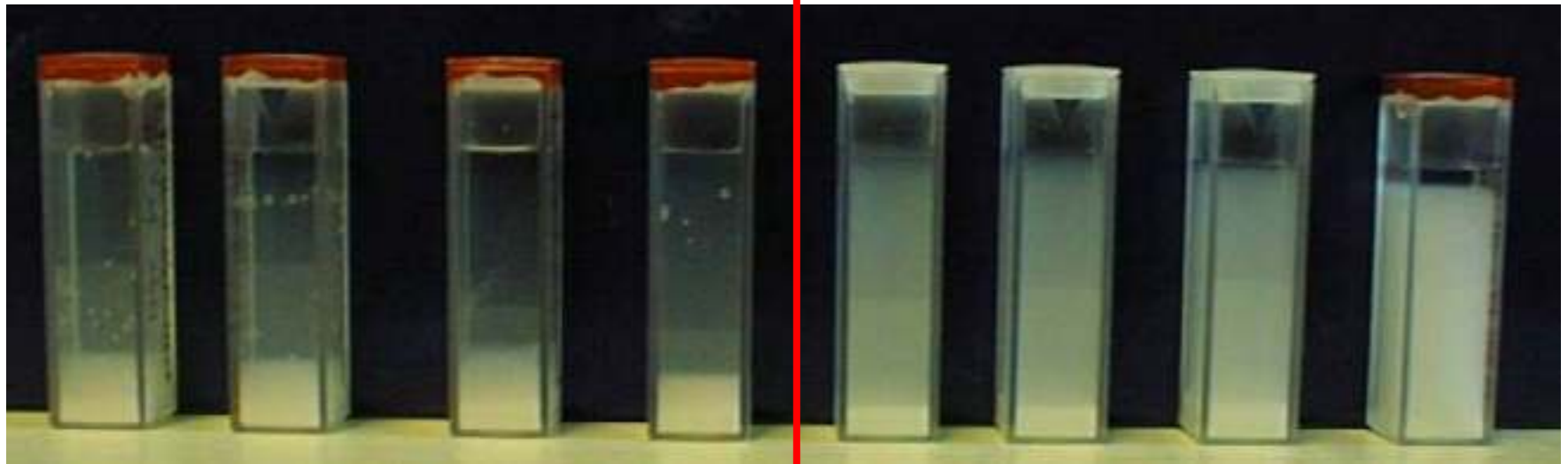


Increasing salt:



"Repulsive nematic"
"Wigner glass"



Particles push each other out
towards container walls,



nematic

at high enough concentration

→ "large" domains

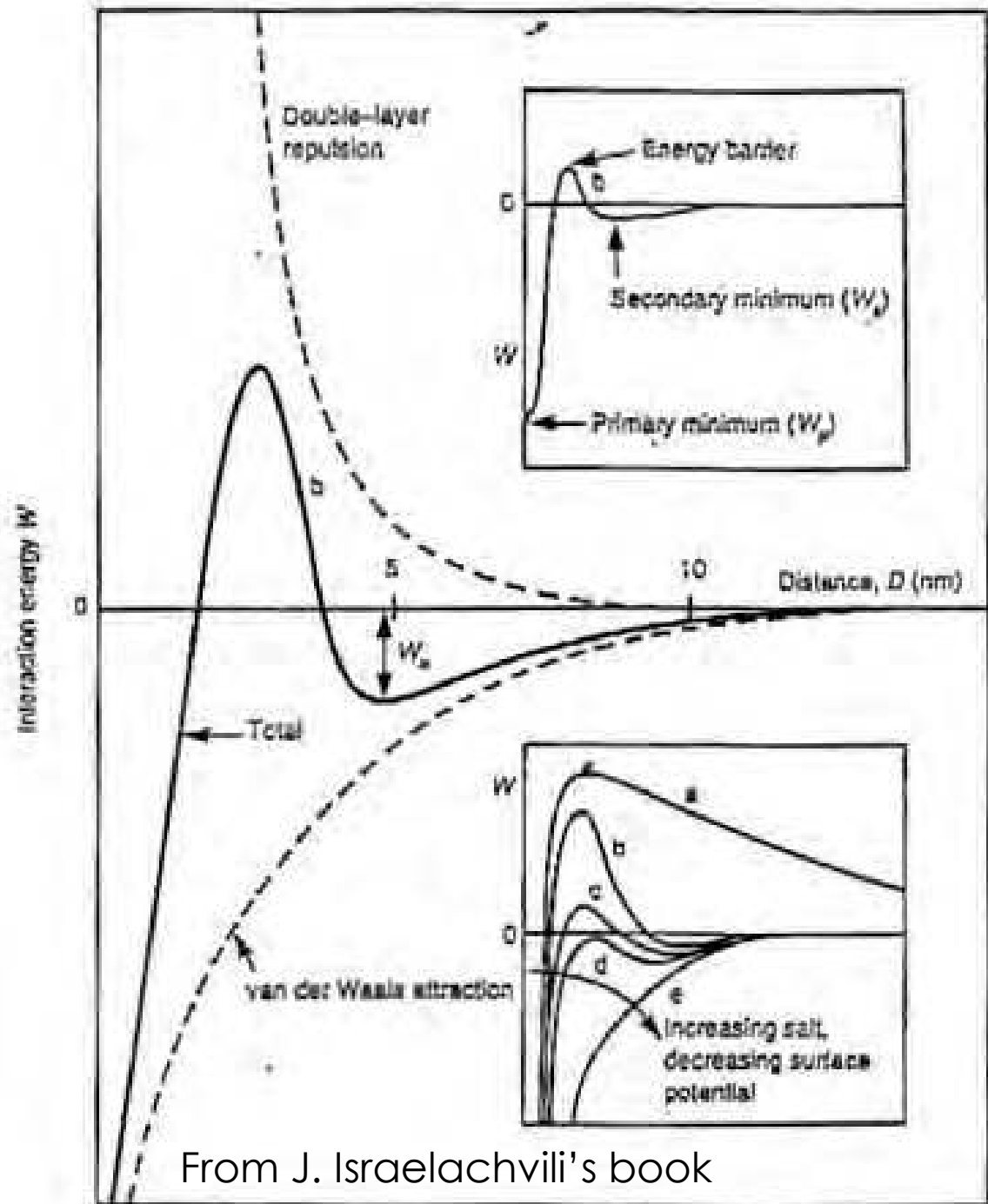
"Attractive nematic"
"Gel"



Particles "catch each other" in
DLVO local minima

→ small domains

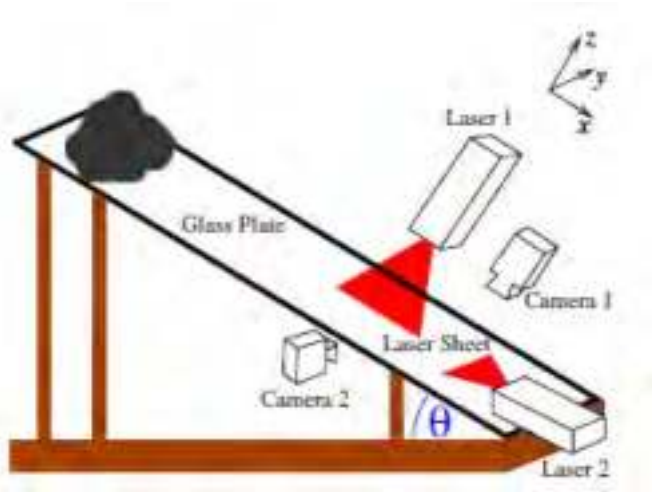
DLVO Theory:
vdW
+ Screened Electrostatic Rep.



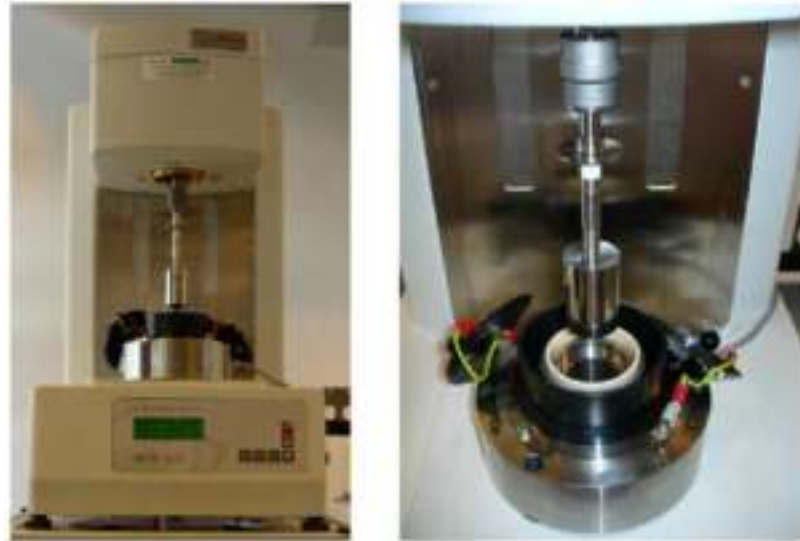
TOOLS

Macroscopic tools:

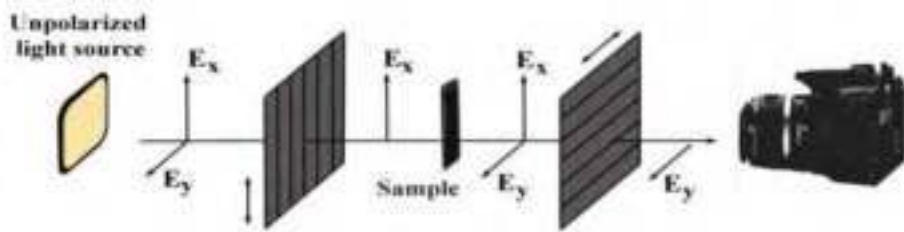
Tilted plane experiments on clays:



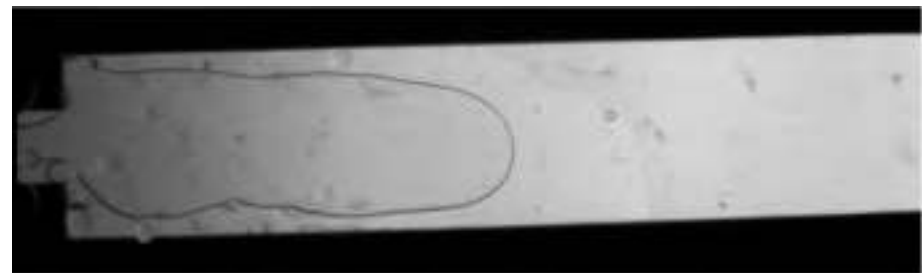
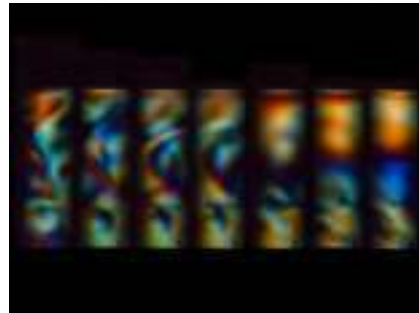
Rheometry:



Birefringence studies of clay nematics:



Observations of fingering and fracturing in clay gels:



Nano-structural tools: X-ray synchrotrons facilities/neutron facilities:

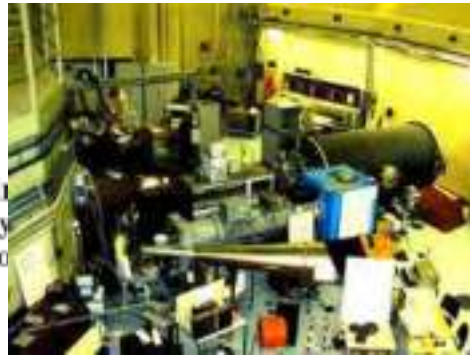
ESRF – Grenoble, France
Maxlab – Lund, Sweden
LNLS – Campinas, Brasil
PLS – Pohang, S-Korea
(In the past: BNL; APS – USA)
+++++



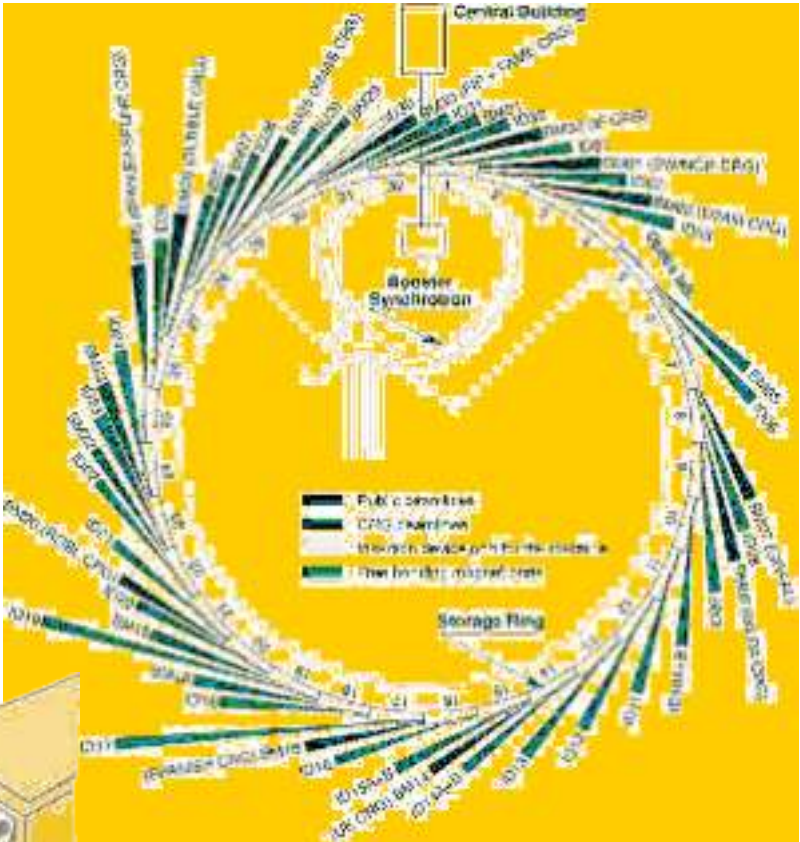
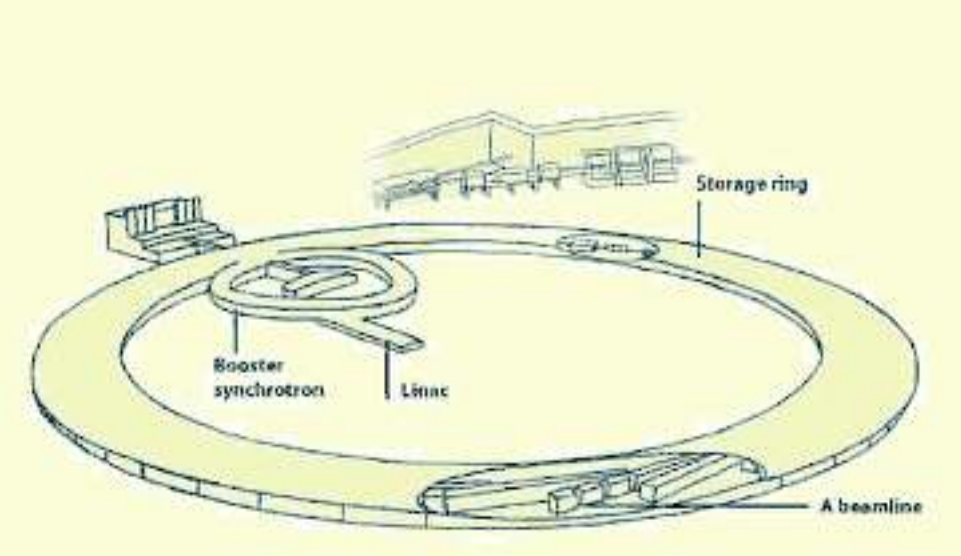
Neutron scattering at IFE – Kjeller, Norway

Jeep II reactor:

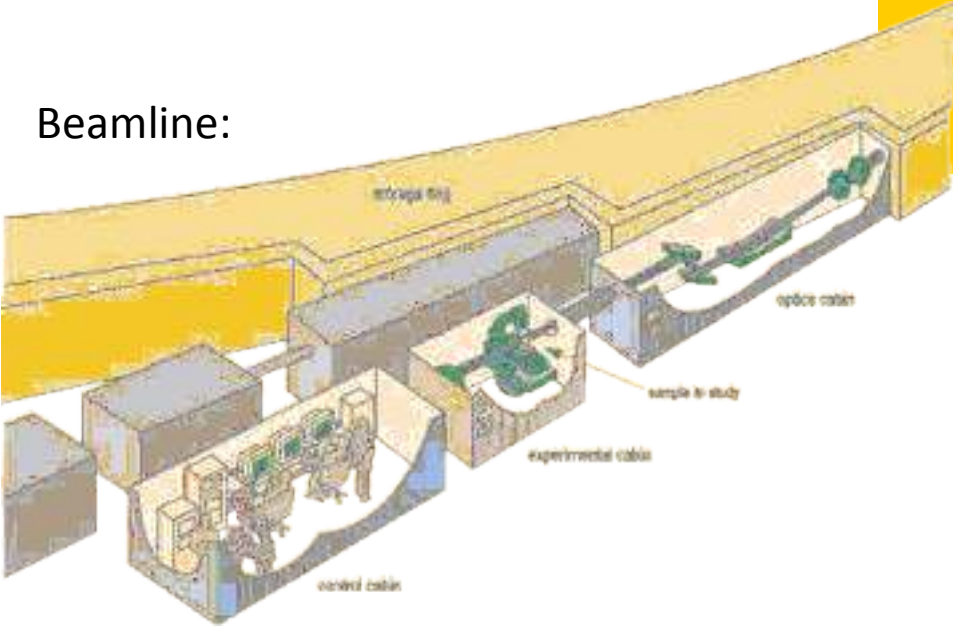
SANS at IFE:



X-ray synchrotron sources:

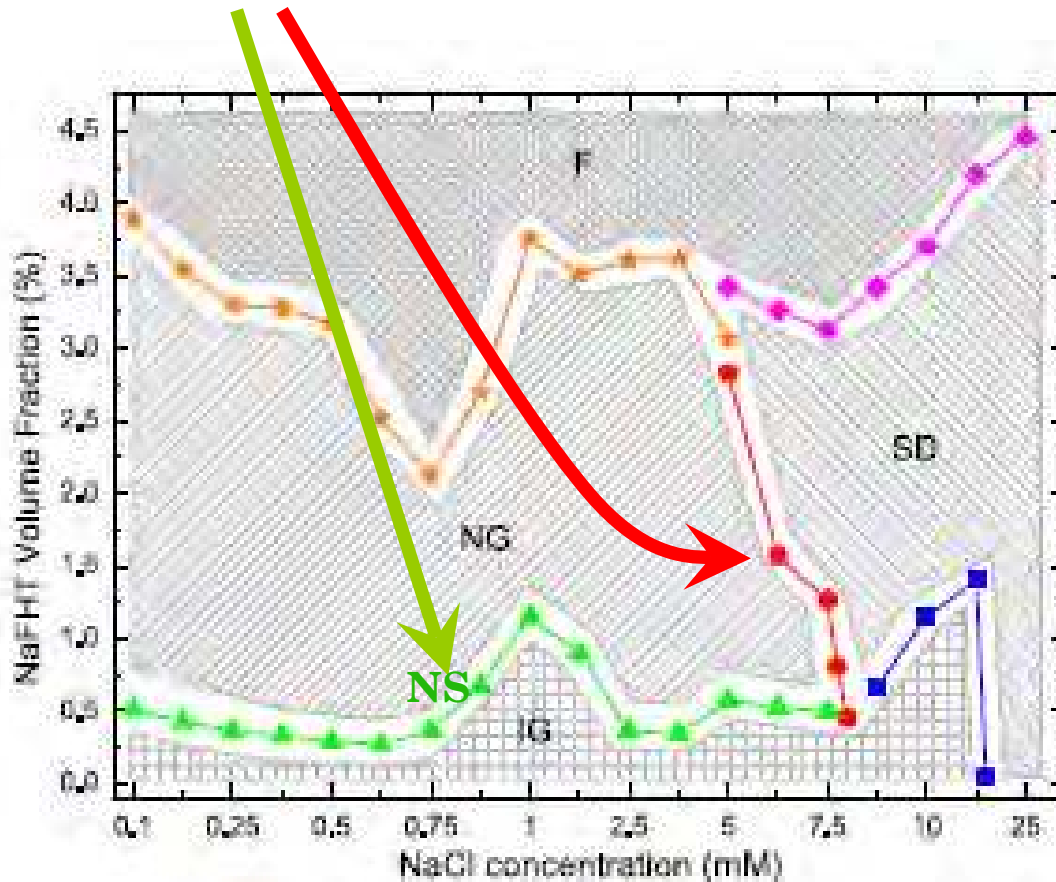


Beamline:



From SAXS experiments at ESRF: "True phase diagram":

Transitions of interest



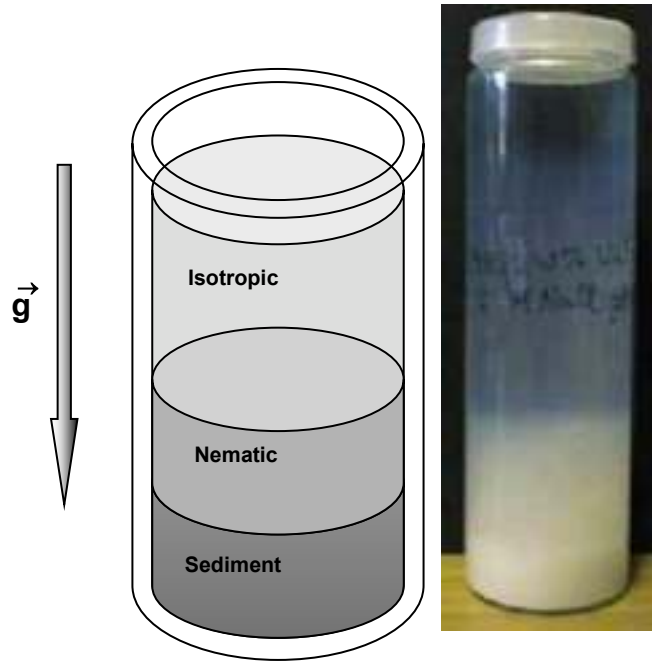
Obtained by combining:

- Eccentricity of SAXS scattering
- Angle of tilt of SAXS scattering
- X-ray transmission



The phase diagram of polydisperse Na-Fluorohectorite–water suspensions: A synchrotron SAXS study, D. M. Fonseca, Y. Meheust, J. O. Fossum, K. D. Knudsen, and K. P. S. Parmar, *Phys.Rev. E* 79, 021402 (2009)

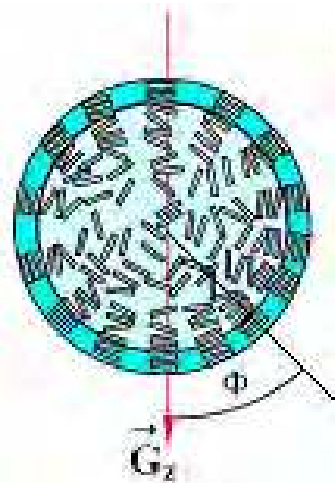
Response to magnetic field: Magnetic field guided self-organization:



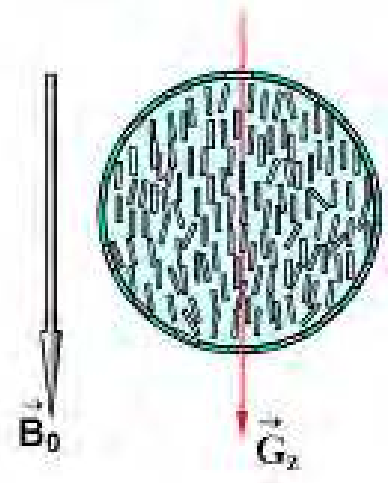
Glass wall anchoring confirmed by spatially resolved MR measurements of anisotropic self-diffusion coefficient of water in the nematic phase.

Magnetic field induced ordering, due to diamagnetic anisotropy of the platelets at fields above about 1 Tesla.

$$S_2 \sim -0.3$$



$$S_2 \sim +0,5$$

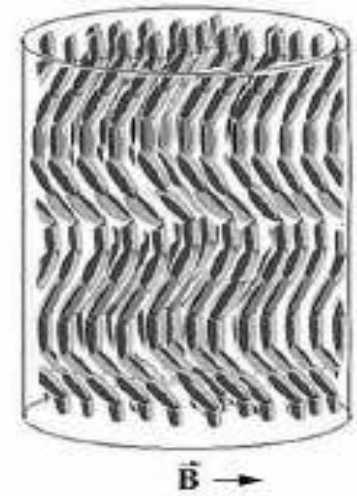
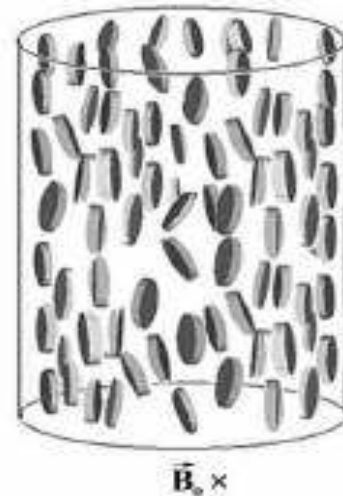


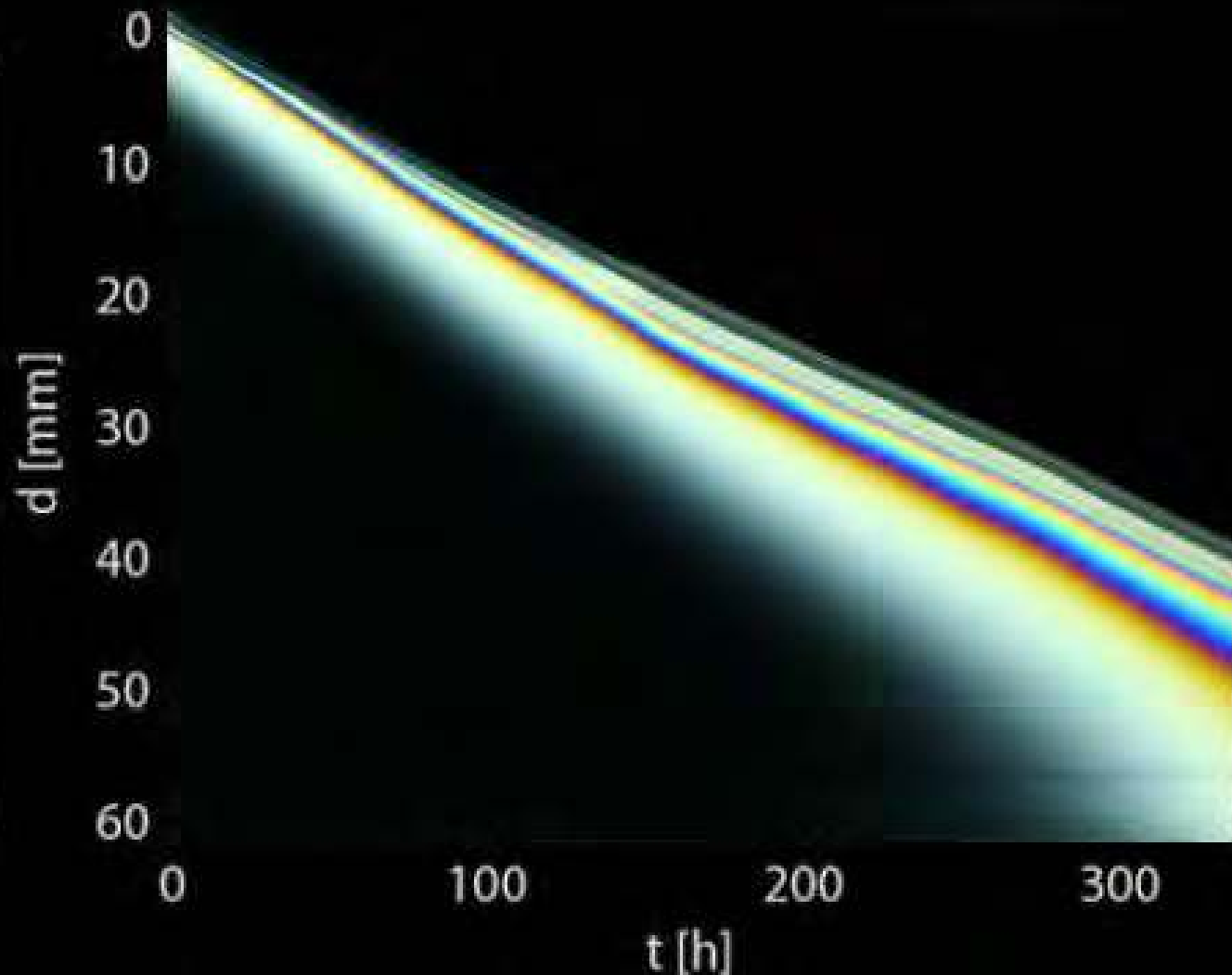
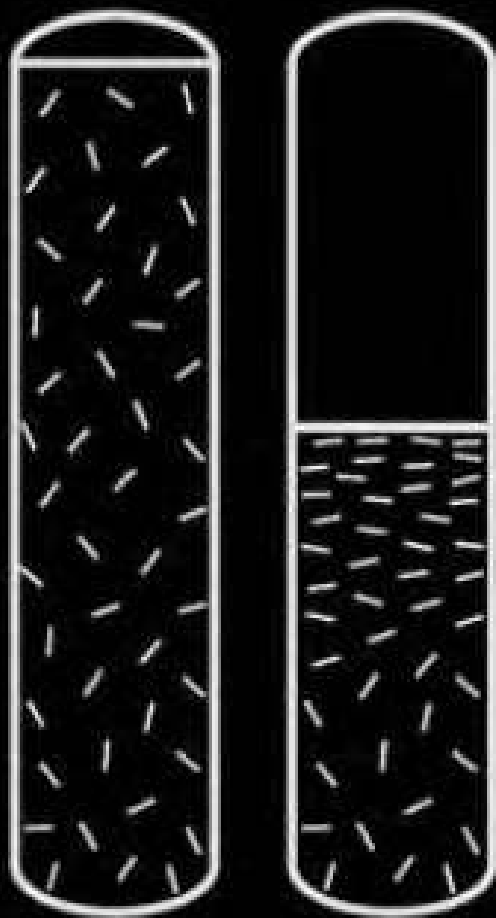
Fredericksz configuration in nematic liquid crystals:

Transient competition between wall anchoring and magnetic field alignment

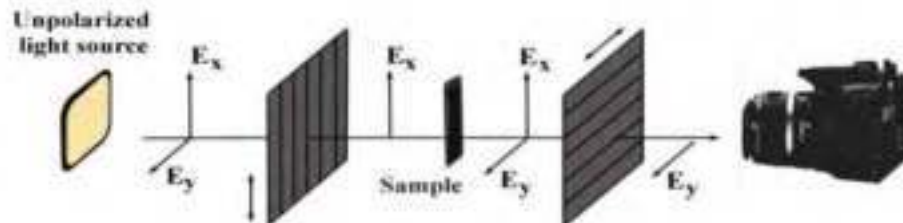


The Fredericks transition in an aqueous clay dispersion,
H. Hemmen, E.L. Hansen, N.I. Ringdal and J.O. