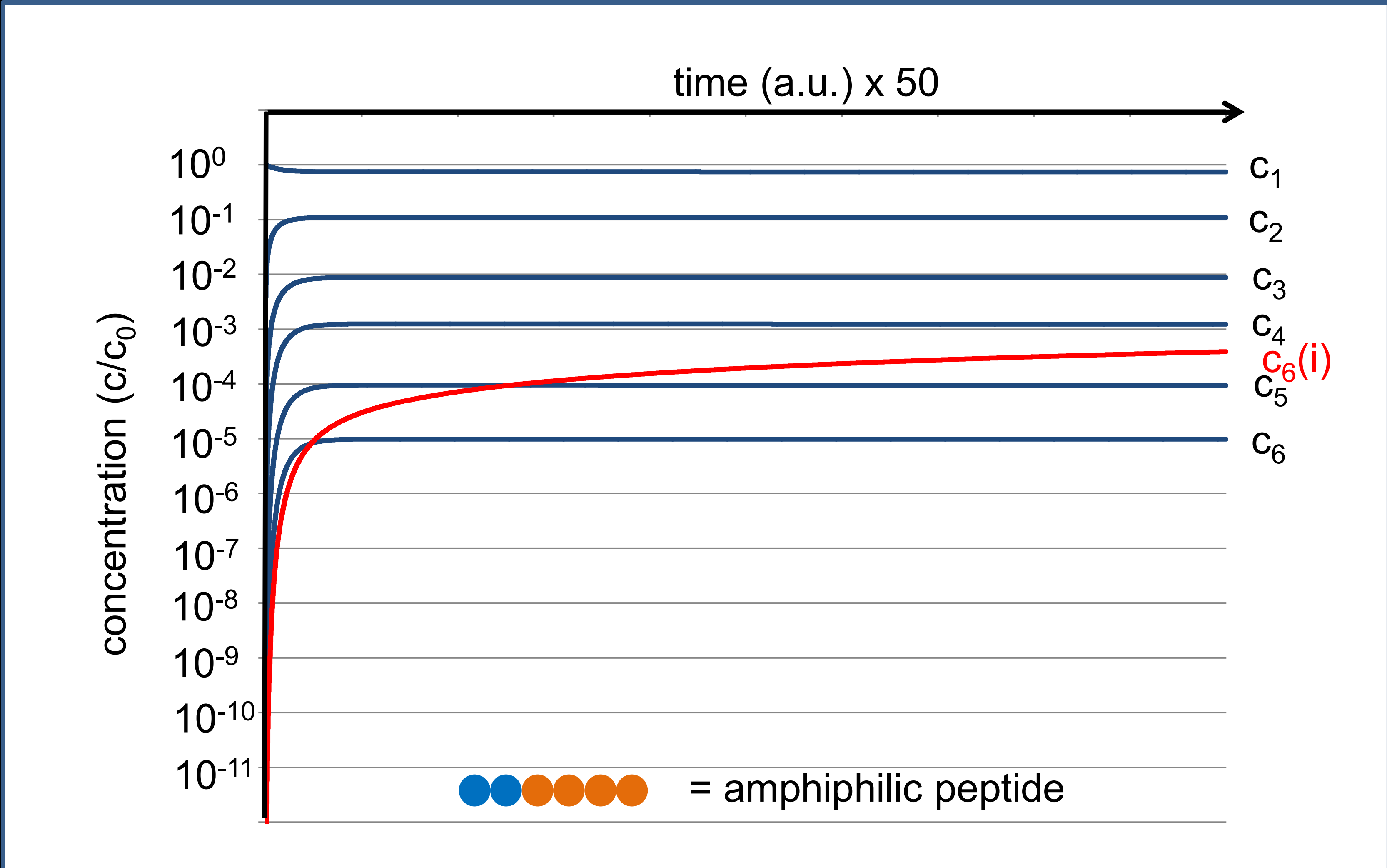


$$\text{amino acids} \underset{\text{hydrolysis}}{\overset{\text{condensation}}{\rightleftharpoons}} \text{peptides}$$

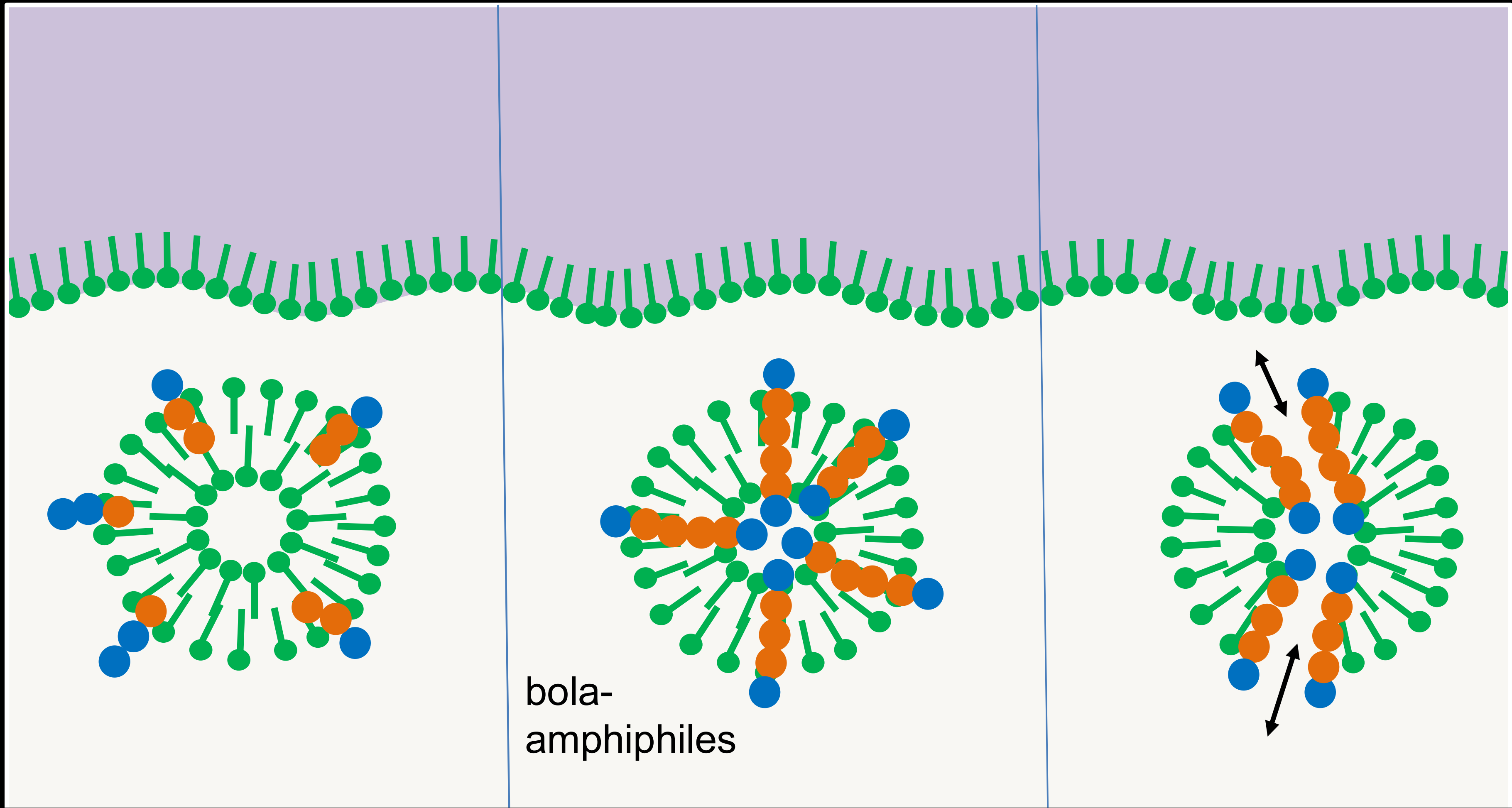
selection of an amphiphilic hexapeptide (short timescale)



selection of an amphiphilic hexapeptide (expanded timescale)



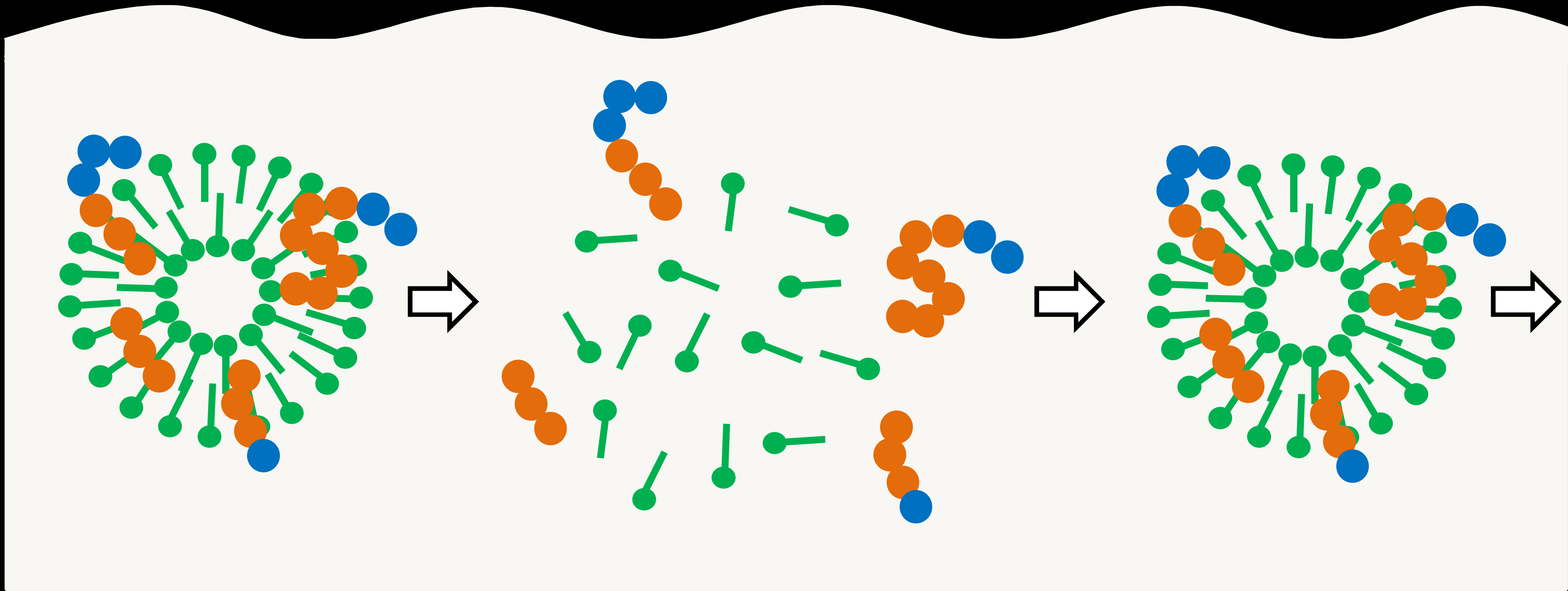
possible targets of peptide selection:



