BELBaR
at ClayTech
WP2, WP4

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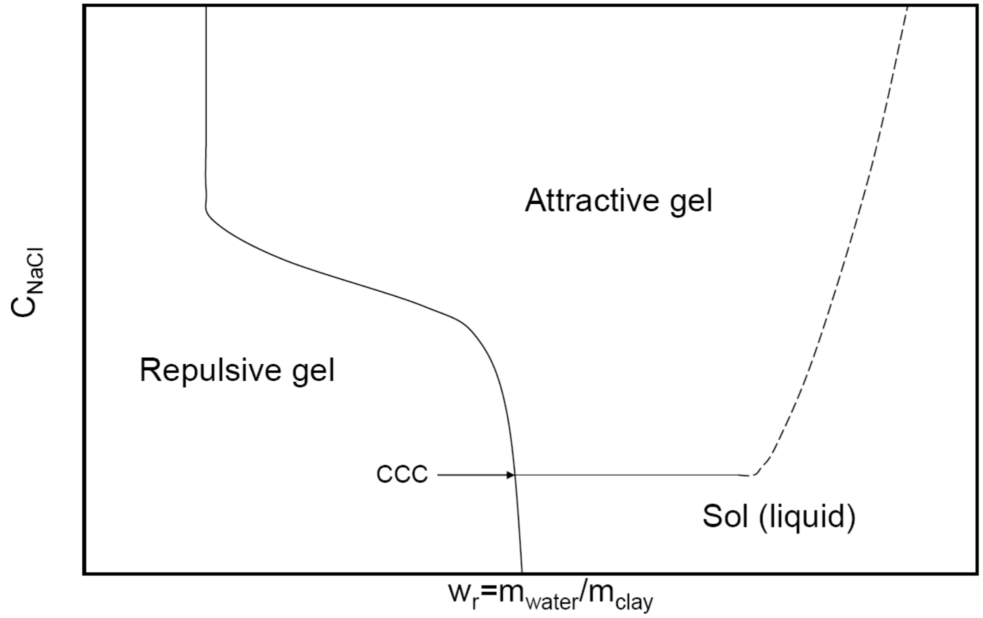
CLAY TECHNOLOGY AB

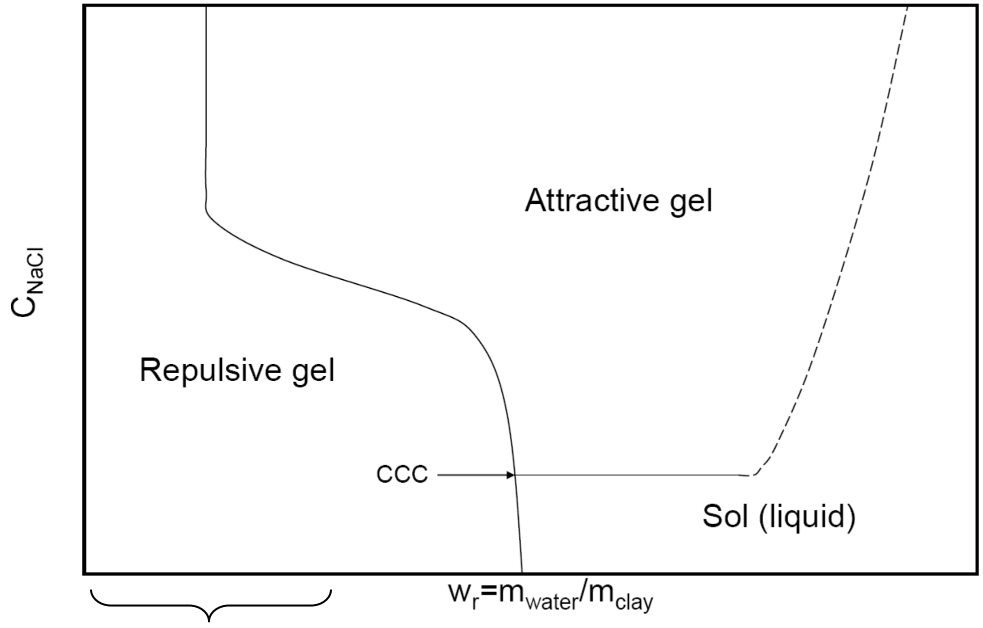
BELBaR Start-up Meeting
Lund, March 7-8 2012

SKB

Phase diagram Na-montmorillonite



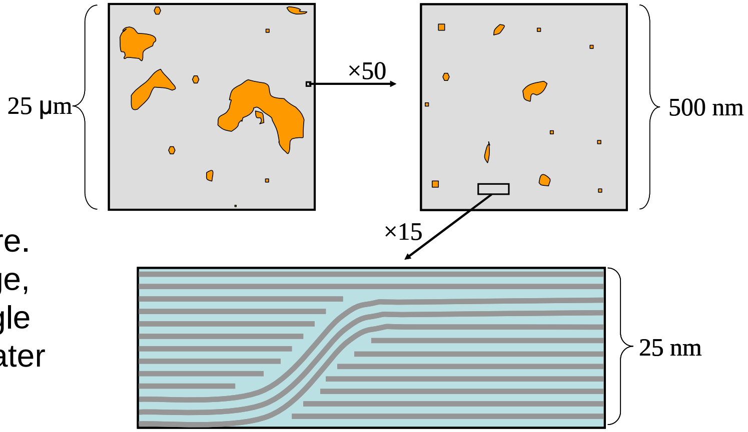
Phase diagram Na-montmorillonite



Dense system
Buffer conditions

Properties at buffer density are well understood

- Swelling pressure/salt effects
  - Karnland, Muurinen, Karlsson in Adv. Understanding Clay Barriers (Eds. Alosno, Ledesma) (2005).
- Freezing
  - Birgersson, Karnland, Nilsson, Phys. Chem Earth 33, S527-S530 (2008).
- Gas
  - Birgersson, Åkesson, Hökmark, Phys. Chem Earth 33, S248-S251 (2008).
- Ion-equilibrium/diffusion/selectivities
  - Birgersson, Karnland, Geochim. Cosmochim. Acta 73, 1908-1923 (2009).
  - Hedström, Karnland, Geochim. Cosmochim. Acta 77, 266-274 (2012).
  - Hedström, Karnland, Phys. Chem Earth 36, 1559-1563 (2011).



Schematic illustration of bentonite structure. Accessory minerals are indicated in orange, hydrated montmorillonite in light gray, single montmorillonite layers in dark gray and water in blue.

Erosion and sol formation less well understood

- SKB Technical report TR-09-34
- Phys. Chem. Earth 36 (2011)
  - 1554-1558, 1559-1563, 1564-1571, 1572-1579
- Two manuscripts in preparation

Clay used in experiments

- Bentonite
  - MX-80, Deponit CA-N, Asha (505)
- Montmorillonite (<2 µm, <0.5 µm) Homo-ionic
  - Wyoming (Wy), e.g. Wy-Na
  - Milos (Mi)
  - Kutch (Ku)
- Mixed montmorillonite Ca/Na
  - Wy-80/20 means mixed clay prepared from 80% Wy-Ca and 20% Wy-Na by mass

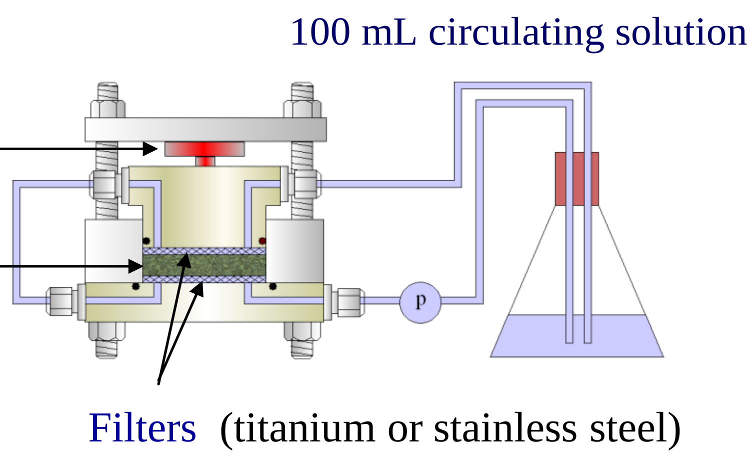
Physical properties of the investigated montmorillonites

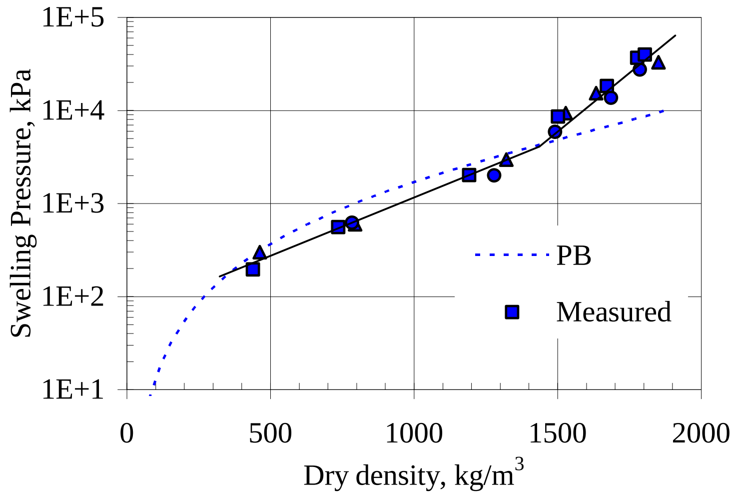
	Wy-Na1	Wy-Na2	Mi-Na1	Mi-Na2	Ku-39-Na
CEC [eq/kg]	0.87	0.88	0.97	1.09	1.04
σ [C/m^2]	-0.11(1)	-0.11(1)	-0.12(3)	-0.14(0)	-0.13(5)
Tetr. Charge [e]	-0.11	-0.05	-0.15	-0.27	-0.38
Octa. Charge [e]	-0.54	-0.60	-0.57	-0.55	-0.42
Total Charge [e]	-0.65	-0.65	-0.72	-0.82	-0.79

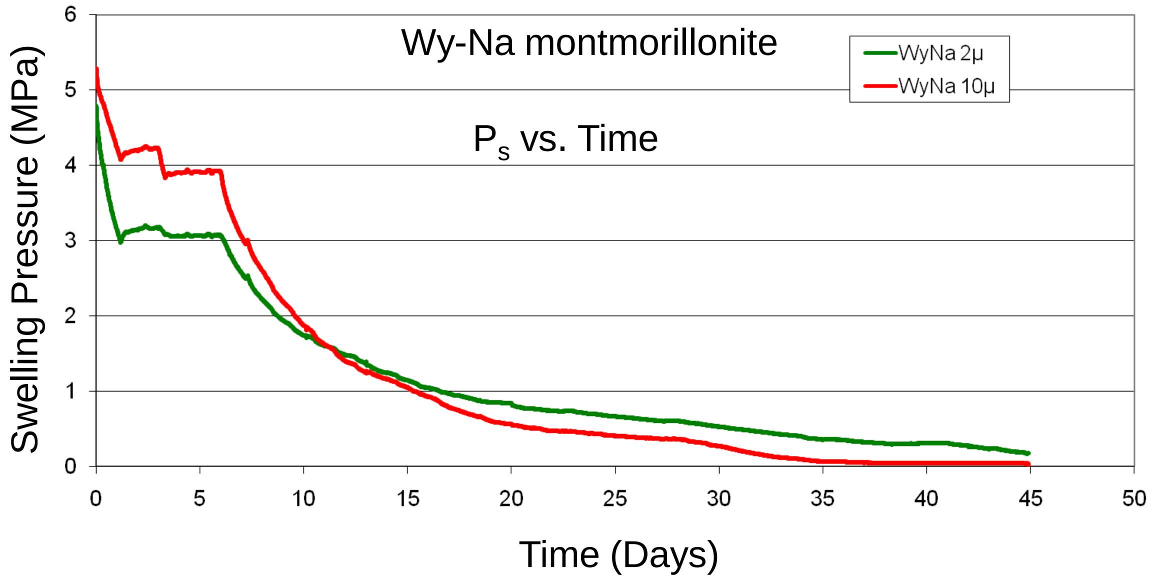
$$\sigma = \frac{q}{a \cdot b}$$

Wyoming MX-80
Milos Deponit CA-N
Kutch Asha-505

The problem of erosion due to sol formation



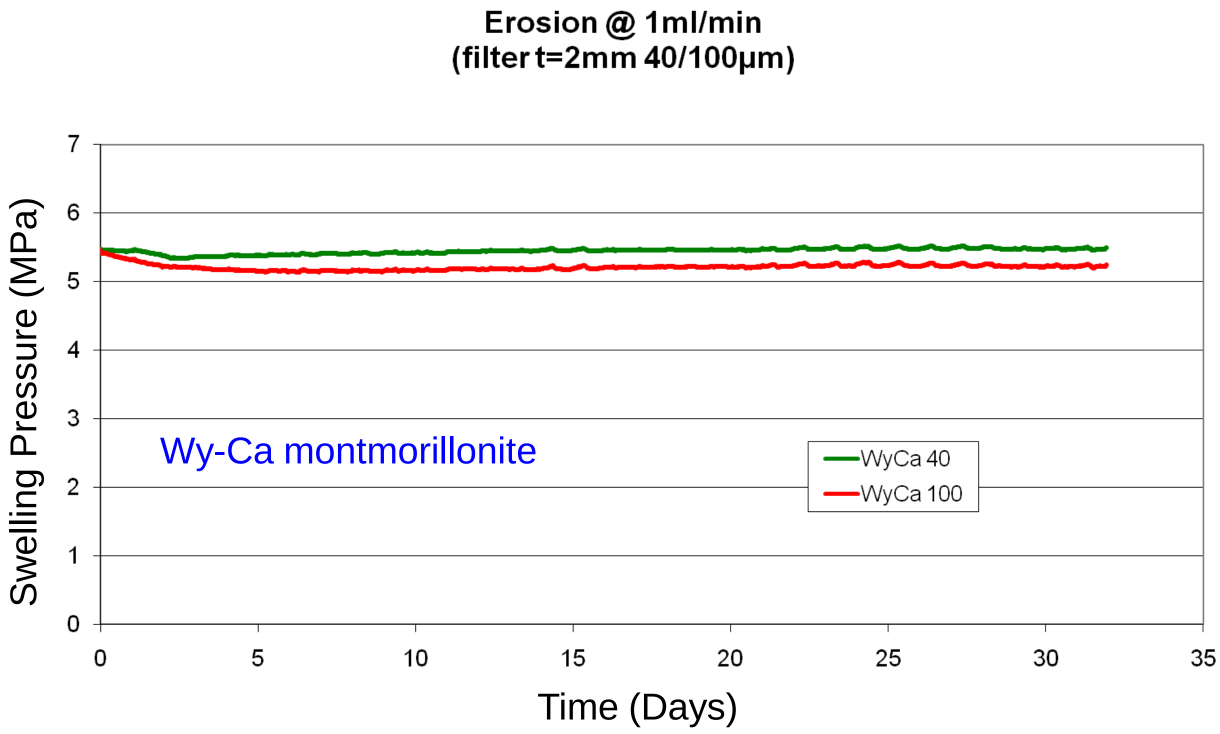




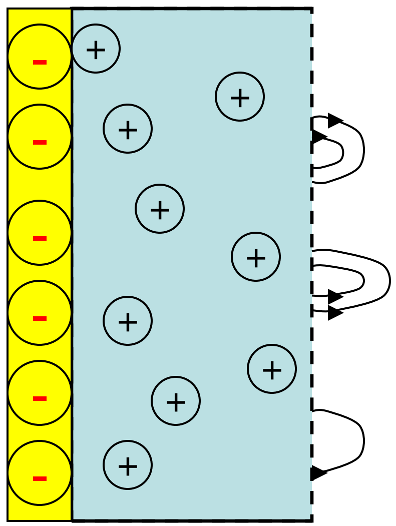
Sodium montmorillonite disperses easily

Filter pore size of 2 µm not enough to hinder erosion

No erosion with Ca-montmorillonite



Ion correlation important for divalent counterions



Cartoon adapted from Evans & Wennerström

No loss of Ca-montmorillonite even when pore size = 100µm

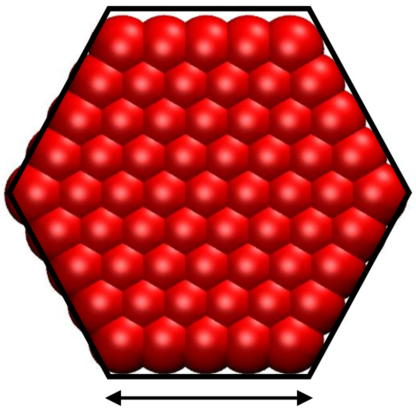
Ca-montmorillonite is not sol forming

MD simulation of Na- and Ca- ”montmorillonite”

Surface charge -100 Å^2/e
$(Si_8)(Al_3Mg)O_{20}(OH)_4$

Each O_{20} unit cell represented by a sphere of diameter ~9 Å

Hexagonal clay platelet 61 spheres



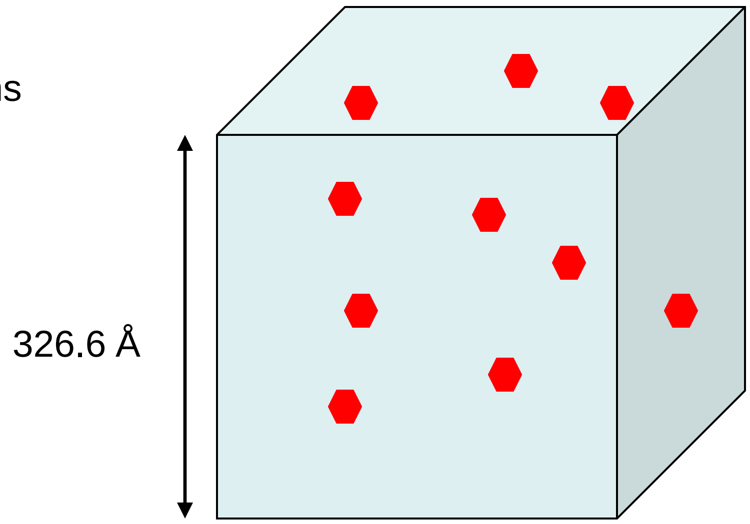
Coarse-grained description

Area about 15-20 times smaller than laponite
and 800 times smaller than montmorillonite

Counterions

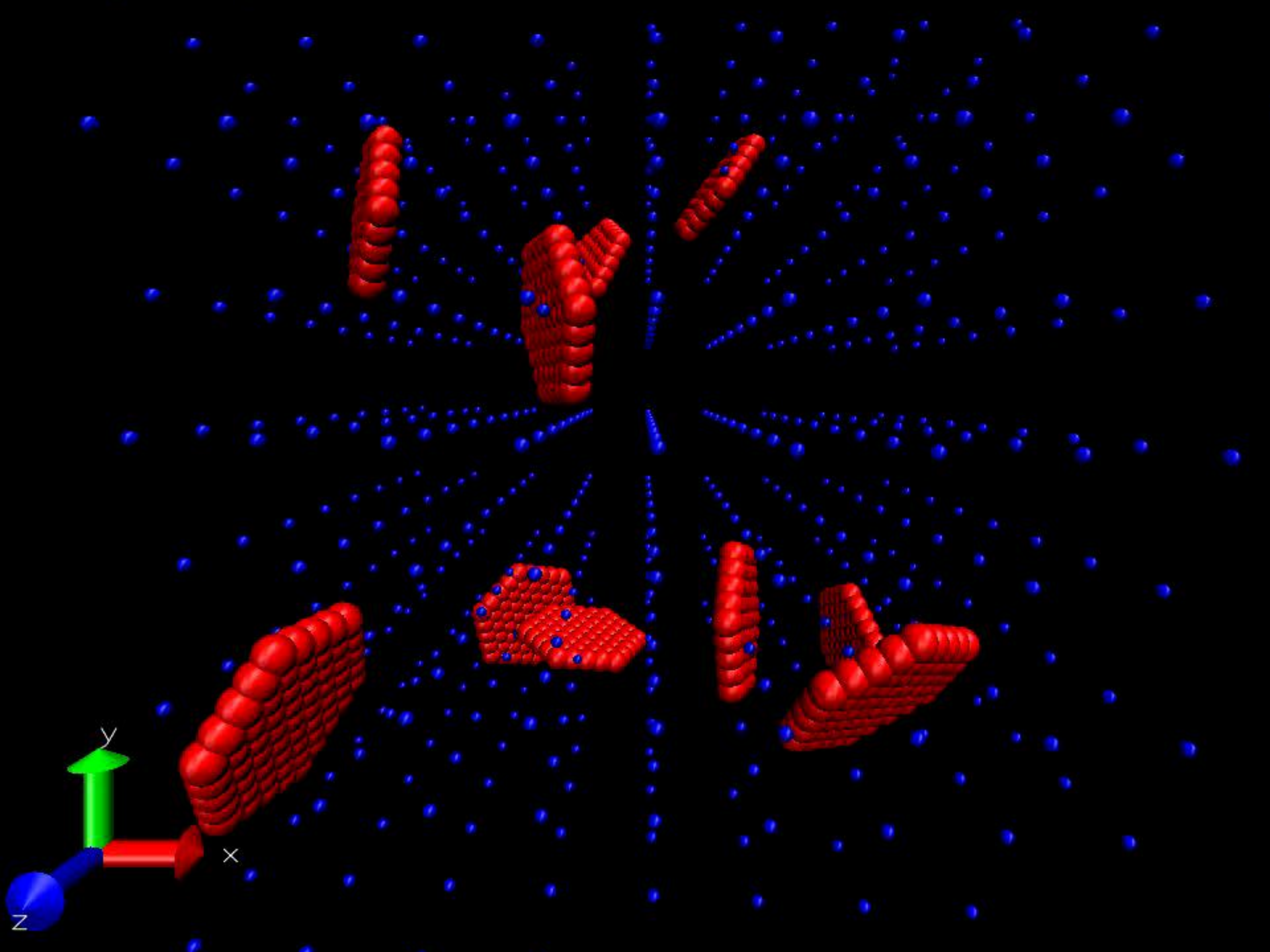
● Na^+

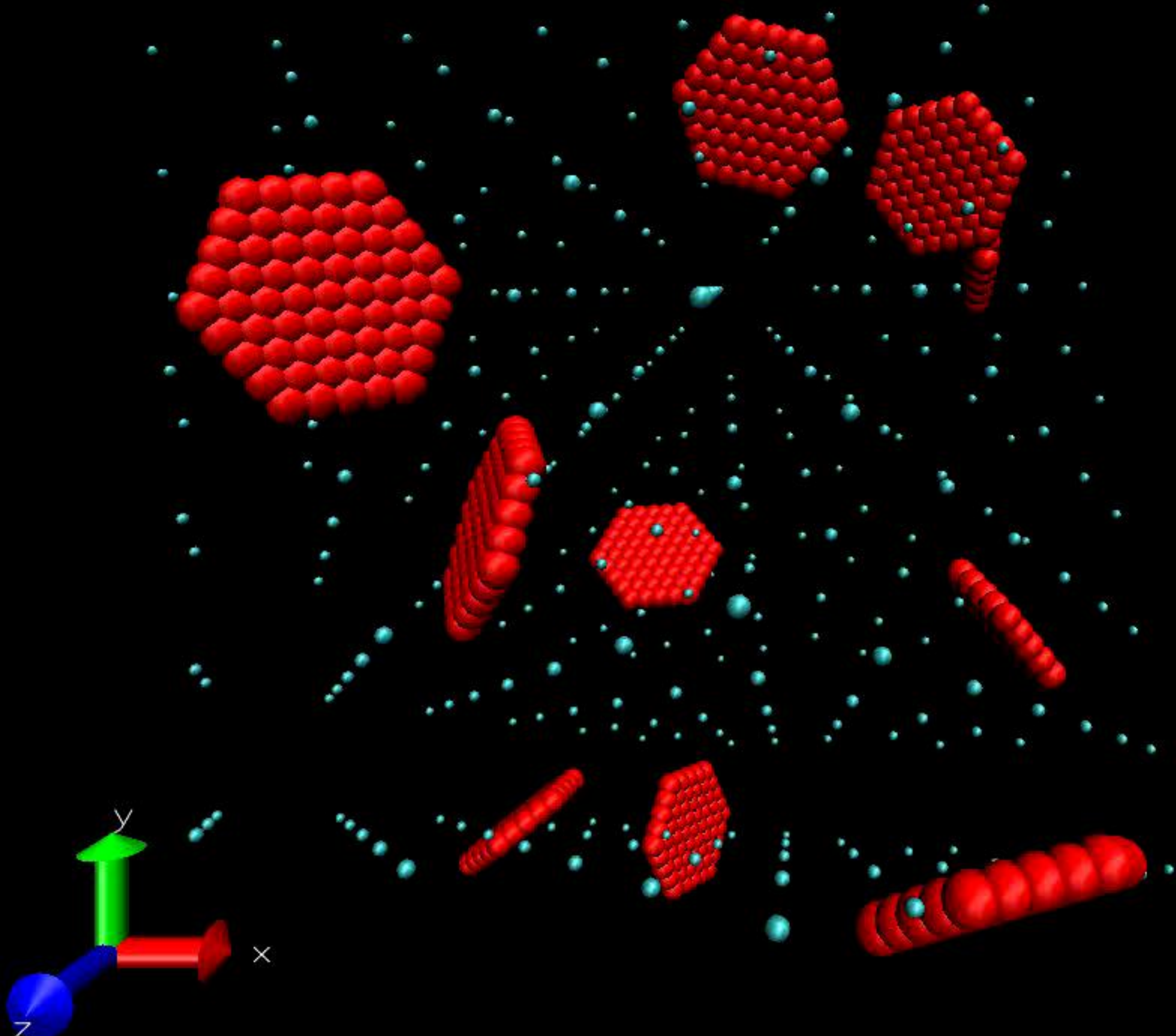
● Ca^{2+}



10 clay particles
10*61/Z counterions
Z=1 or 2

Volume fraction ϕ = 0.008

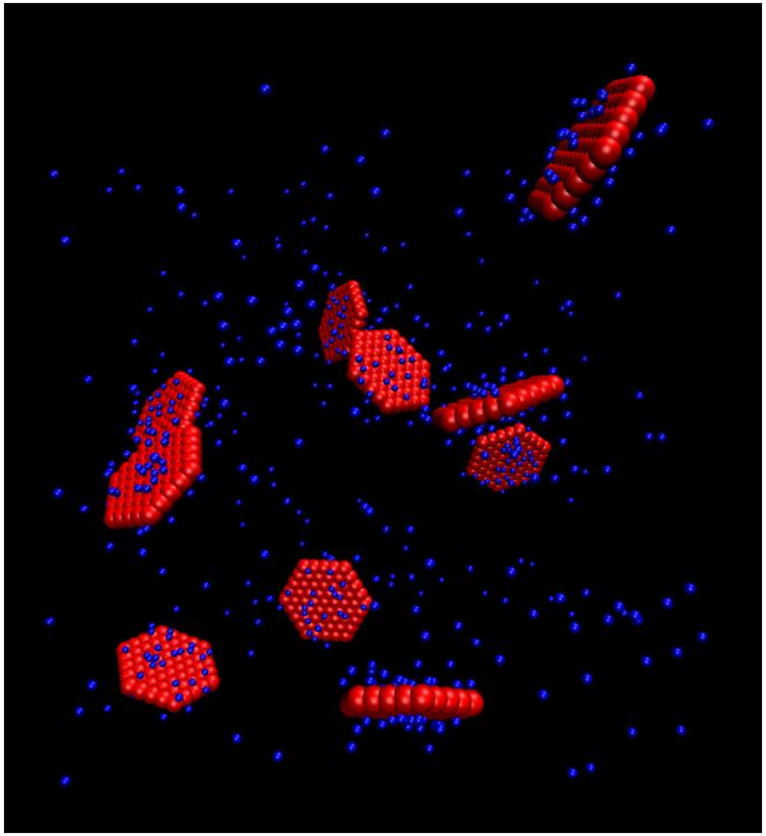

y
x
z



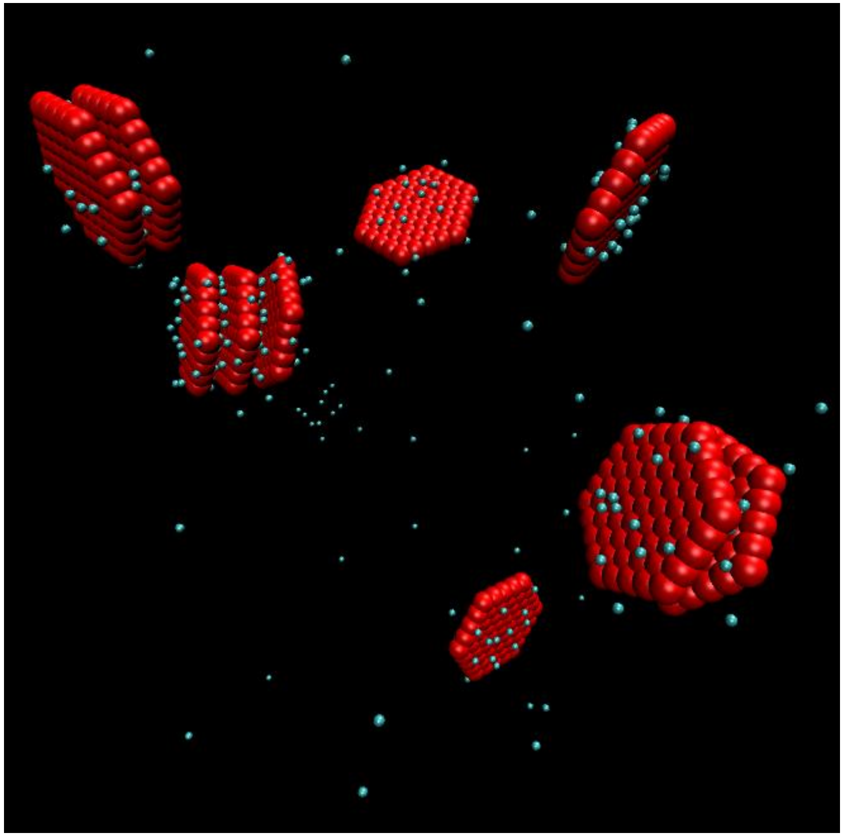
y
x
z

Snapshot at the end of simulation

Na-mmt (sol phase)



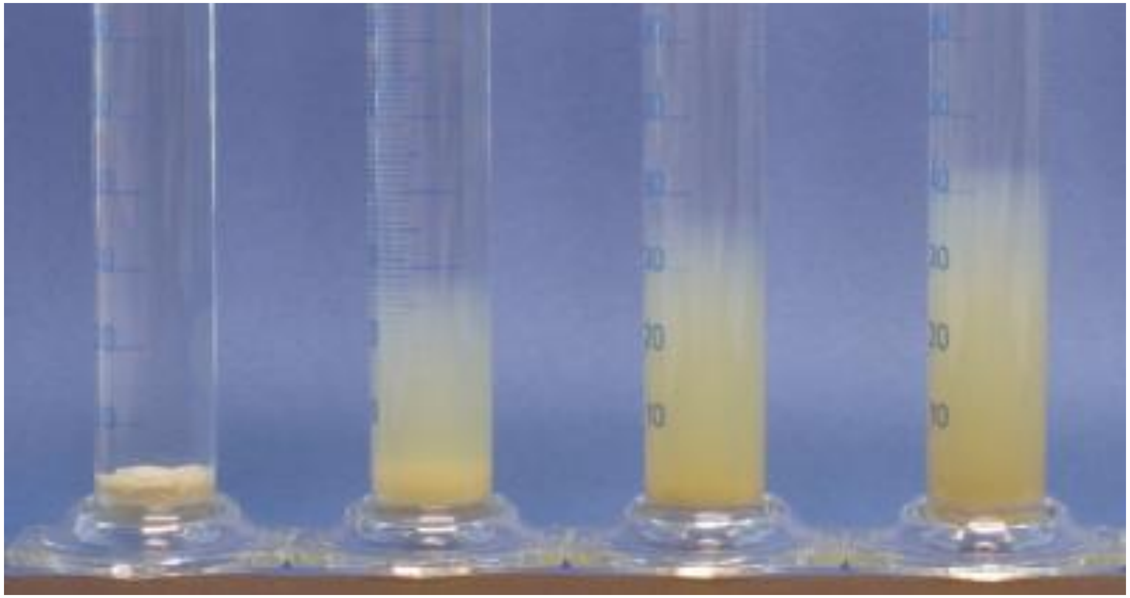
Ca-mmt (phase separation)



Montmorillonite colloid sol formation

Measurement cylinder tests: Wy-Ca/Na

Deionized water

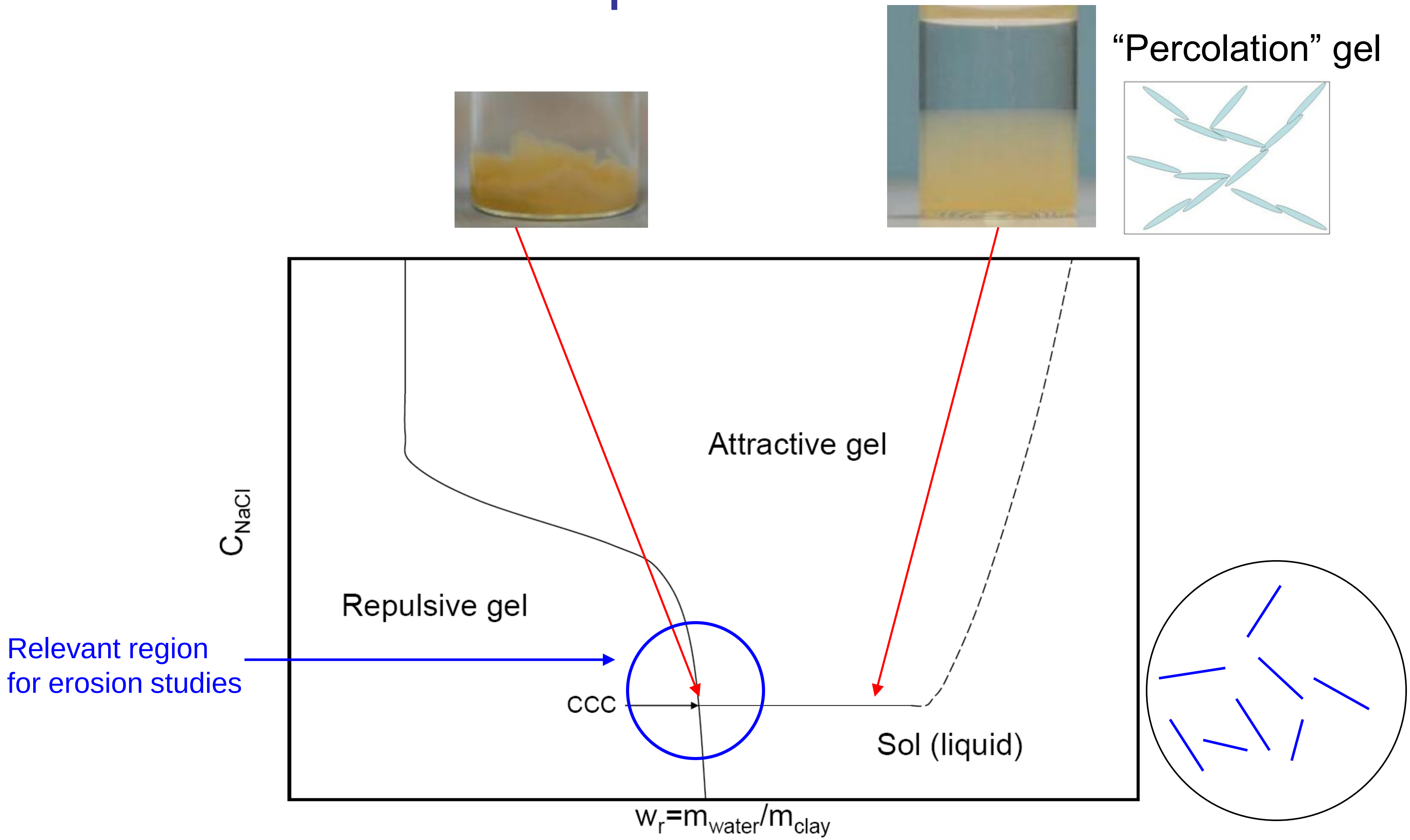


100/0 80/20 60/40 0/100

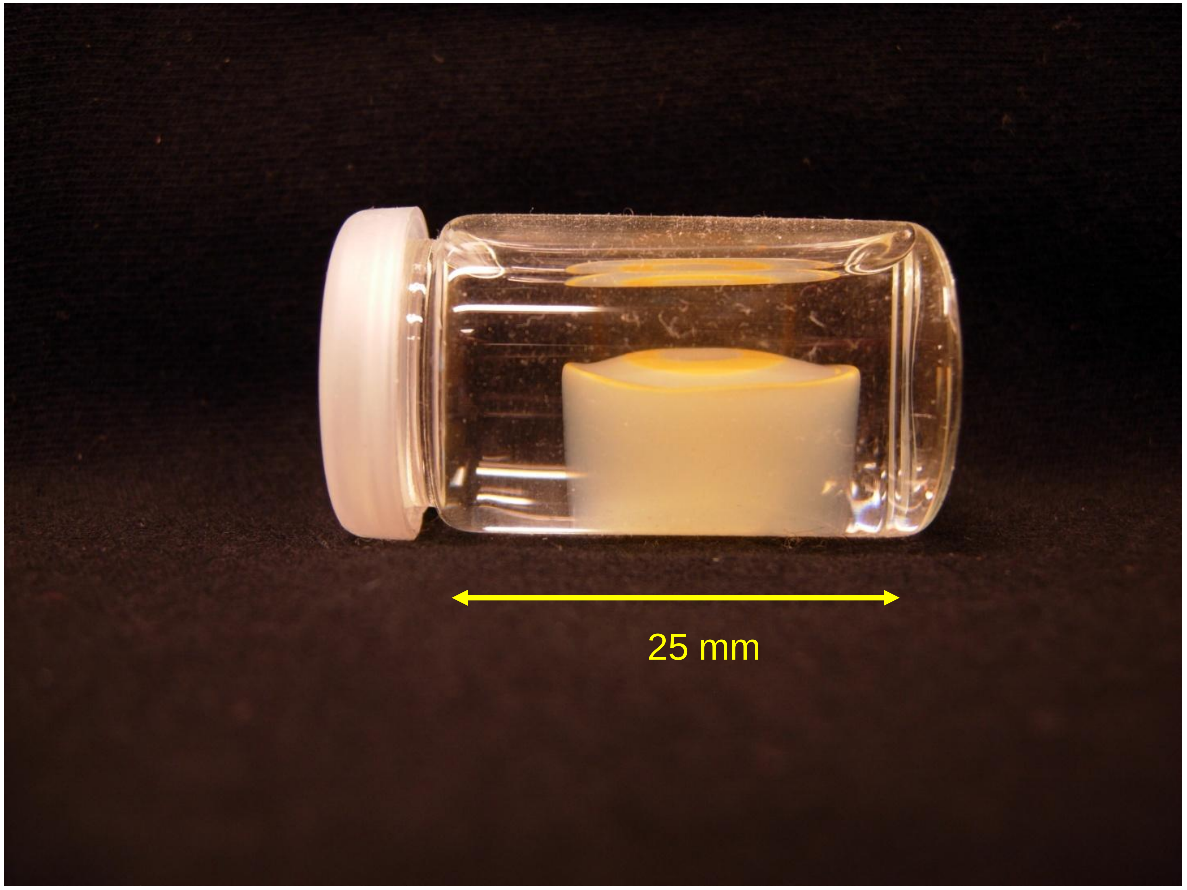
In order for correlation attraction to dominate the calcium charge fraction needs to be 90% or higher

Can also be understood from simulations using primitive model

Phase diagram for Na-montmorillonite macroscopic observations

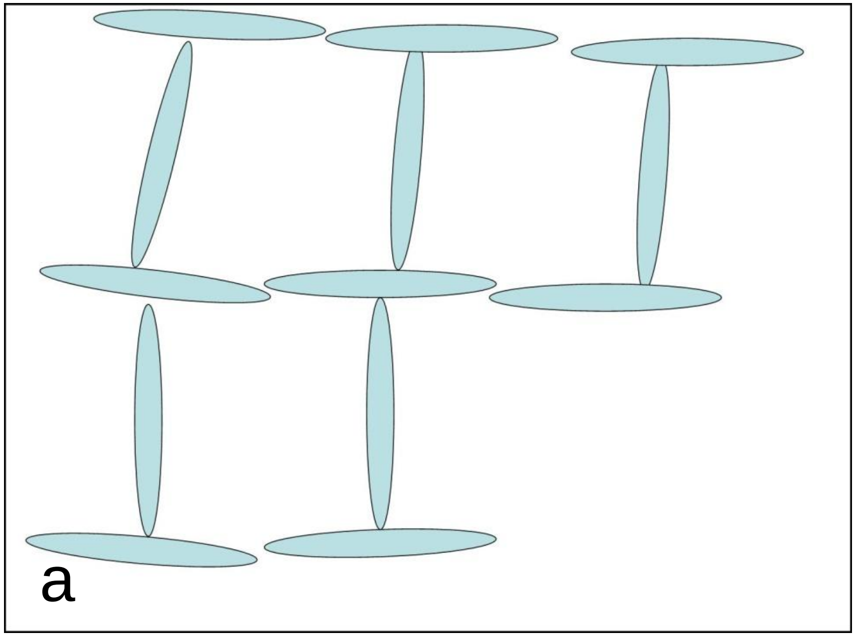


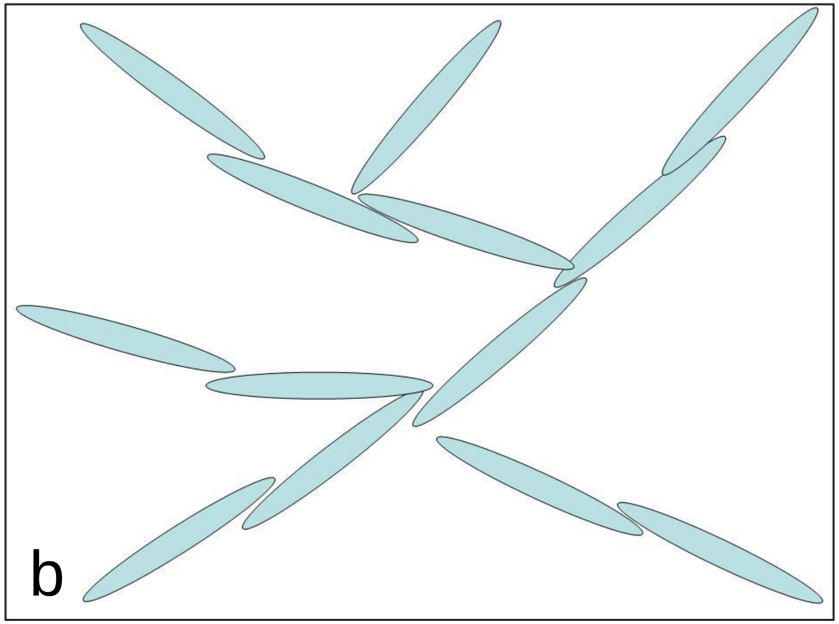
Attractive gel: Na-montmorillonite
$[Na^+]$=15 mM



~2g clay/l, density 1.002 g/l, ~1400 nm of water between clay layers assuming parallel layers
Diameter of typical clay platelet 100-500 nm

Attractive percolation gels



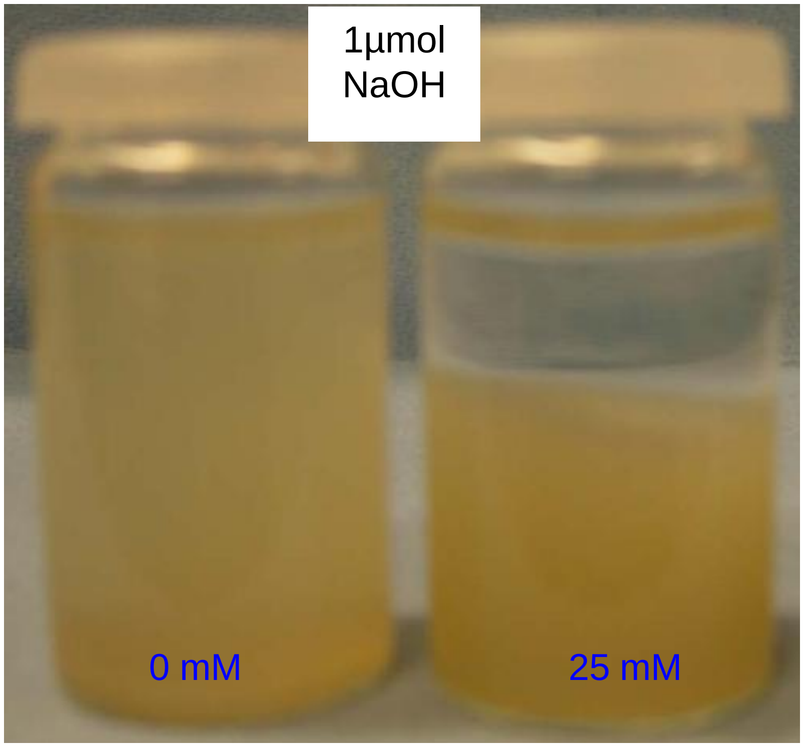


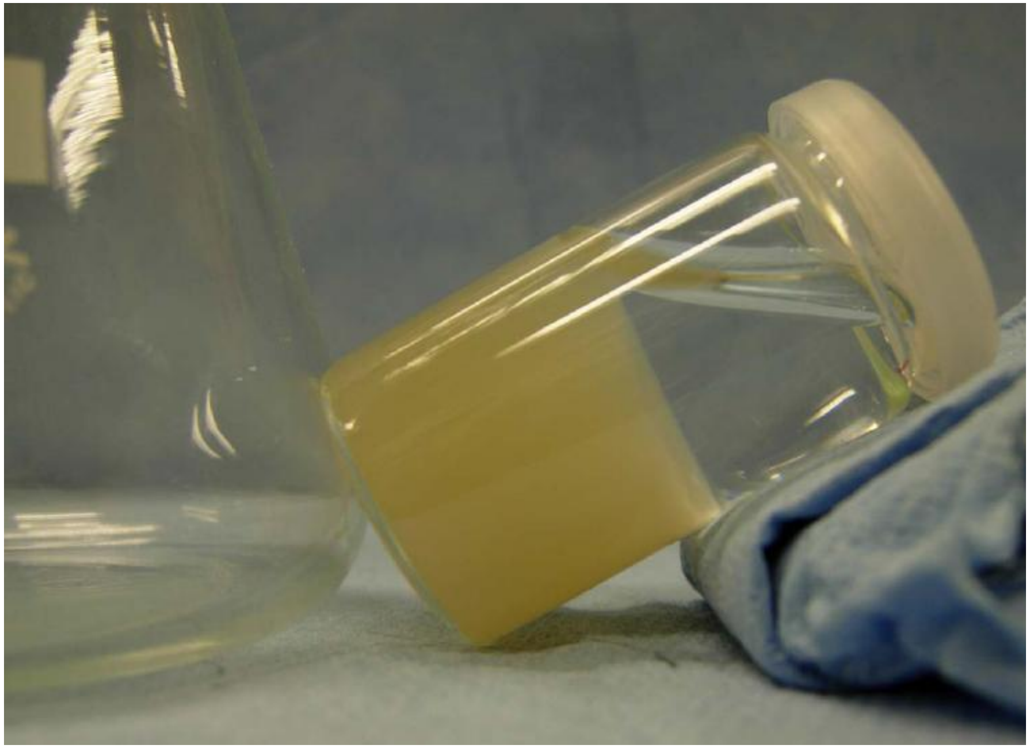
House of cards cannot fill space
in the extremely dilute cases
Favoured structure for attractive gels
at higher clay content

Possible space-filling structure
Branched chains of “overlapping coin” configurations
Edge-face interactions govern gel formation

pH and gel formation (Wy-Na)

Phase separation after centrifugation





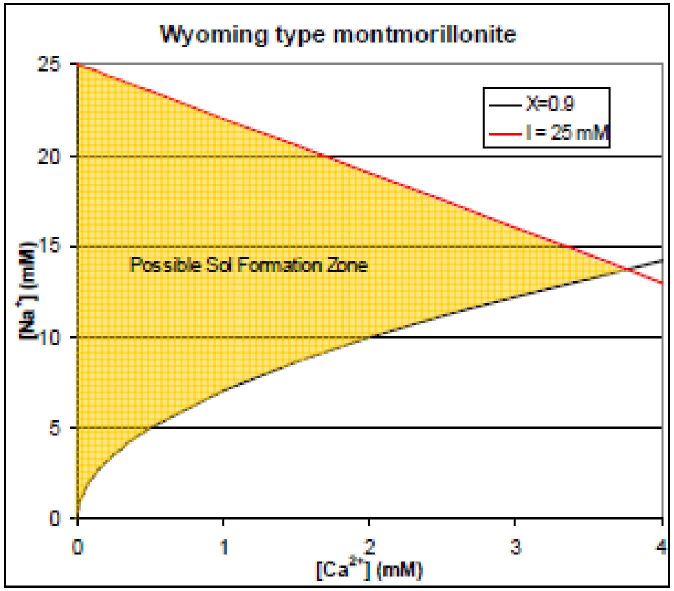
pH 9.9 pH 9.1

Clearly an attractive gel and not a dense fluid!
Still looks the same after more than1 month

Still gel formation at 25 mM NaCl but increasing pH 7.8 to 9.1 gives weaker structure.
Fewer positive charges on the edges.

Mixed Ca/Na clays with excess ions

Ionic strength 25 mM



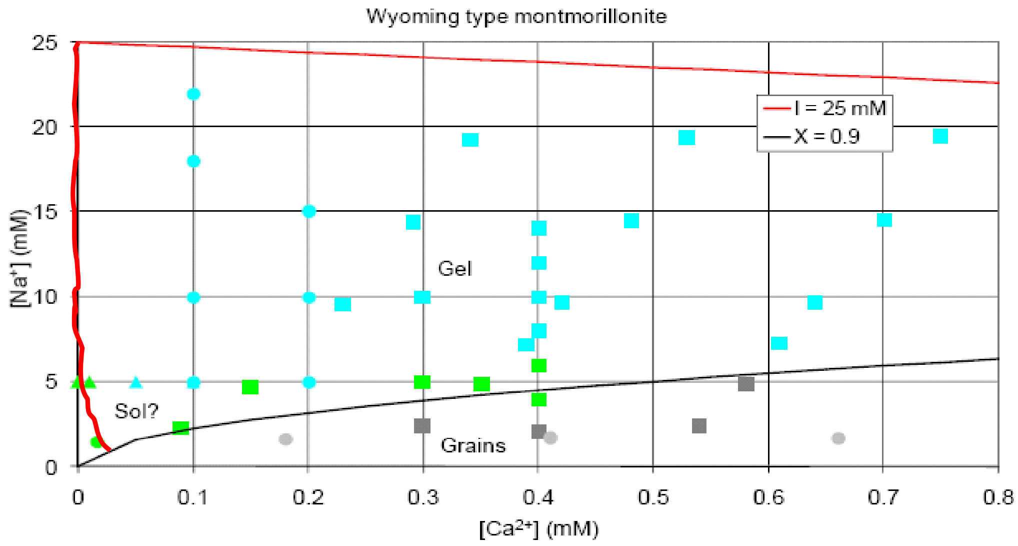
90% calcium in exchange position
assuming K_{GT}=4.5

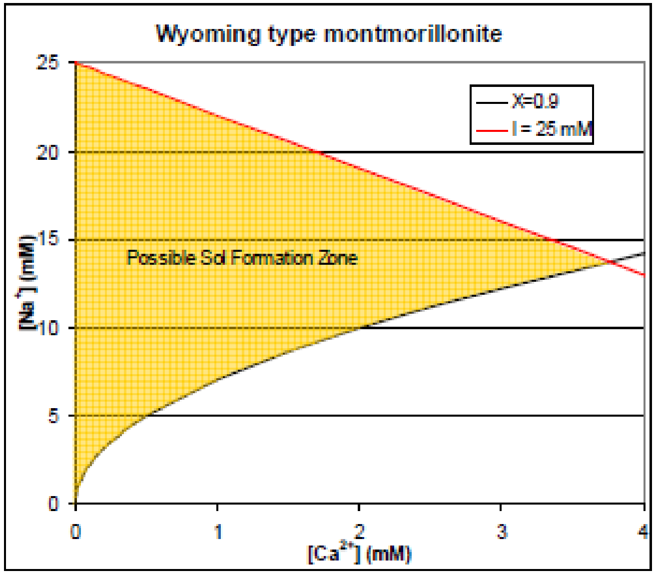
More complicated phase diagram
CCC is not a good variable
Needs both sodium and calcium concentration

Ion-exchange equilibrium key concept

Note that chloride is the anion

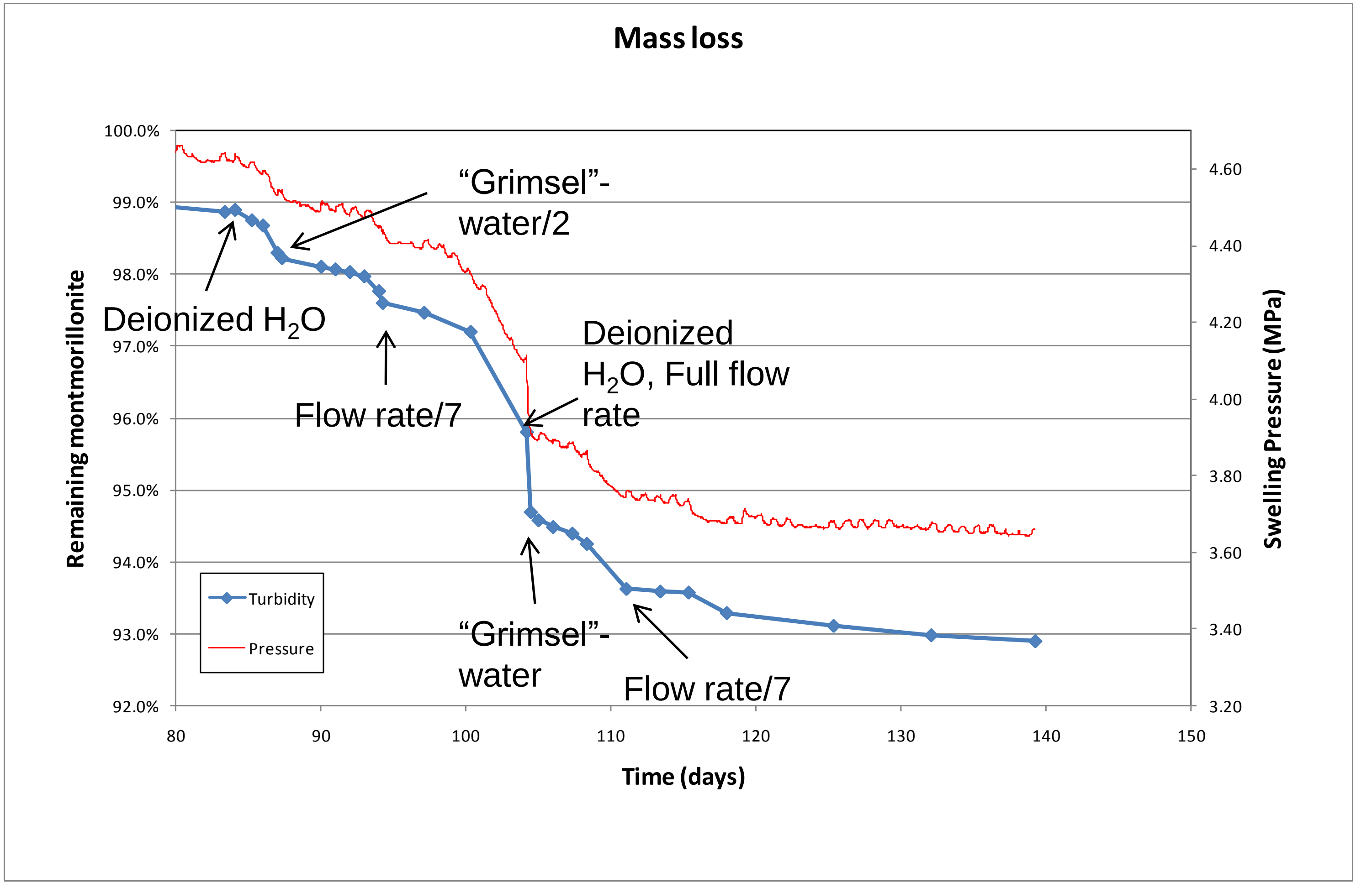
The experimental sol formation zone



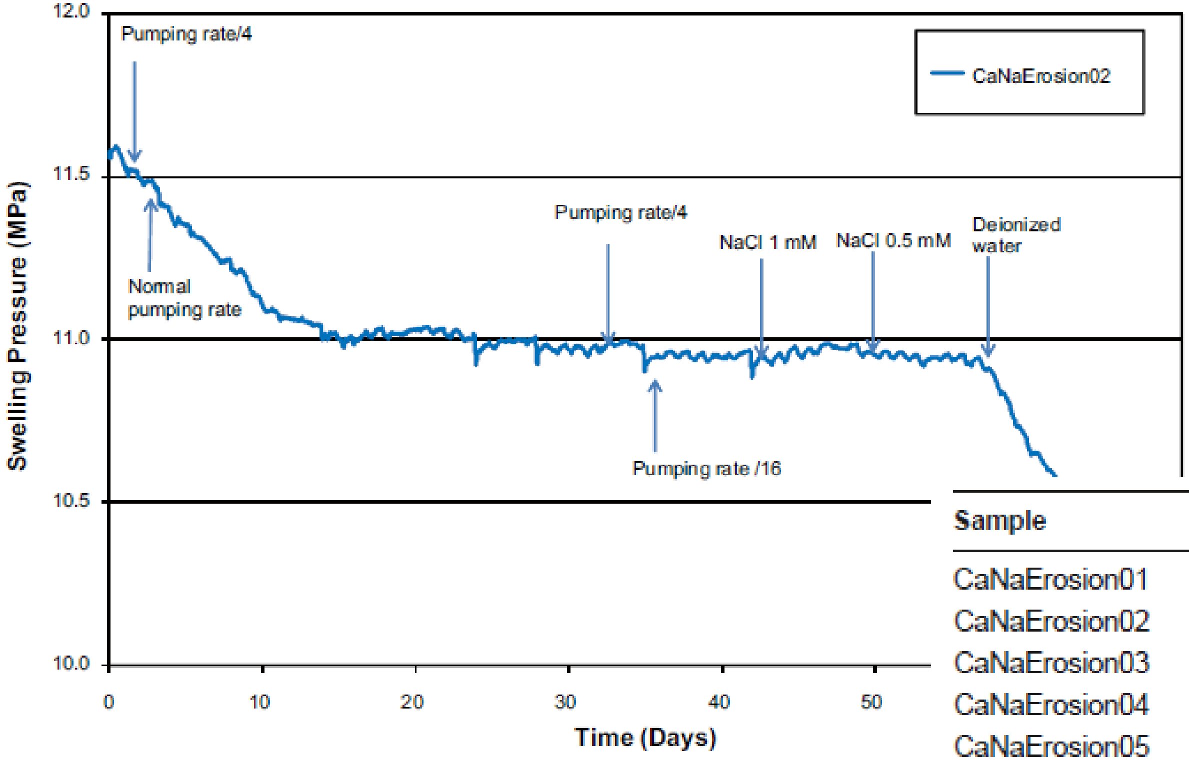


- Motivation for a large part of CT's work
- Map the thermodynamic equilibrium states before investigating the dynamics
- Exchange equilibrium between monovalent and divalent counterions essential
- Small SFZ →Possible to control ionic strength using 1:1 salt e.g. NaCl
- Questionable if this is the usual correlation effect seen in parallel clay layer configuration and divalent cations. More tests needed!

Erosion test of MX-80



Ca/Na-Montmorillonite
Effect of excess ions



Milos type
50% Ca, 50% Na

Sample	Clay Type	X	Observed stability
CaNaErosion01	Milos	0.5	2 mM
CaNaErosion02	Milos	0.5	0.5 mM
CaNaErosion03	Milos	0.25	1 mM
CaNaErosion04	Milos	0.75	3 mM
CaNaErosion05	Wyoming	0.5	4 mM
CaNaErosion06	Kutch	0.5	1 mM

Erosion of clays with a mixture of Na^{+} and Ca^{2+} (20%<CaX<90%) is prevented by groundwaters with charge concentrations above 2-4 meq/L

BELBaR WP2 & WP4

- Artificial fracture (Plexiglas)
  - Erosion experiments
  - Swelling experiments
- Rheology on attractive gels
- Viscosity measurements
- Why is Ca^{2+} so important for gelling?

Artificial fracture

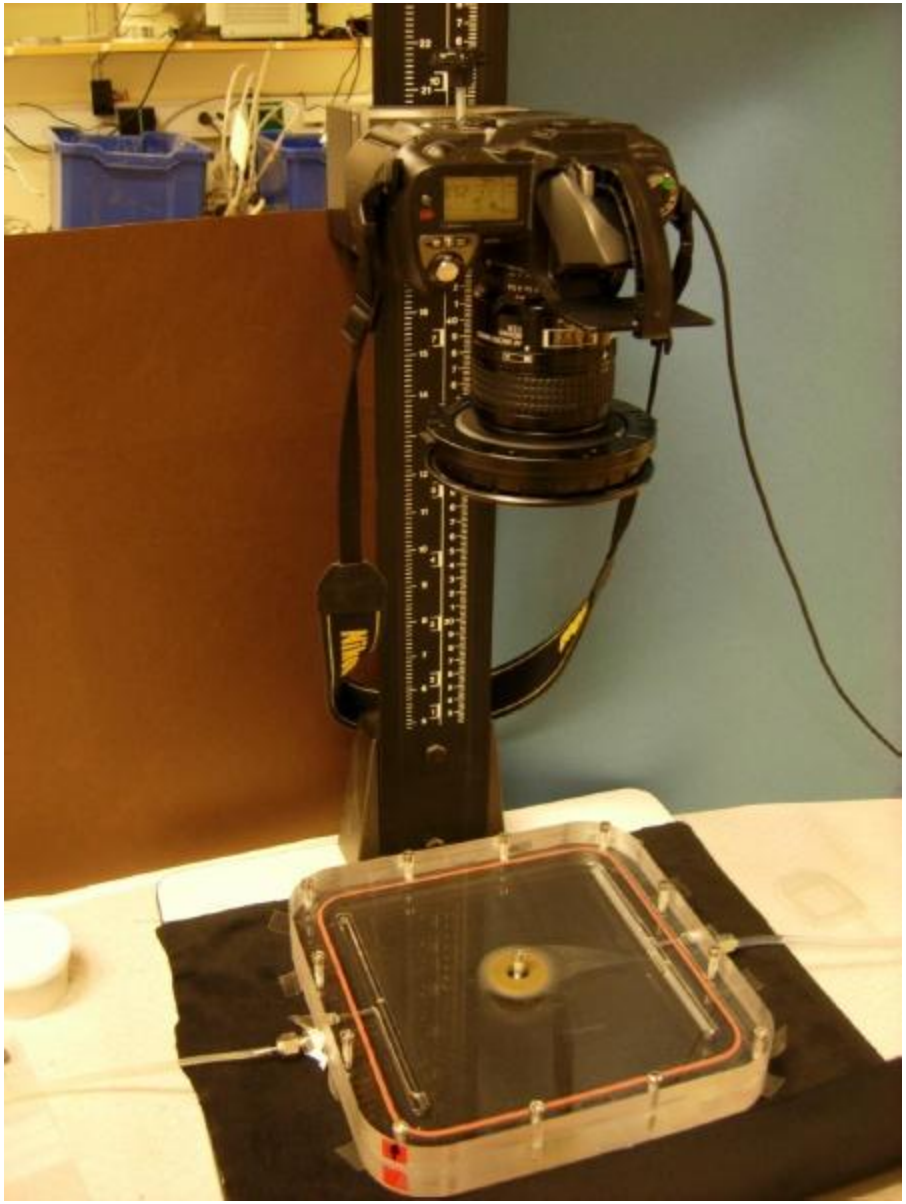
Compacted montmorillonite/bentonite

Aperture

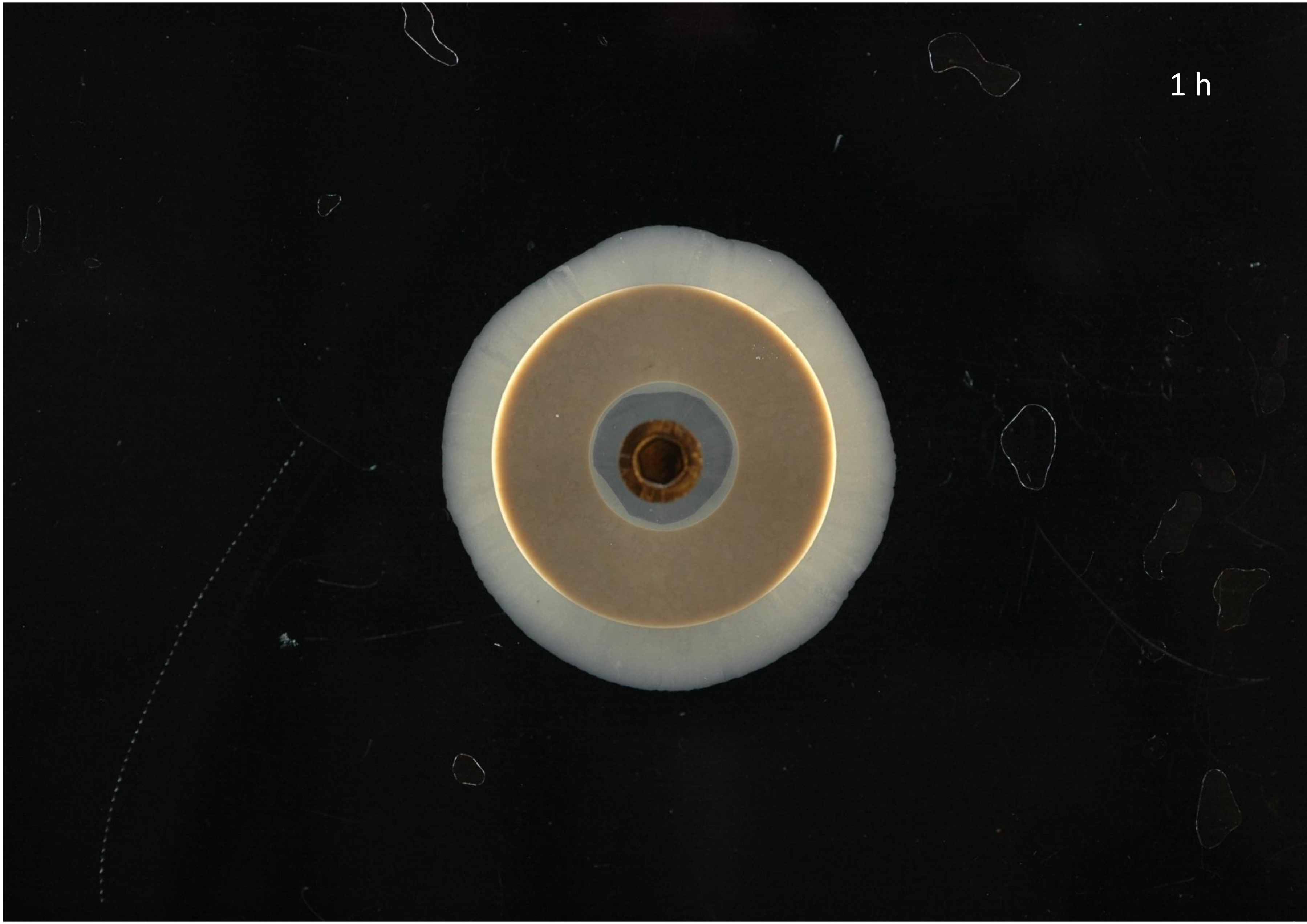
Flow rate

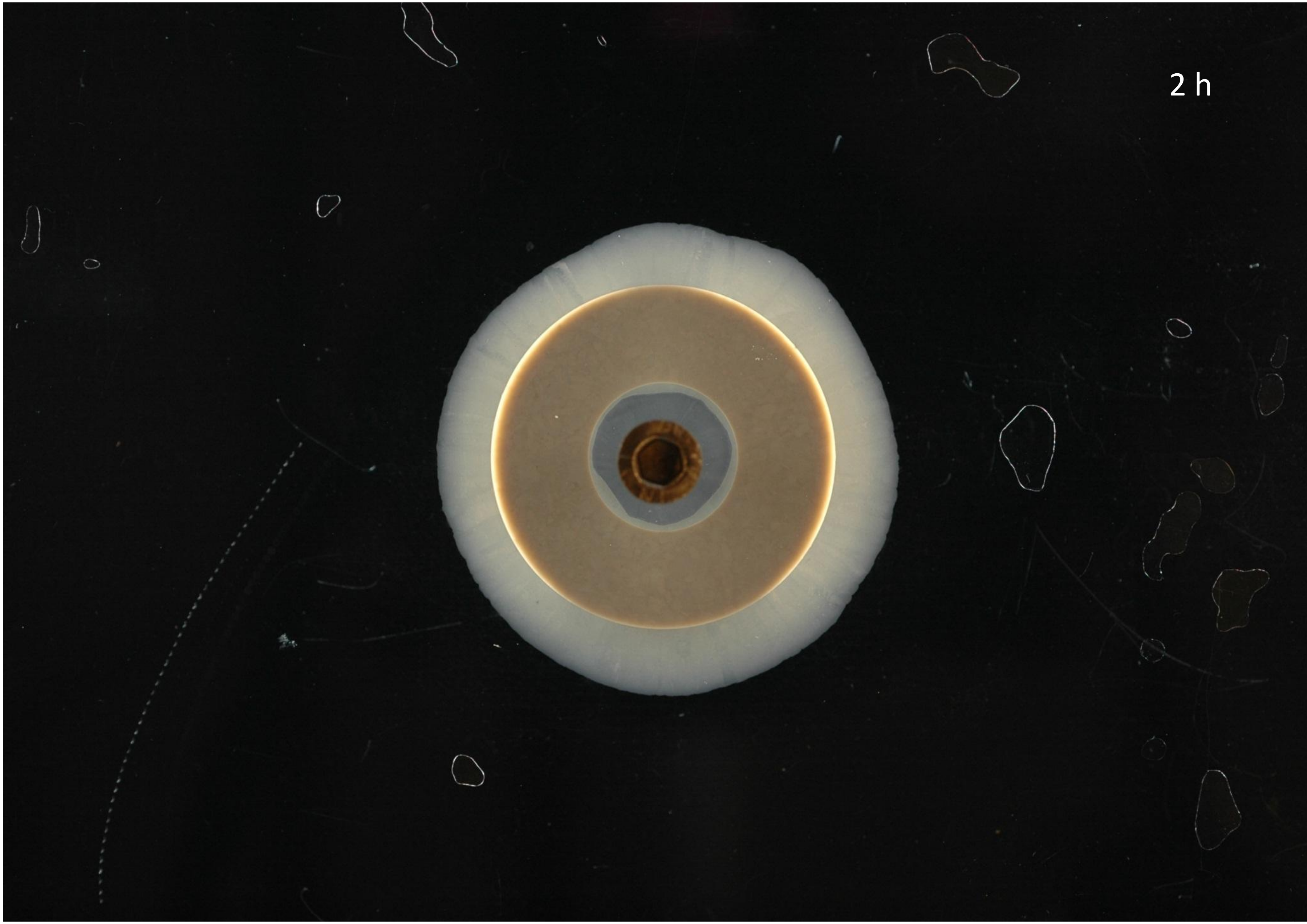
Ionic strength

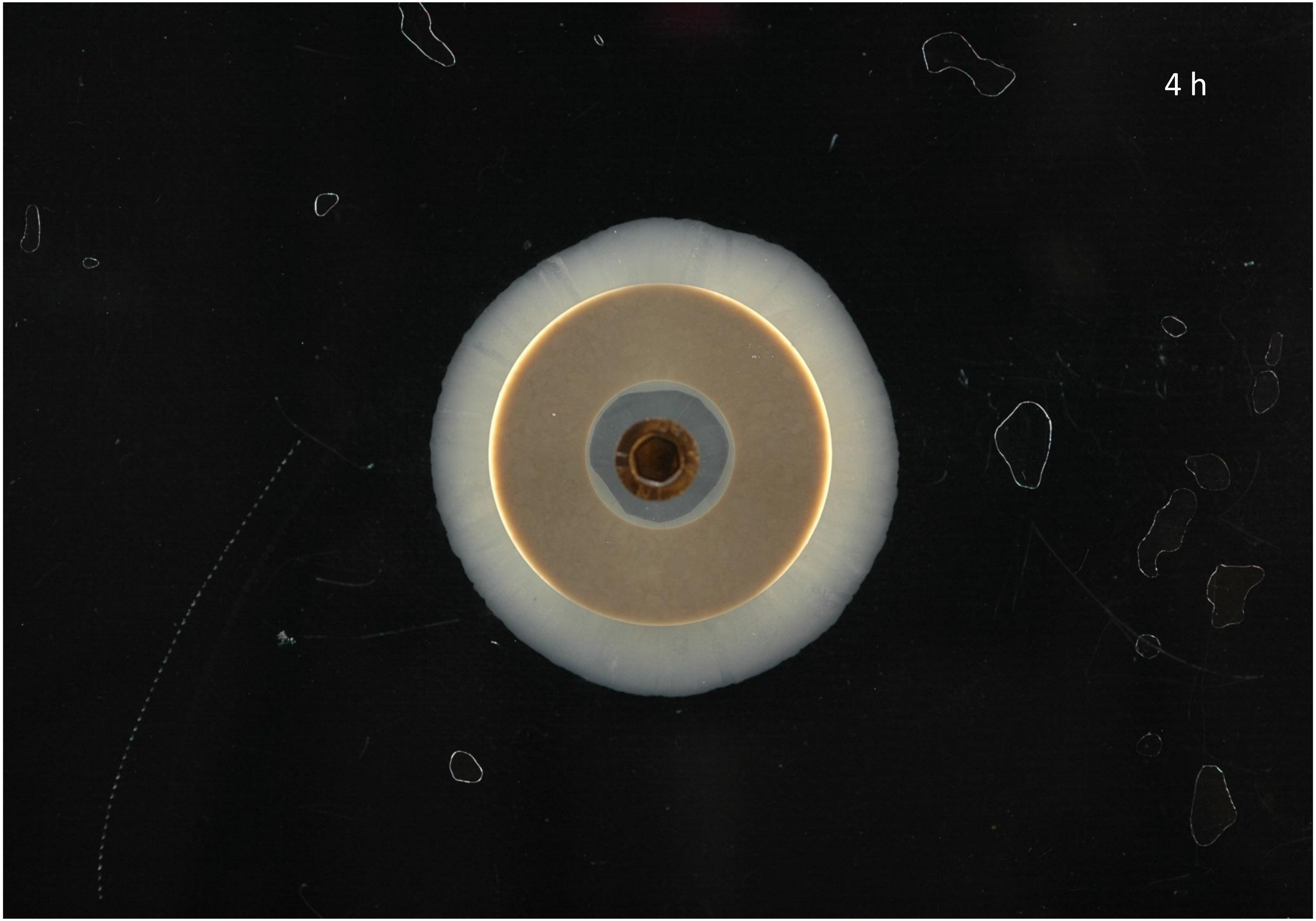
Montmorillonite composition

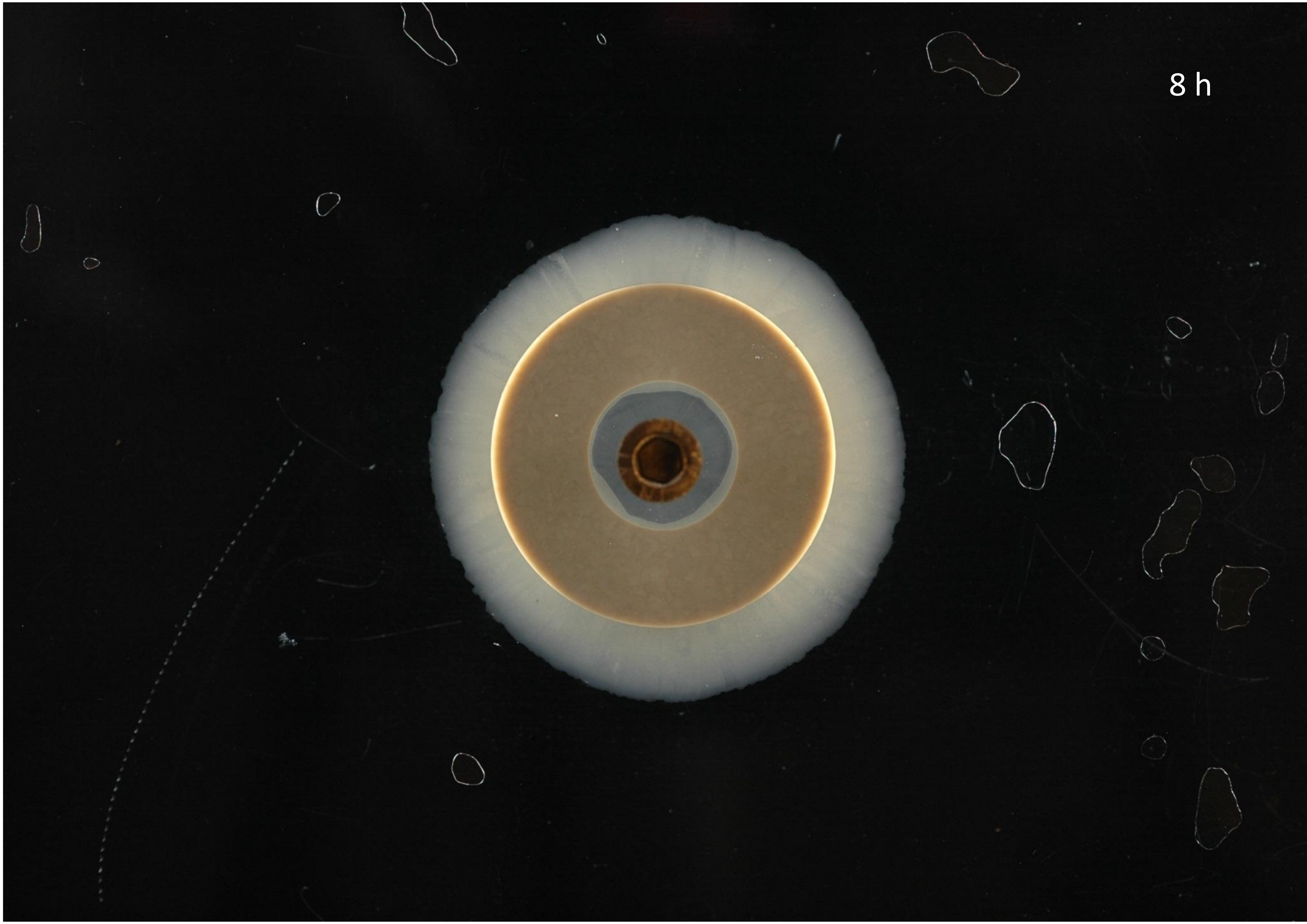


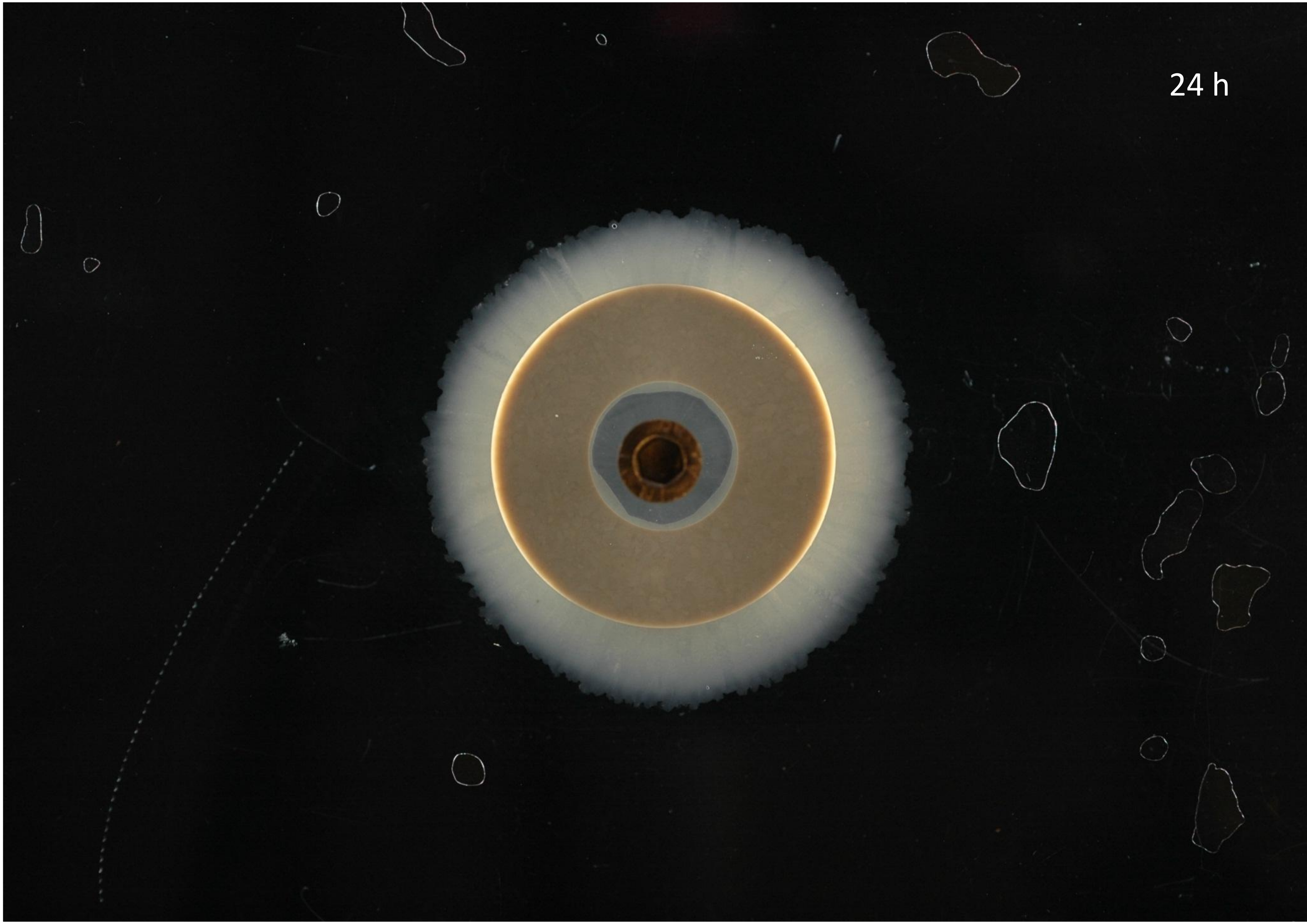

0 h
No solution yet in fracture
Gel extruded at preparation
Wy-Na montmorillonite
25 mM NaCl (aq) added just after
picture taken


1 h


2 h


4 h


8 h


24 h