„parasitic“ „symbiotic“ functional

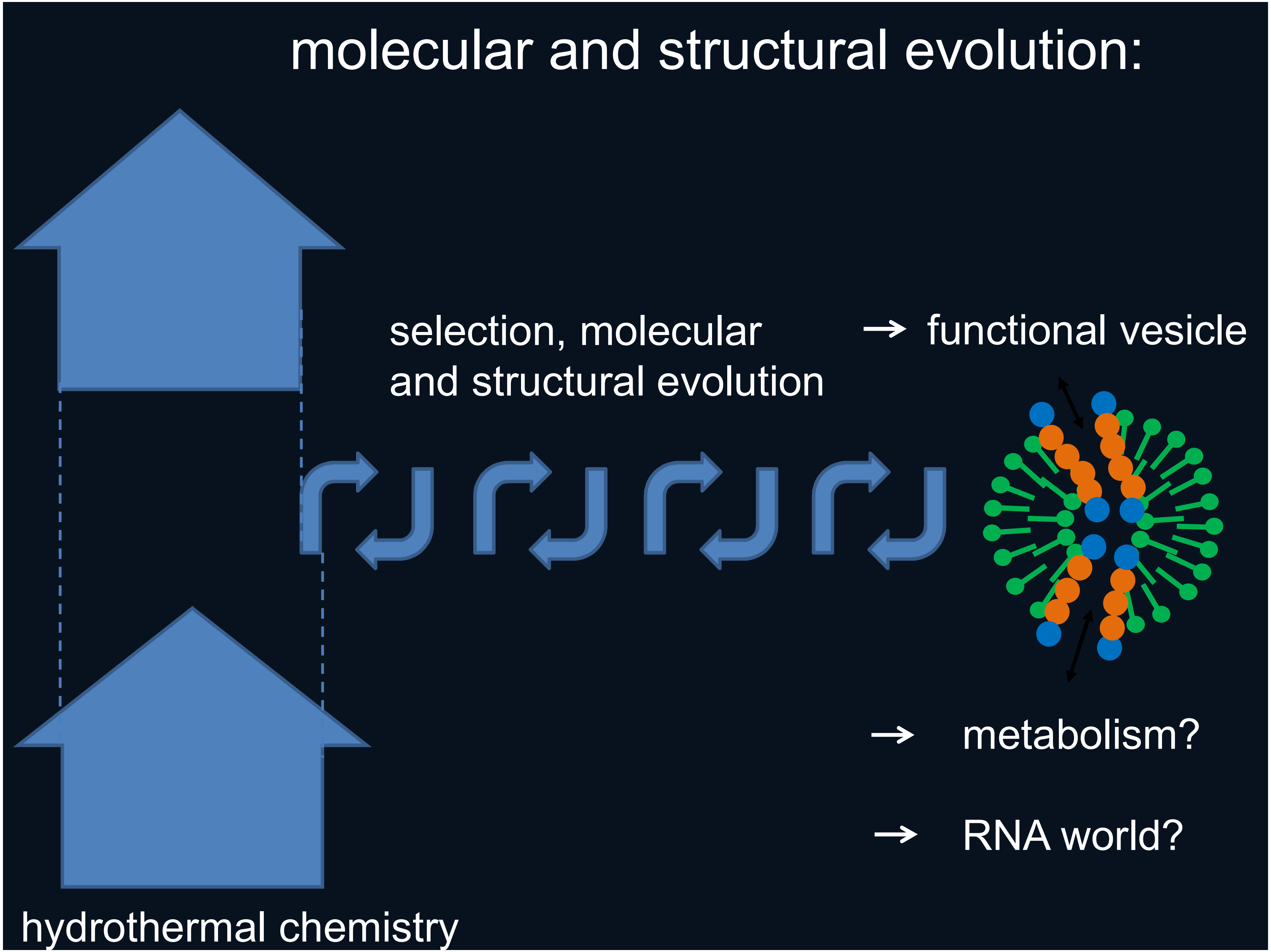
subsequent steps of optimization:

evolution?

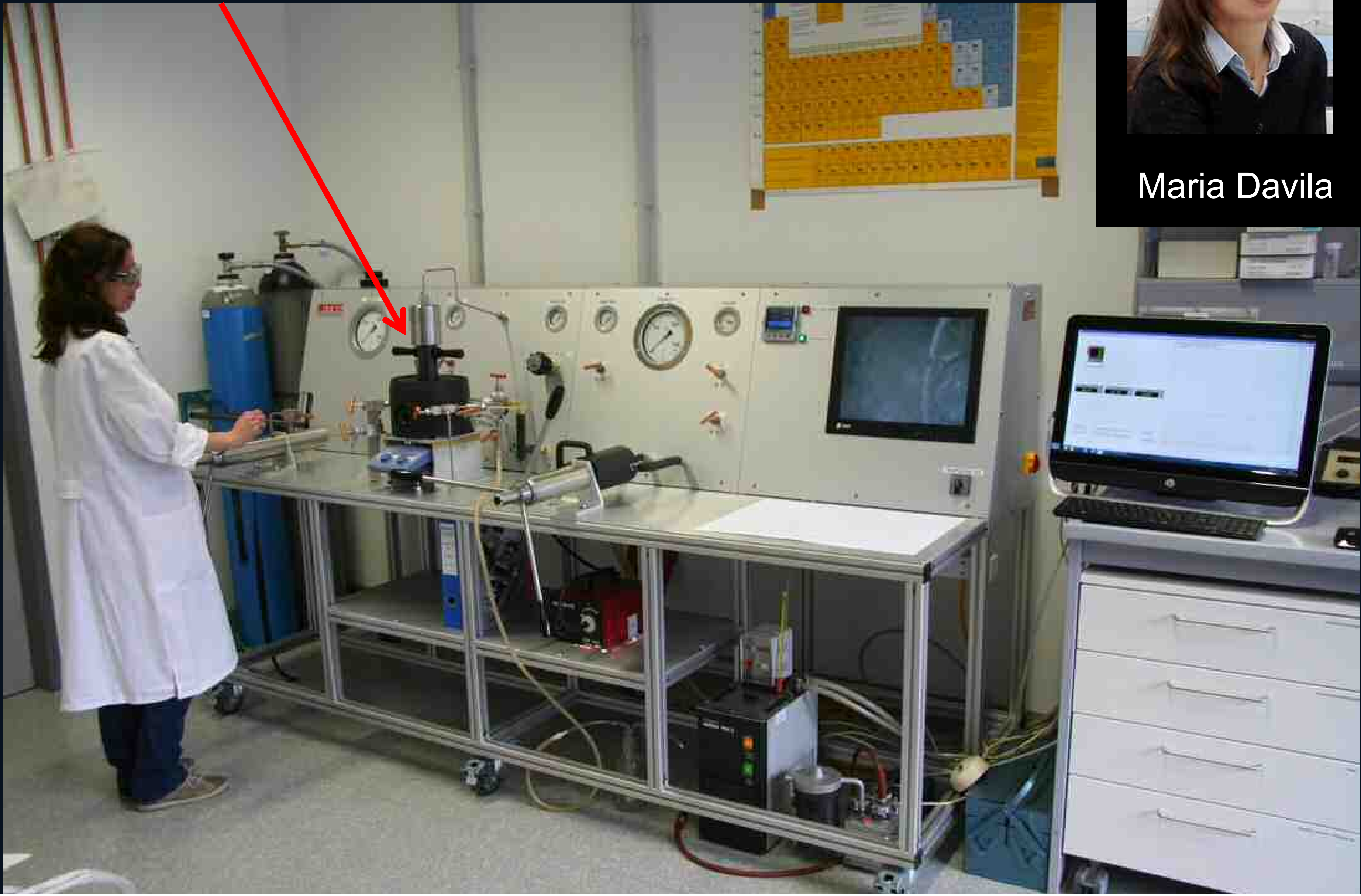


vesicles, selected for thermal stability ➡ stabilizing peptides, accumulated in the vesicle formation zone ➡ vesicles, selected for thermal stability ➡

phenotype ➡ (collective) genotype ➡ phenotype ➡


molecular and structural evolution:
selection, molecular
and structural evolution
→ functional vesicle
→ metabolism?
→ RNA world?
hydrothermal chemistry

high pressure cell



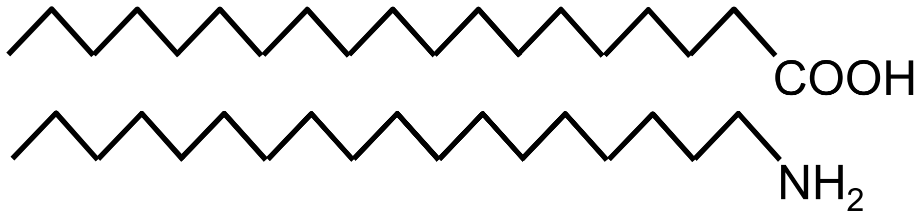
Maria Davila

materials:

bulk solvents:

water + carbon dioxide

amphiphiles for vesicle formation:



0.01 M

0.01 M

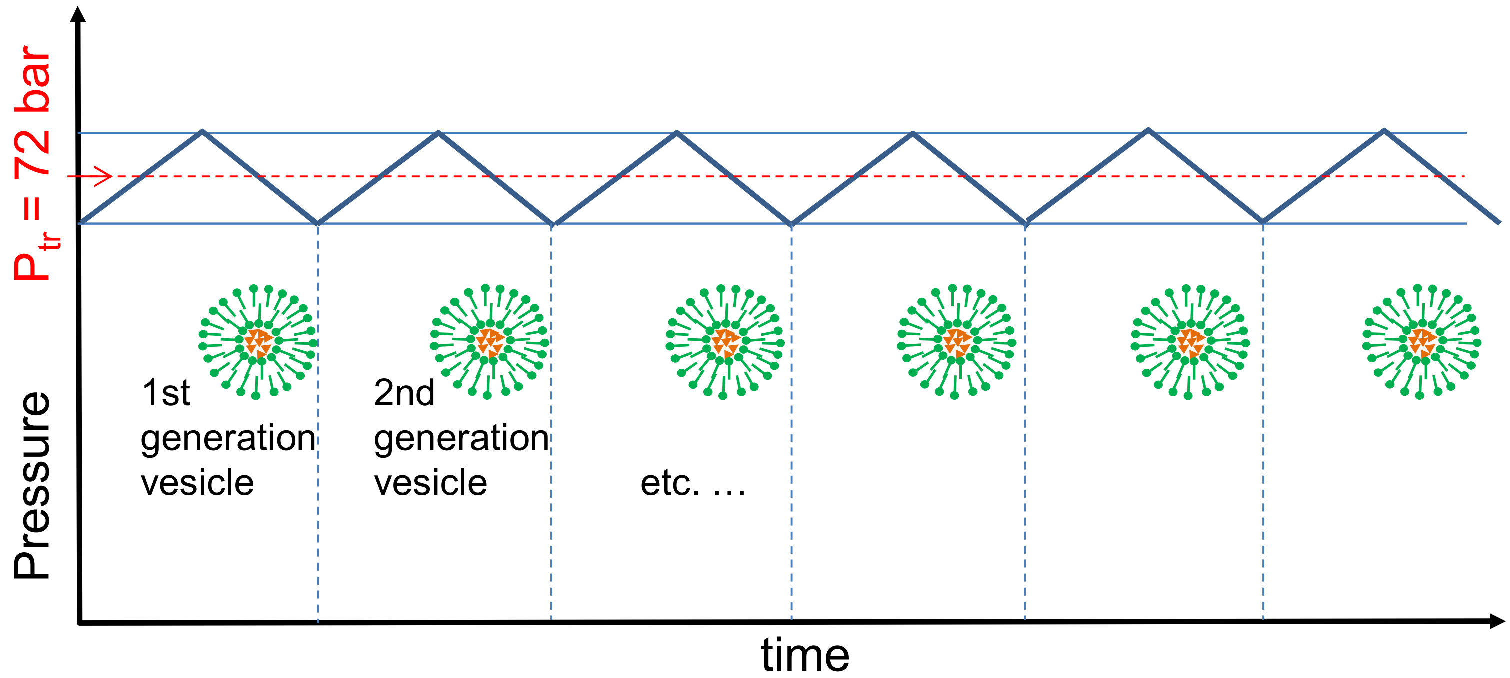
amino acids for peptide formation:

polar:	non-polar:
Glycine	Alanine
Serine	Proline
Threonine	Valine
Aspartic acid	Leucine
Glutamic acid	Isoleucine
Lysine	Phenylalanine

0.067 M each

conditions:

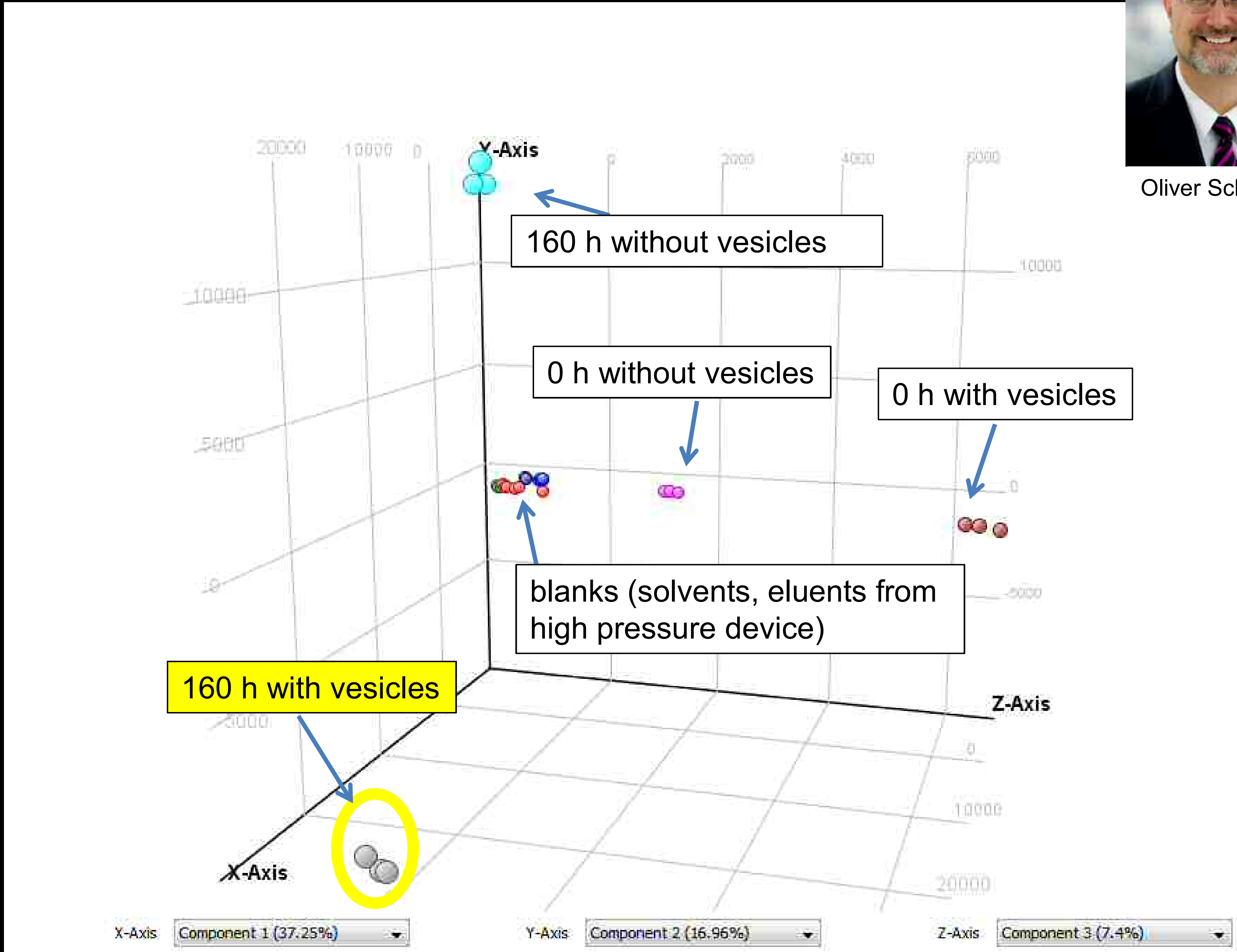
induction of multiple vesicle generations by periodic pressure variations



conditions for peptide formation:

pH ~ 3, T = 120°C

principal component analysis



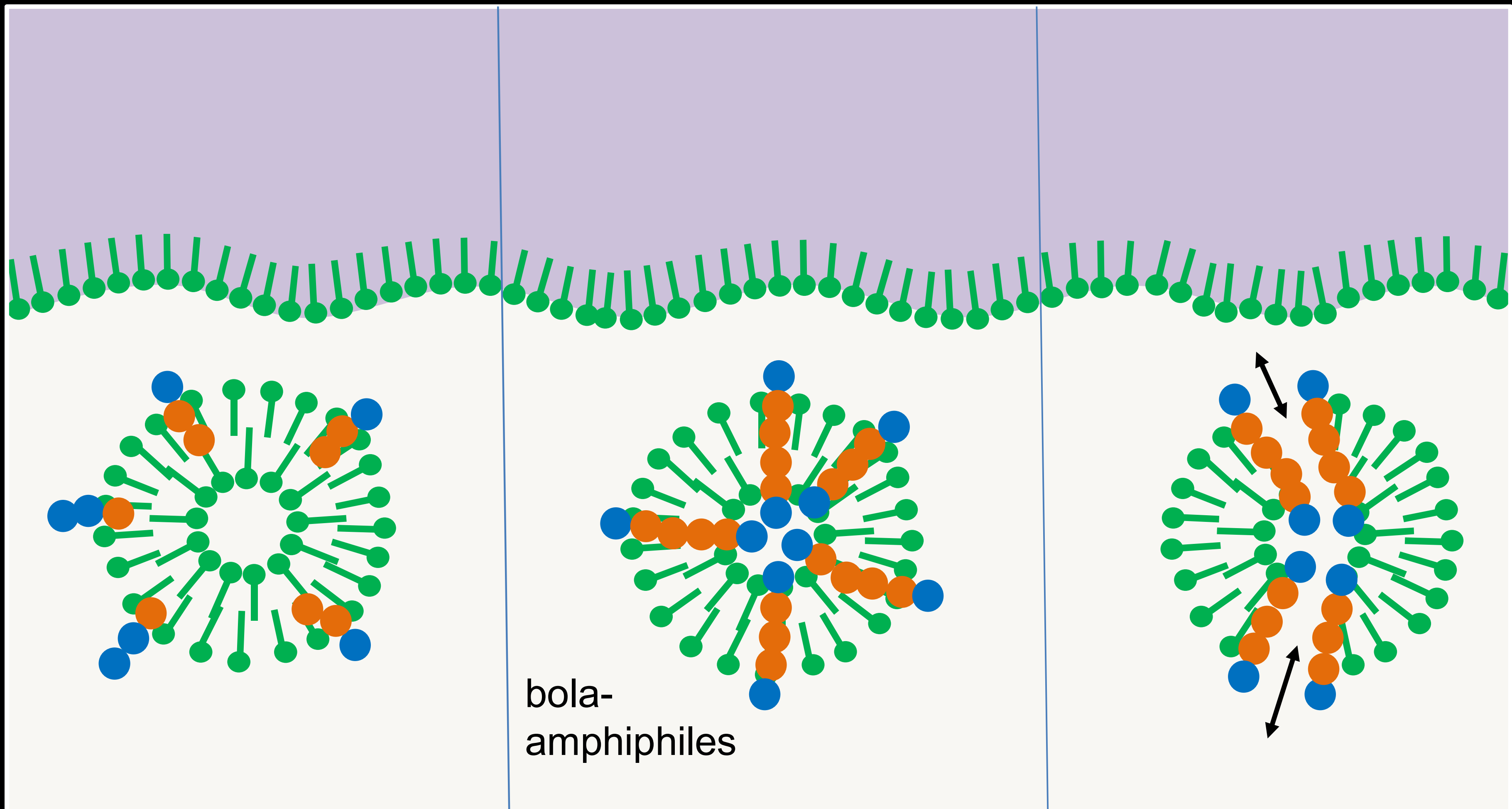
Oliver Schmitz

peptides accumulated by vesicles:

Amino Acid Composition	Exp. 1	Exp. 2	Exp. 3
Thr Thr Pro	X	X	0
Lys Pro Pro Phe	X	X	X
Lys Lys Gly Pro Ala	X	0	X
Lys Ser Pro Ala Phe	X	0	0
Lys Pro Gly Gly Gly Phe	0	X	0
Lys Ser Pro Phe Pro Phe Ala Ala	0	0	X

H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-$COOH$

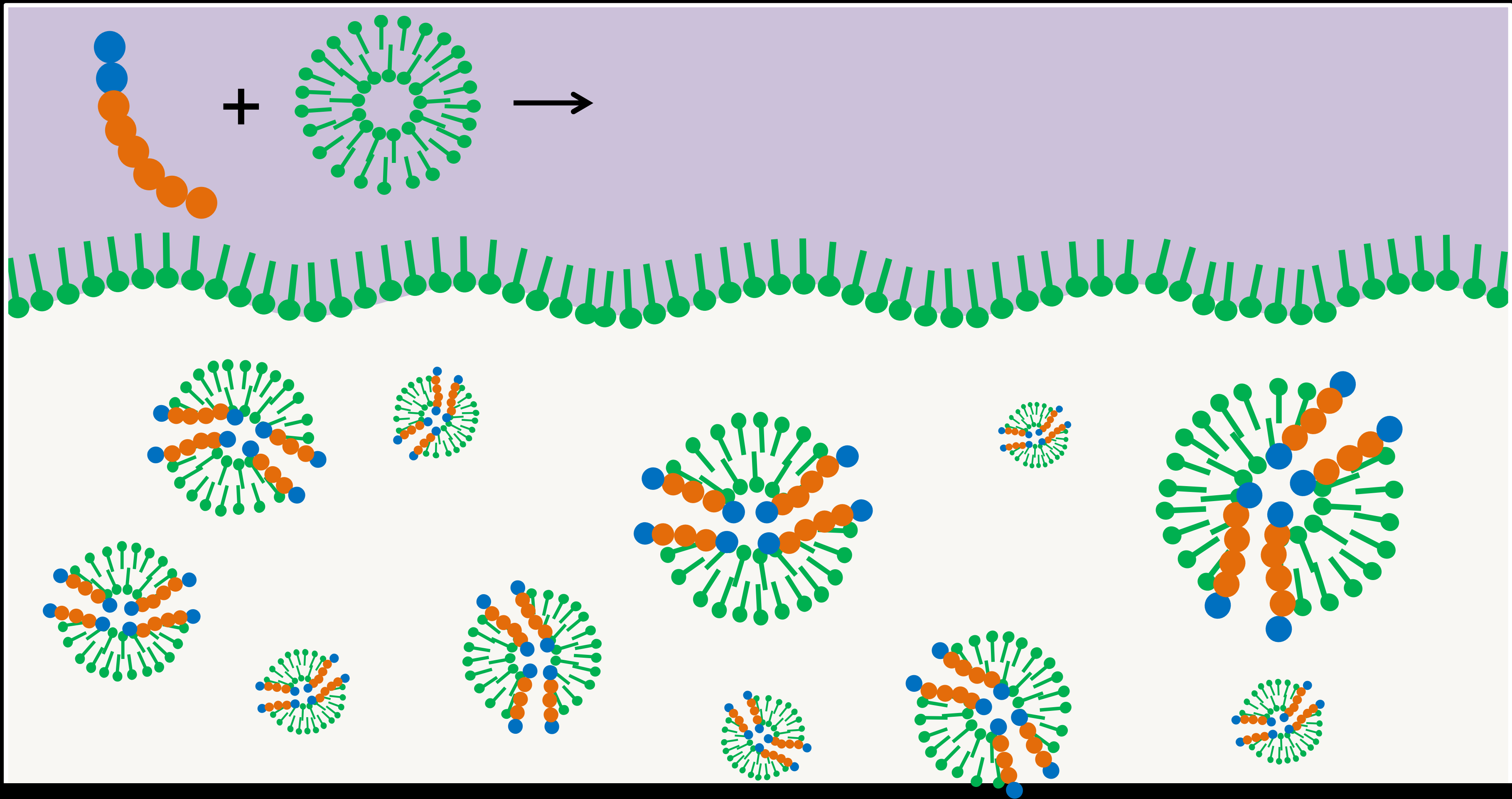
stage of evolution?



„parasitic“ „symbiotic“ functional

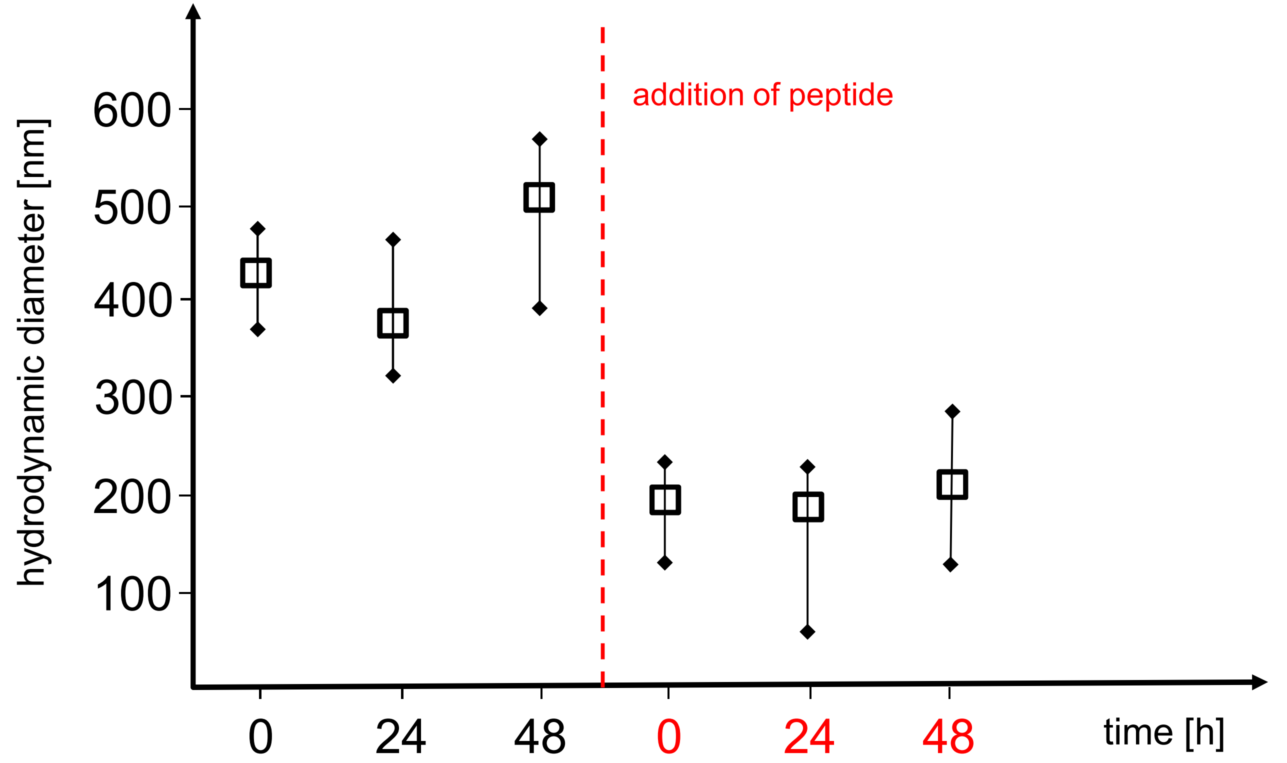
H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

peptide synthesis and artificial re-assembly of vesicles



H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-$COOH$

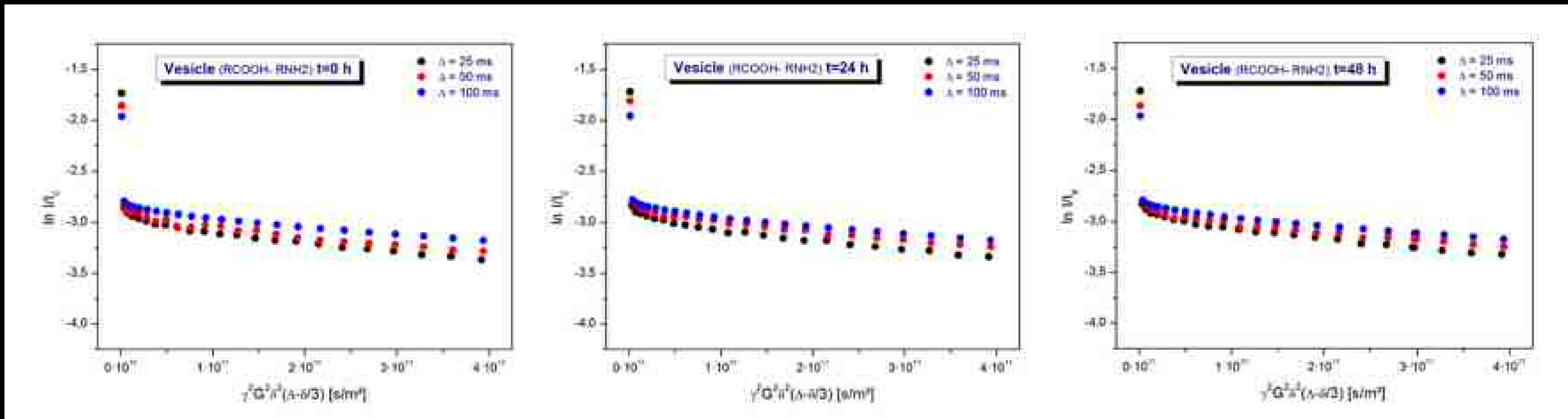
variation of vesicle size



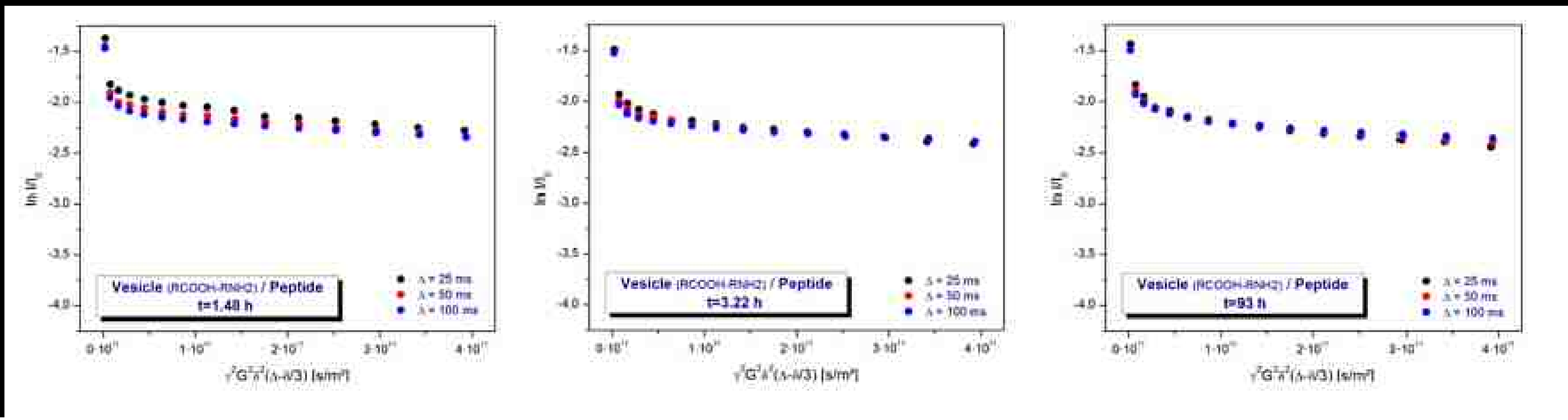
H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

variation of vesicle permeability

a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water



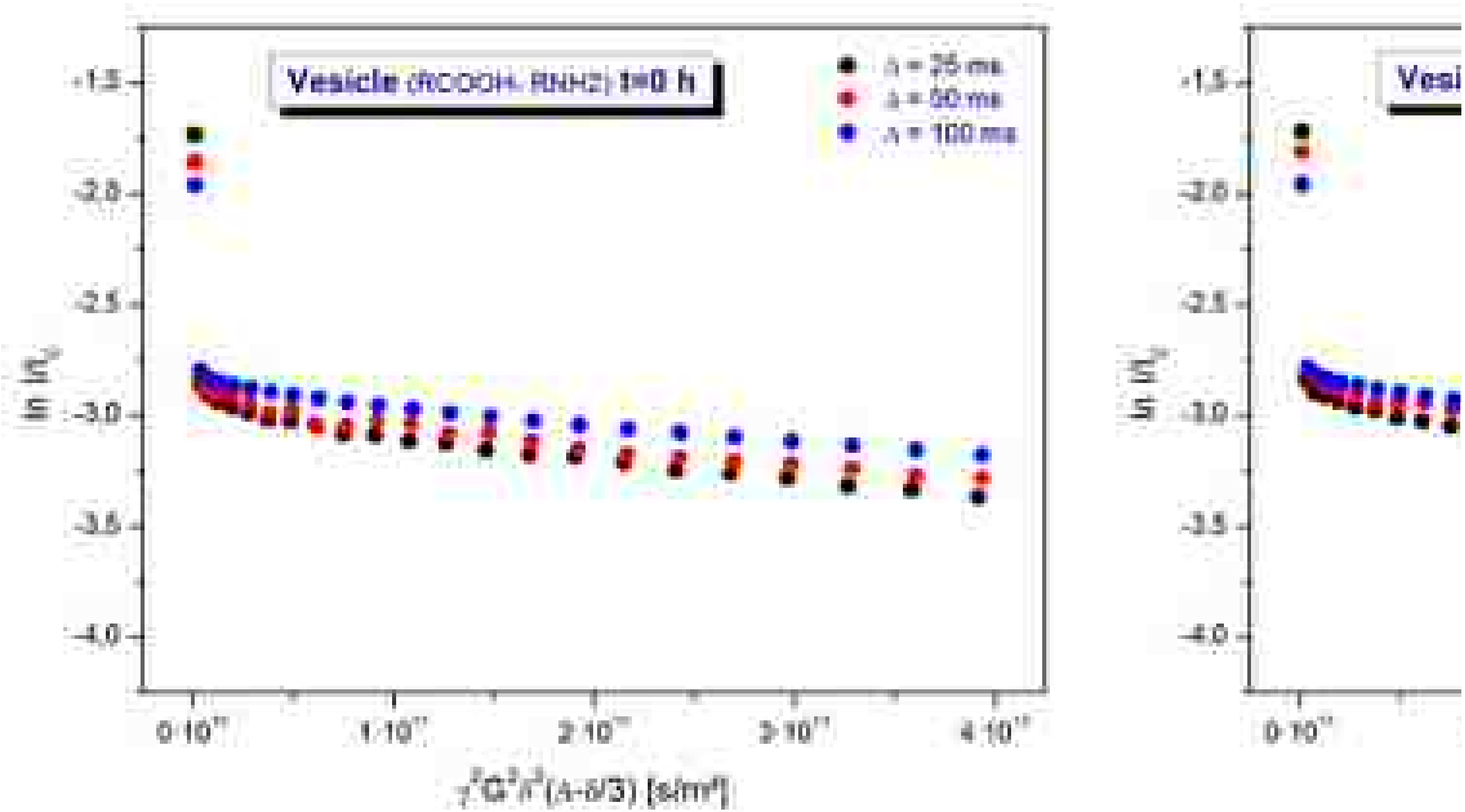
b) Vesicles with H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH (0-93 h)
high permeability for 2 h, then decreasing…



H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

variation of vesicle permeability

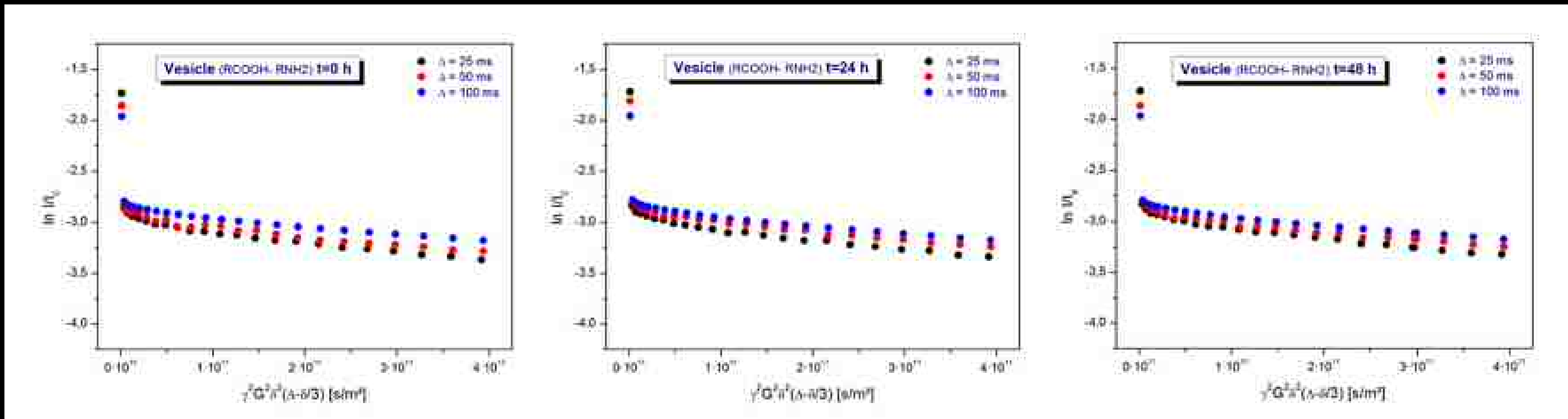
a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water



H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

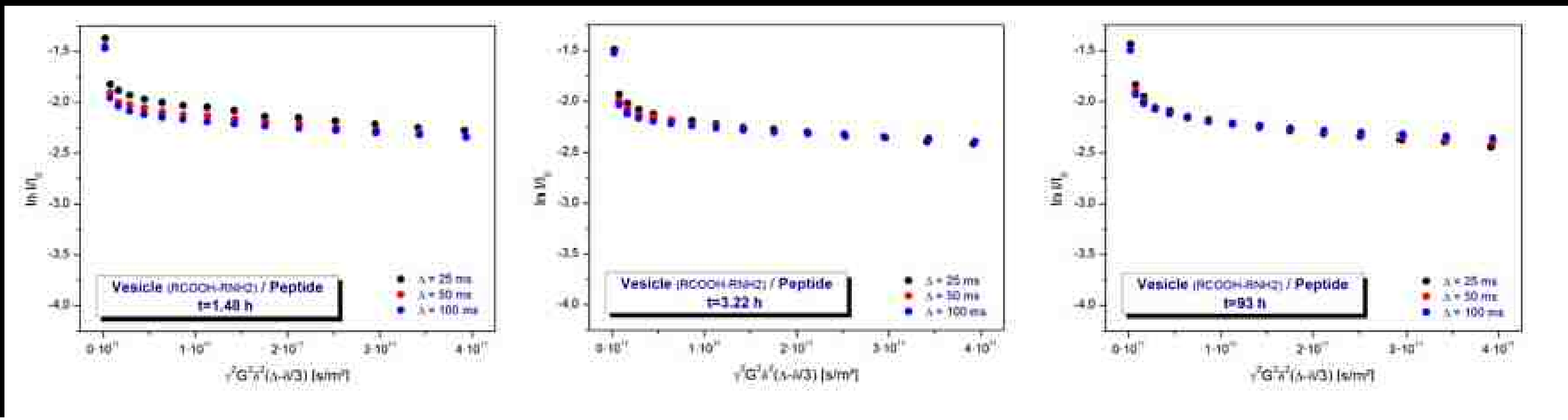
variation of vesicle permeability

a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water



b) Vesicles with H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH (0-93 h)

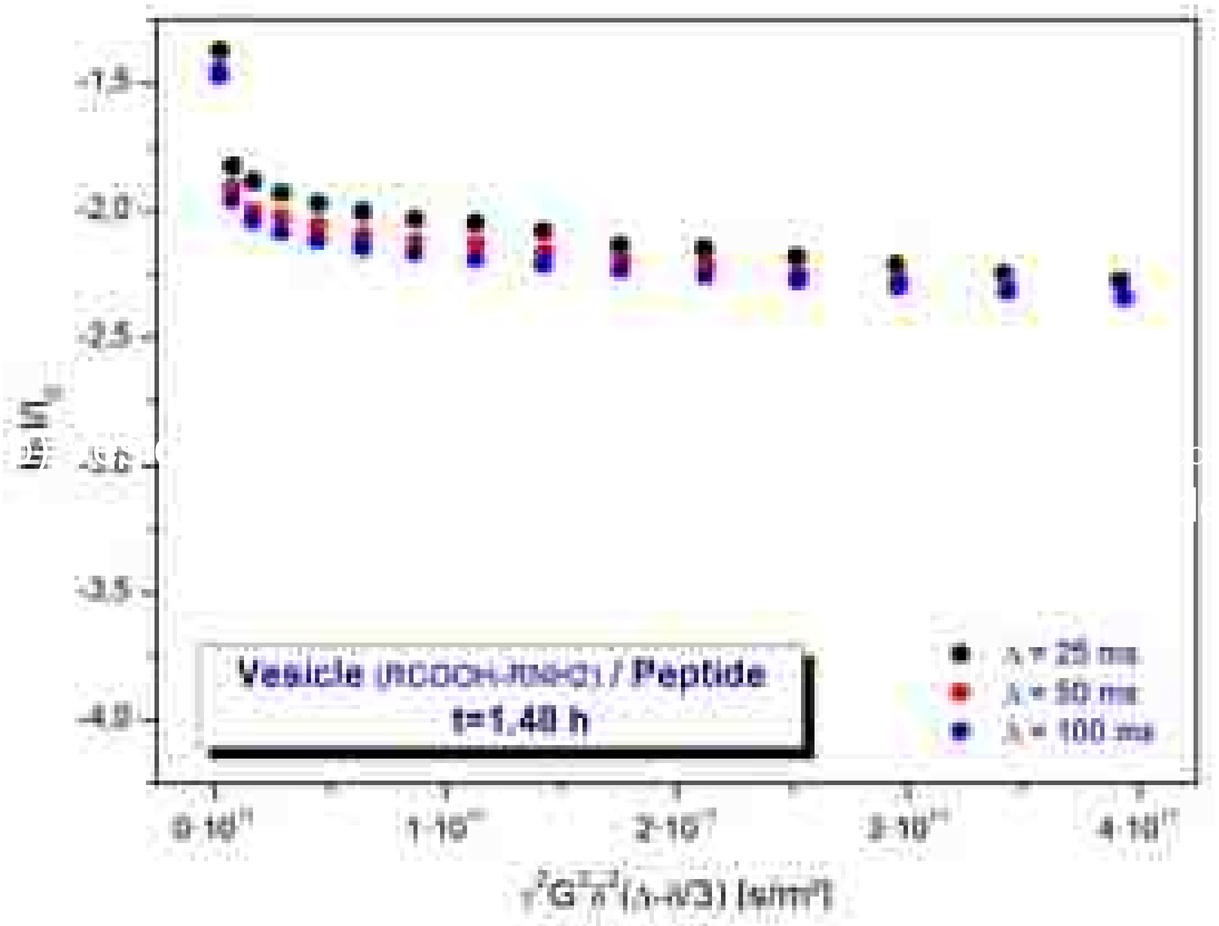
high permeability for 2 h, then decreasing…

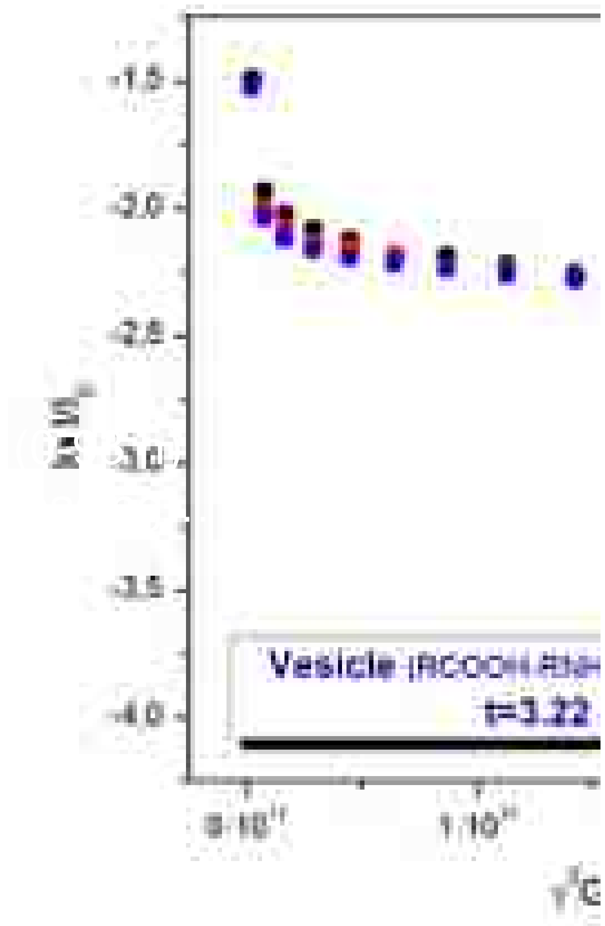


H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

variation of vesicle permeability

a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water

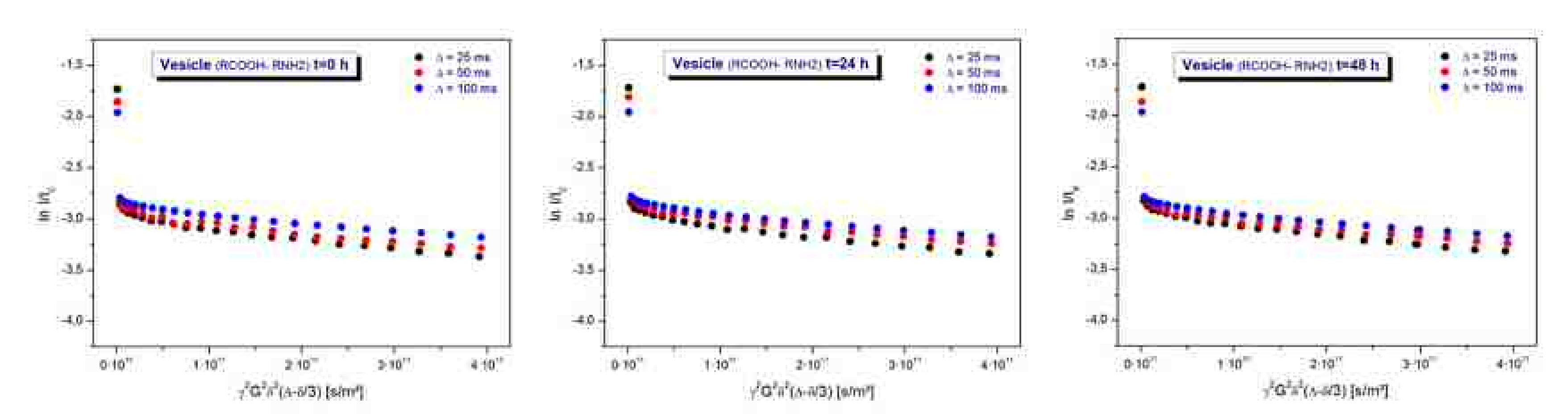




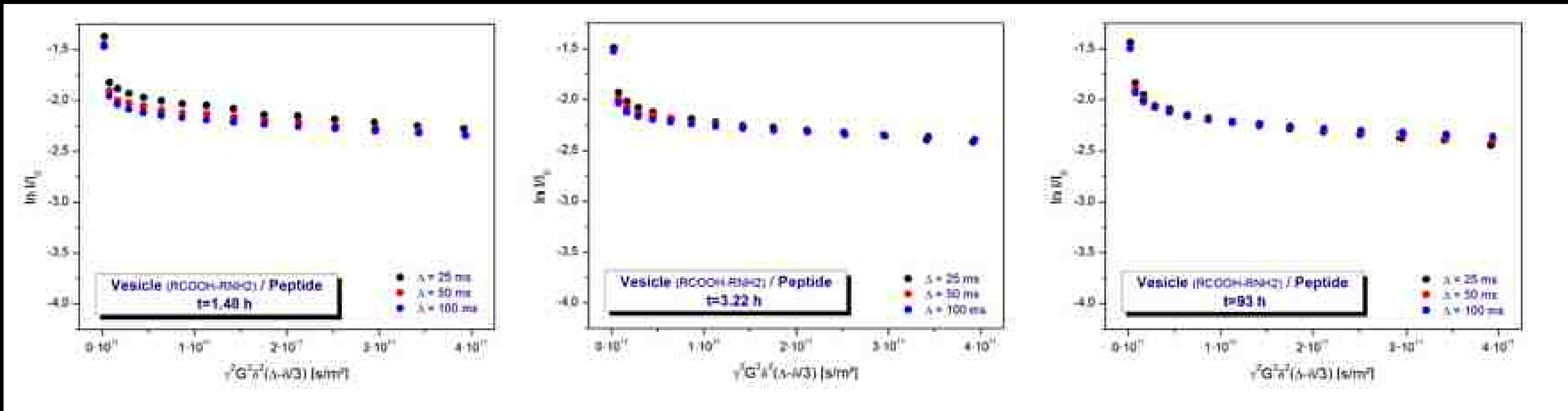
H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

variation of vesicle permeability

a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water



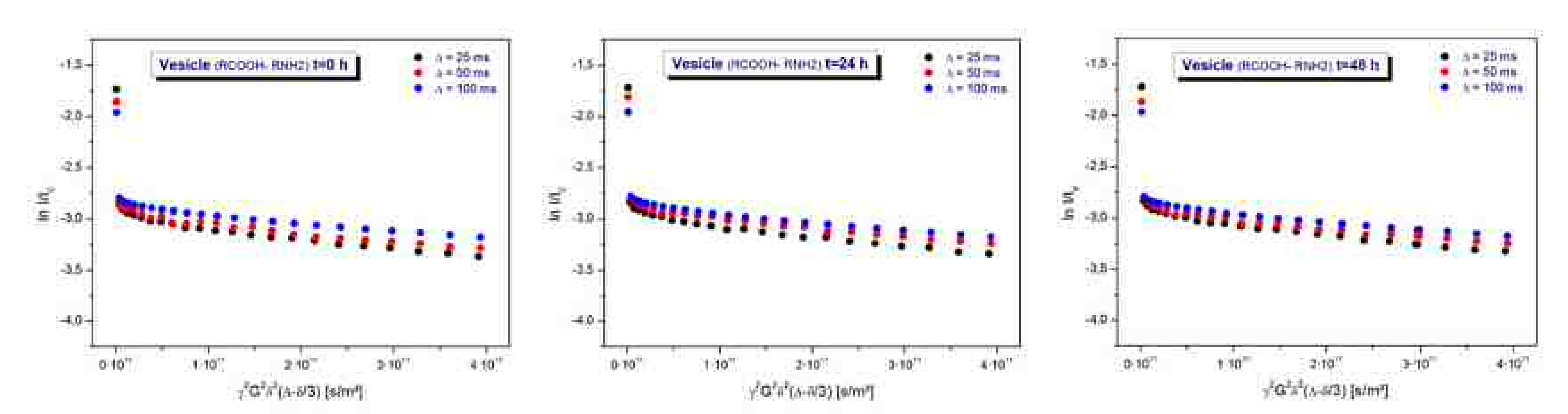
b) Vesicles with H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH (0-93 h)
high permeability for 2 h, then decreasing…



H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

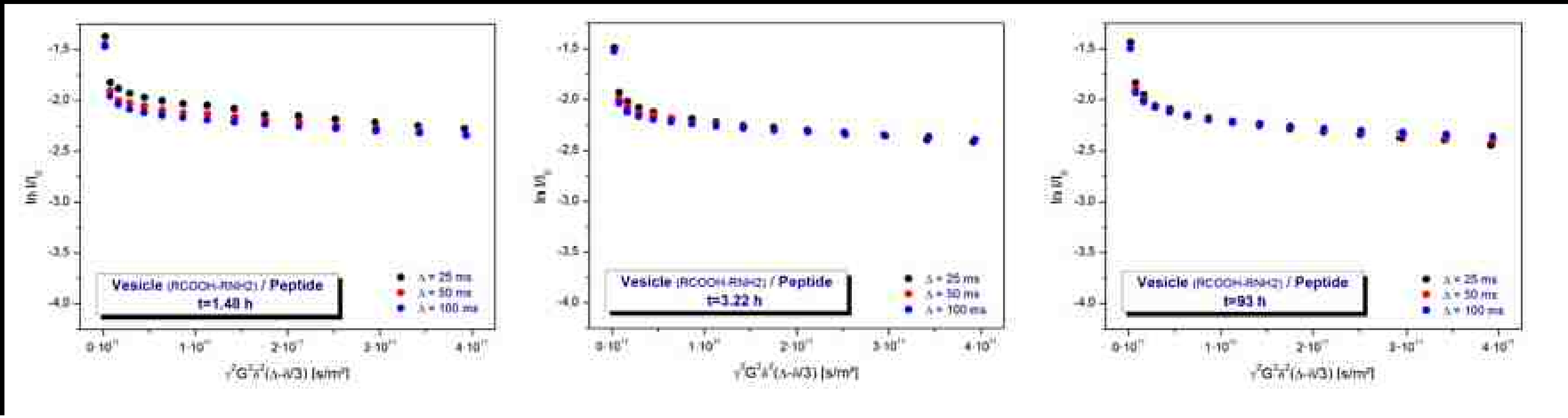
variation of vesicle permeability

a) Reference: Vesicles without peptide (0-48 h): constantly low permeability for water



b) Vesicles with H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH (0-93 h)

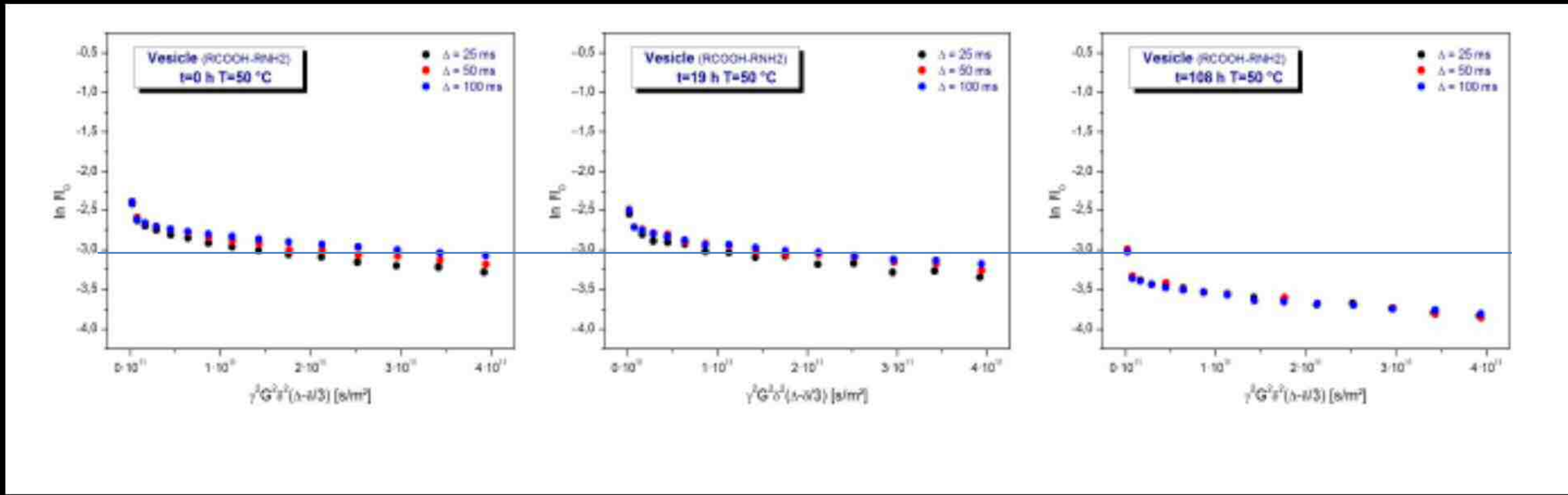
high permeability for 2 h, then decreasing…



H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

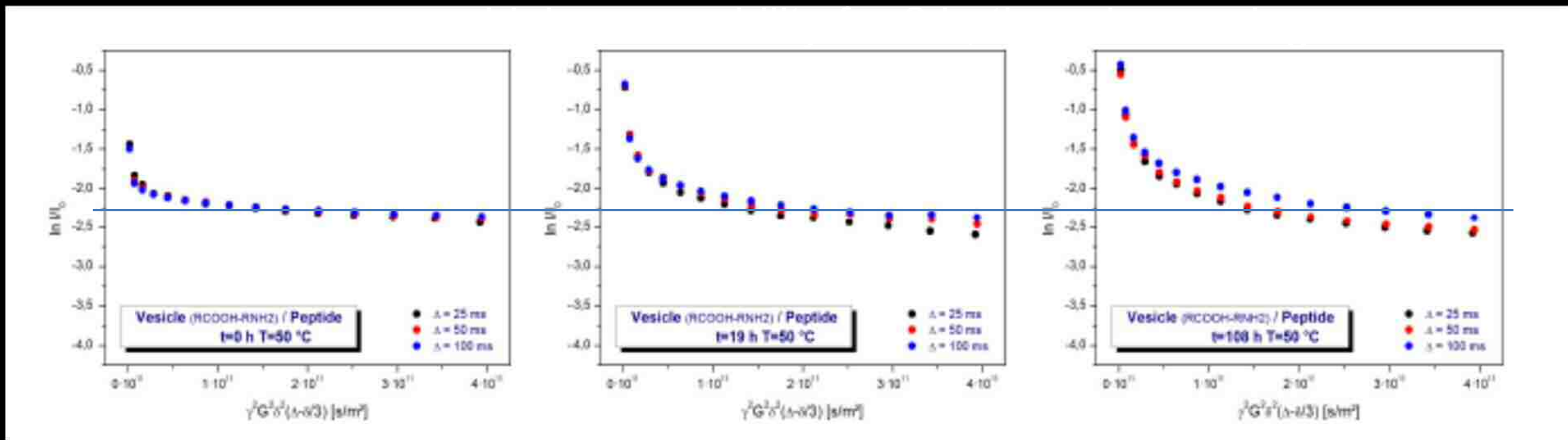
variation of vesicle stability

a) Reference: Vesicles without peptide (0-100 h, 50°C): significant degradation



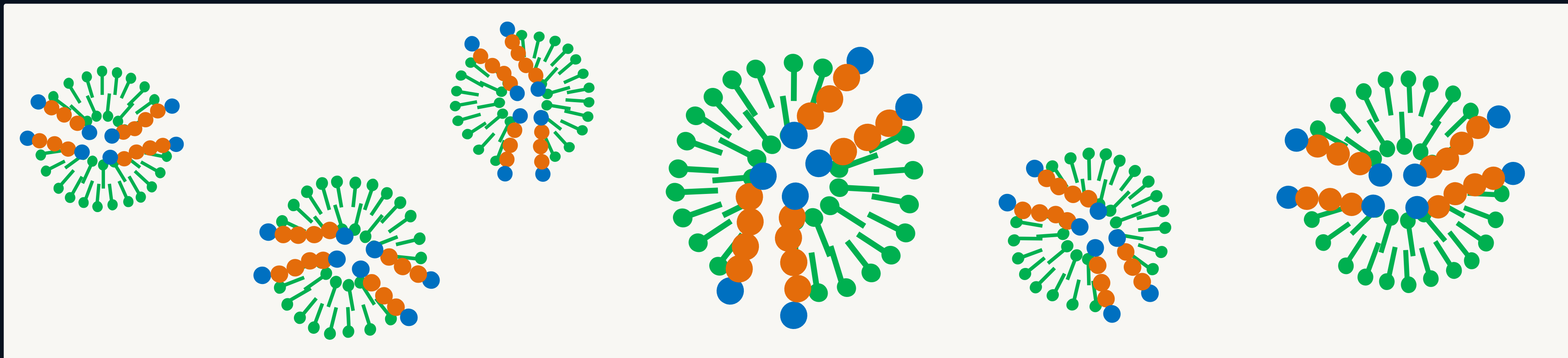
b) Vesicles with H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH (0-100 h)

no detectable degradation



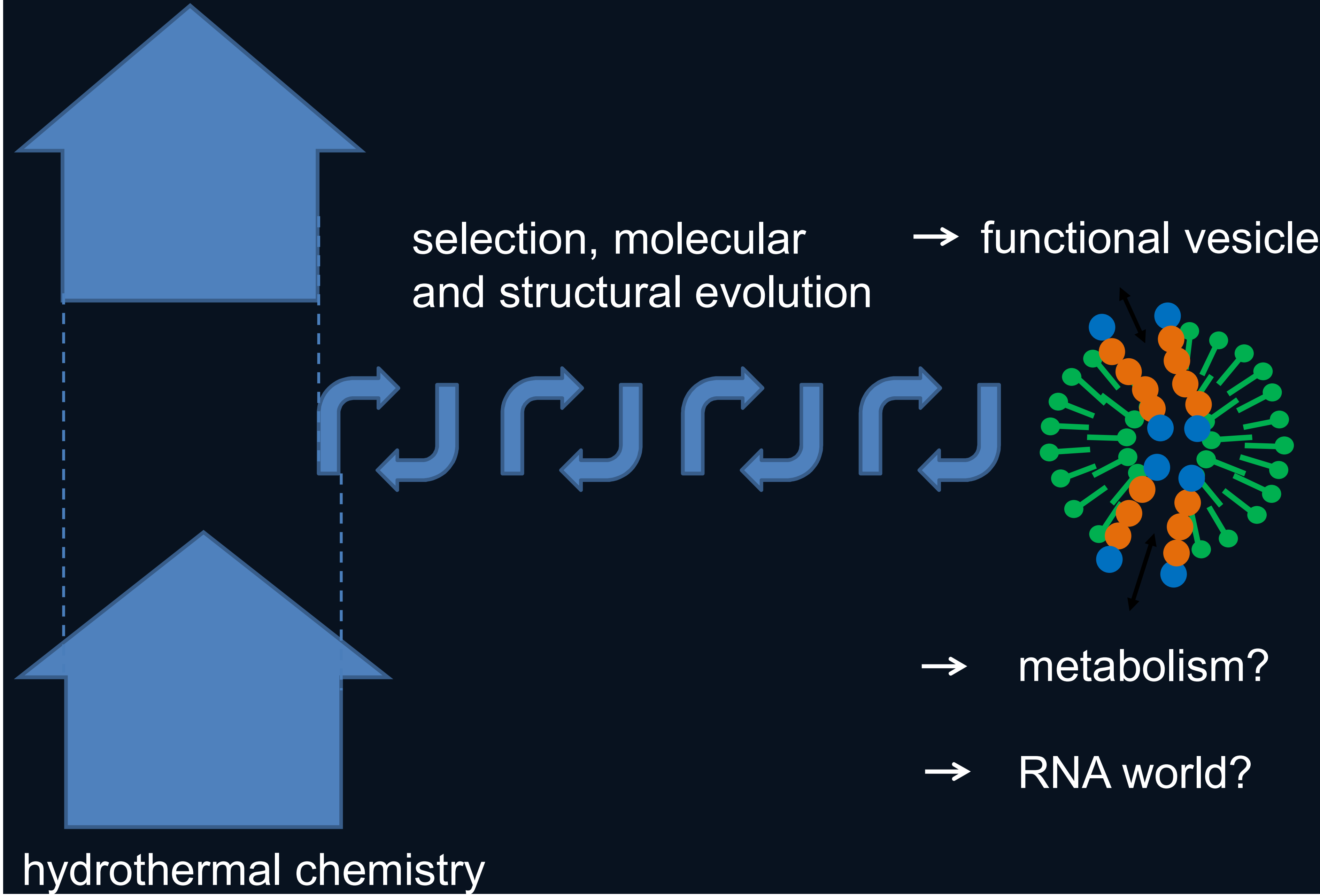
H_2N-Lys-Ser-Pro-Phe-Pro-Phe-Ala-Ala-COOH

overall effect on vesicles

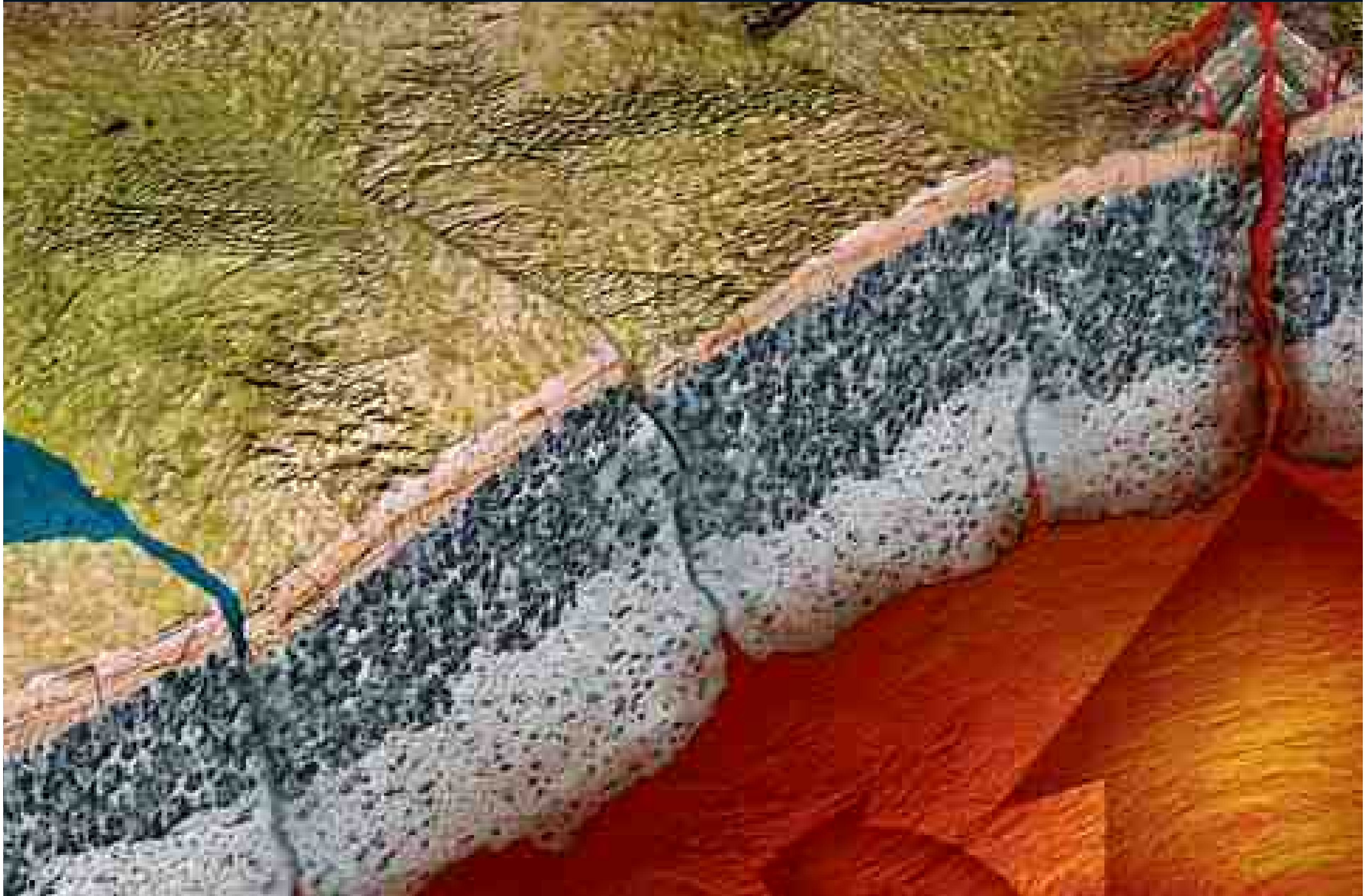


1) The peptide reduces the vesicle size by 50%
2) The peptide increases the vesicle permeability by 100%
3) The peptide increases the vesicle stability (half-life time at 50°C is increased by a factor of five!)

molecular and structural evolution:



tectonic fault zones in the planetary crust



Definitions of life…

…in Physics:

„Life is a system which maintains low entropy by feeding on negative entropy“

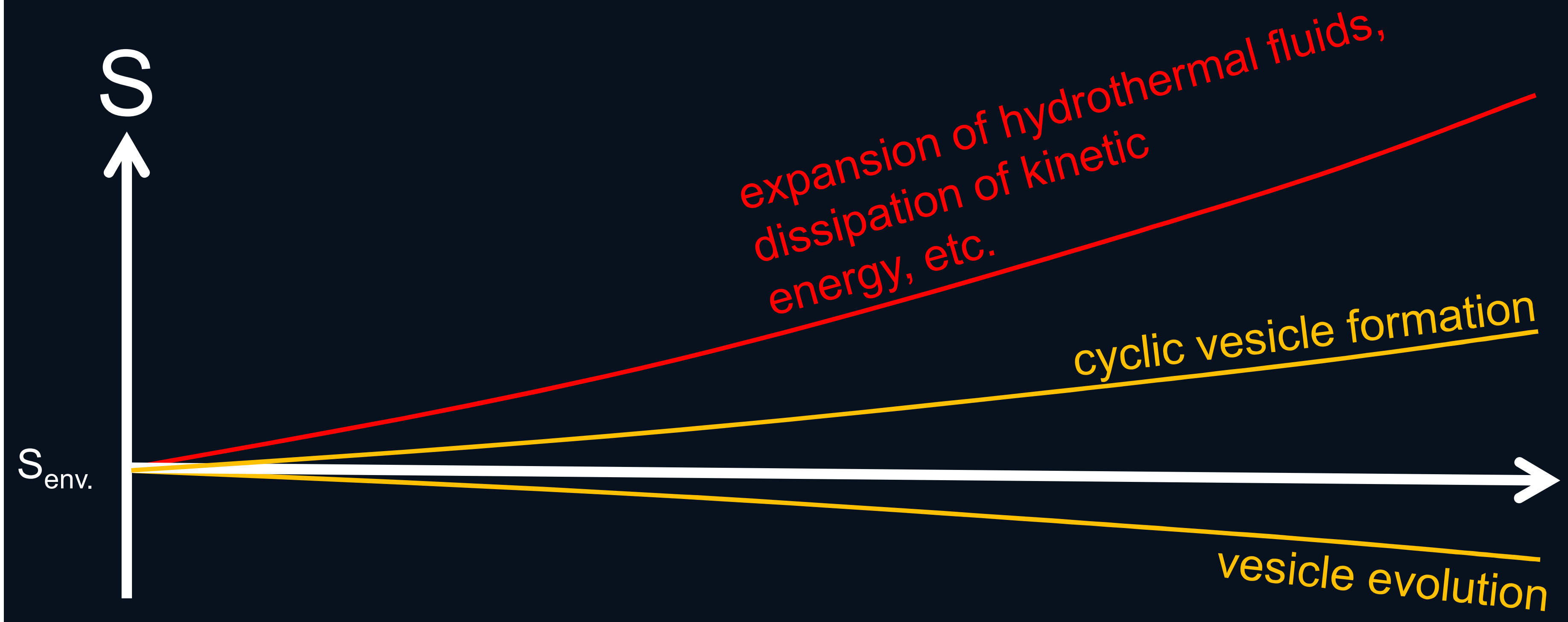
(from „What is Life“
by Erwin Schrödinger)

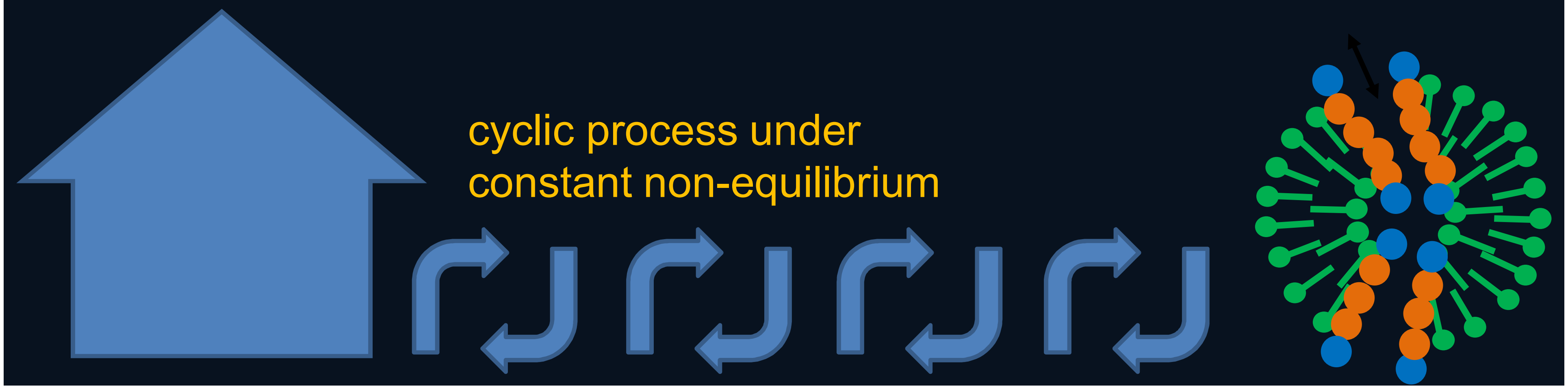
…in Biology:

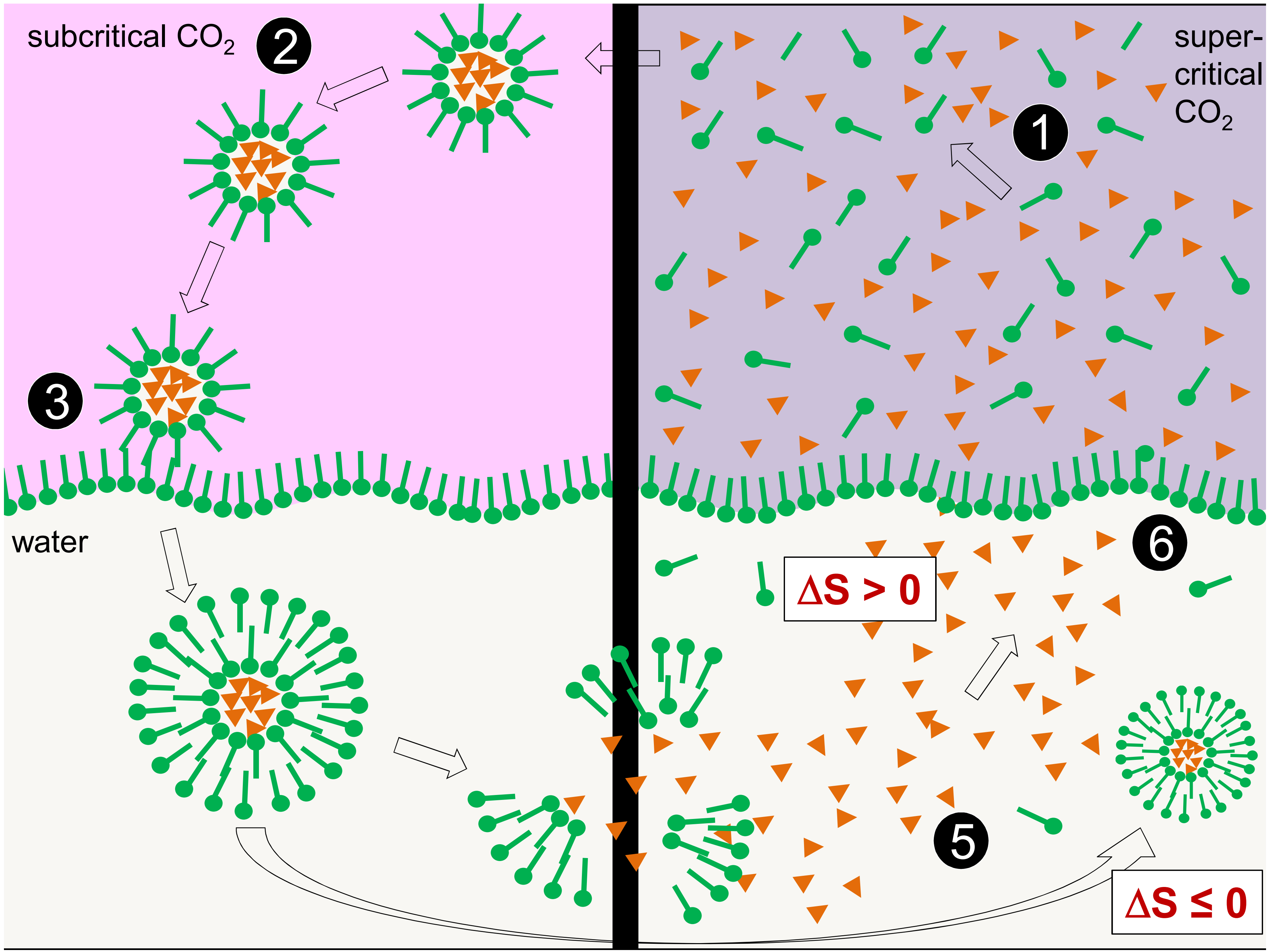
The seven characteristics of life:

1) Homeostasis
2) Organization
3) Metabolism
4) Growth
5) Adaption
6) Stimuli Response
7) Reproduction

entropy changes during evolution

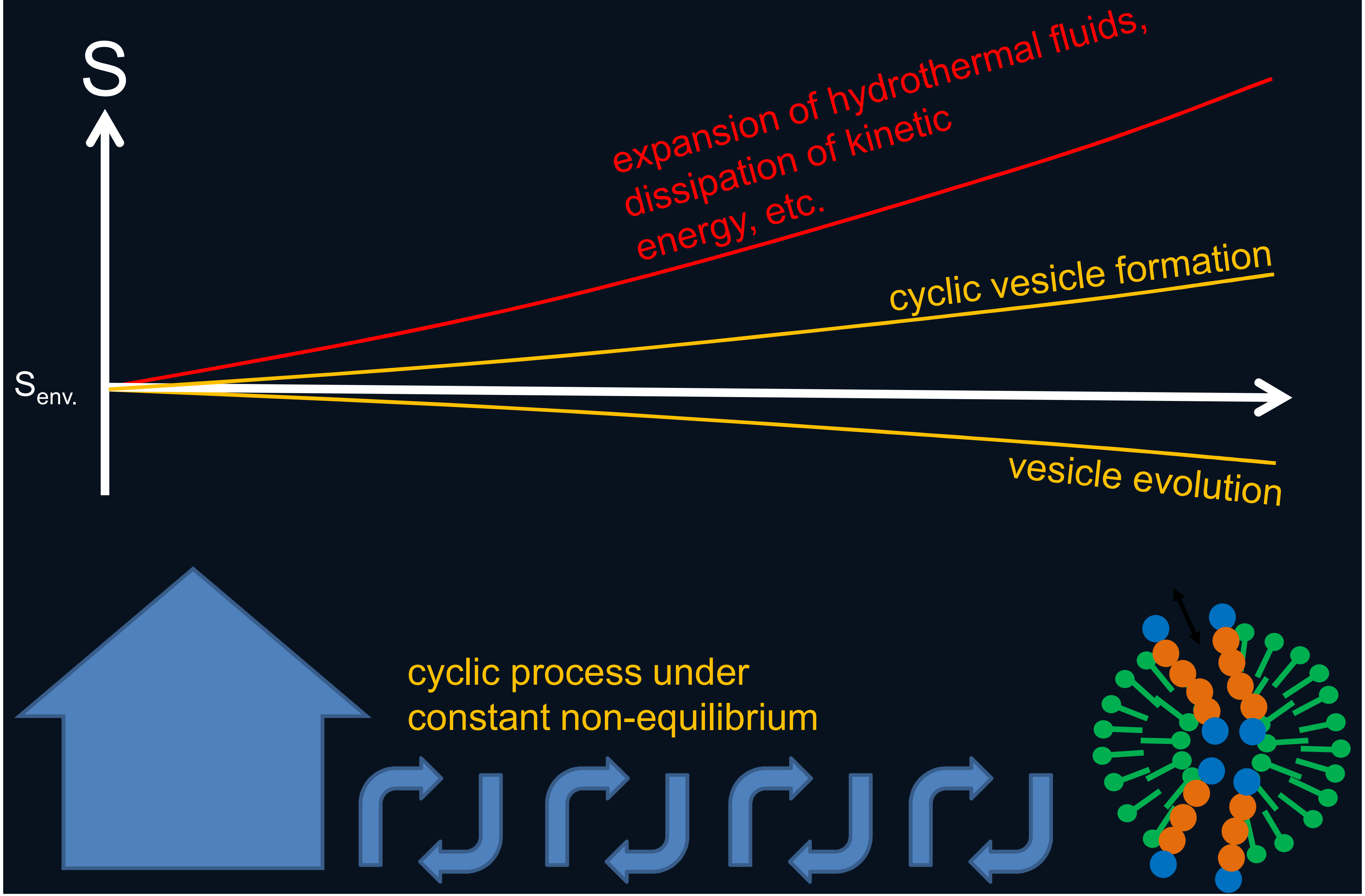


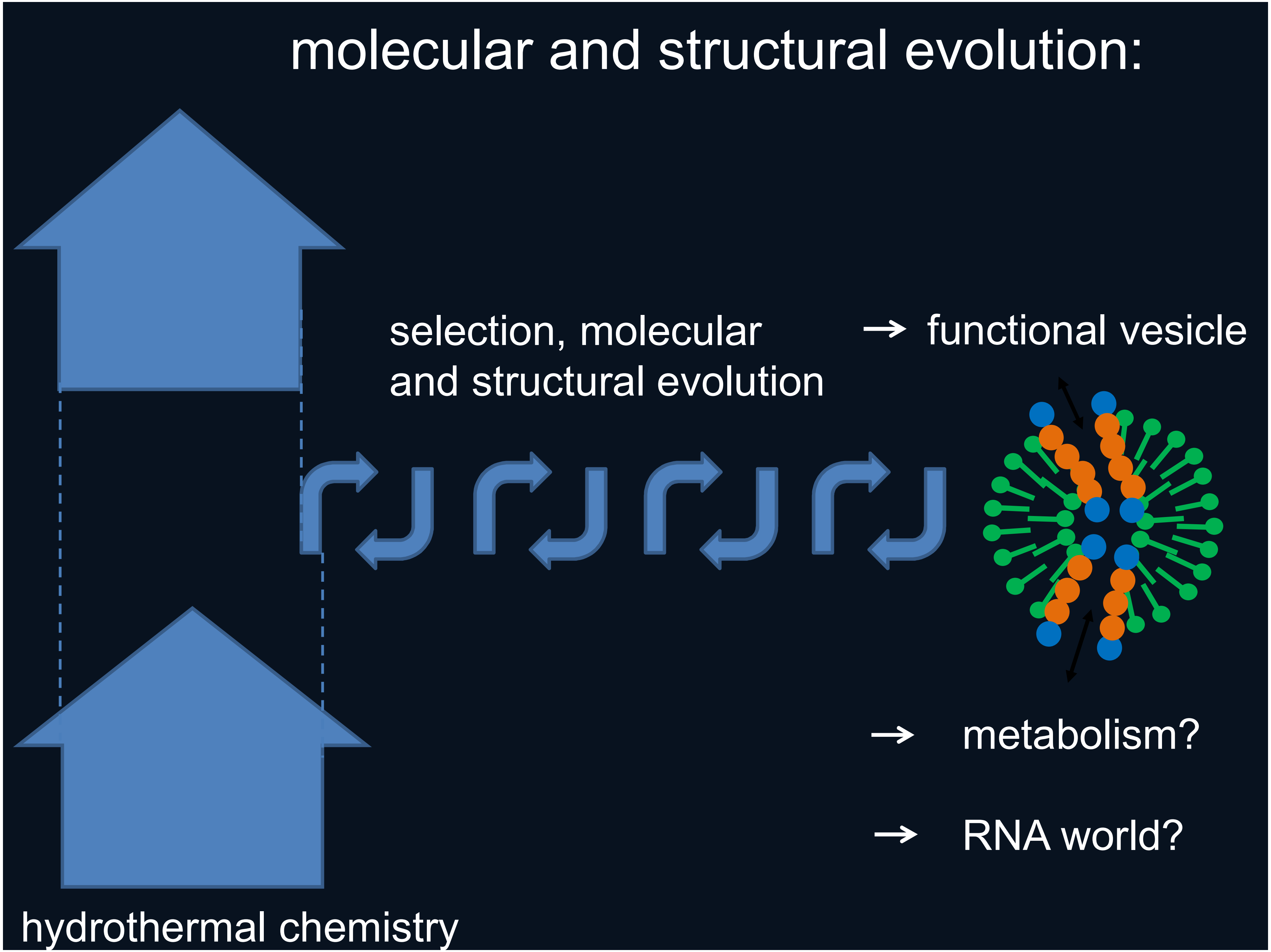




subcritical CO_2
2
super-critical CO_2
1
3
water
6
$\Delta S > 0$
5
$\Delta S \leq 0$

entropy changes during evolution




molecular and structural evolution:
selection, molecular
and structural evolution
→ functional vesicle
→ metabolism?
→ RNA world?
hydrothermal chemistry

Summary 1: Hypothesis

1) Tectonic fault zones are ideal environments for extended and undisturbed molecular evolution
2) Natural pressure variations lead to periodic vesicle formation
3) Amphiphilic peptides are selected and accumulated in vesicle membranes
4) Vesicles and peptides will be optimized for extended lifetime
5) This leads to a structural evolution with three possible targets: parasitic, symbiotic, and functional integration
6) Over extended periods of time, functional vesicles can develop
7) Entropic driving force: the huge entropy increase of expanding media

Summary 2: Experimental Reproduction

1) The vesicle evolution process is artificially reproduced in long-term experiments in a high-pressure cell
2) The peptides selected by vesicles are identified and sequenced
3) The selected peptides will be synthesized in larger quantities
4) The corresponding vesicle-peptide structures will be re-assembled
5) Re-assembled vesicles are characterized by PFG-NMR
   effects of the peptide: -size +permeability +stability

Christian Mayer
Physical Chemistry

Oliver J. Schmitz
Analytical Chemistry

Ulrich Schreiber
Geology

Pia Rosendahl
Amela Bronja

Maria Dávila
post-doc

Frank Keppler
Heinz F. Schöler
Markus Greule
Ines Mulder
Tobias Sattler
Inst. of Earth Sciences, Heidelberg

Summary 1: Hypothesis

1) Tectonic fault zones are ideal environments for extended and undisturbed molecular evolution
2) Natural pressure variations lead to periodic vesicle formation
3) Amphiphilic peptides are selected and accumulated in vesicle membranes
4) Vesicles and peptides will be optimized for extended lifetime
5) This leads to a structural evolution with three possible targets: parasitic, symbiotic, and functional integration
6) Over extended periods of time, functional vesicles can develop
7) Entropic driving force: the huge entropy increase of expanding media

Summary 2: Experimental Reproduction

1) The vesicle evolution process is artificially reproduced in long-term experiments in a high-pressure cell
2) The peptides selected by vesicles are identified and sequenced
3) The selected peptides will be synthesized in larger quantities
4) The corresponding vesicle-peptide structures will be re-assembled
5) Re-assembled vesicles are characterized by PFG-NMR
   effects of the peptide: -size +permeability +stability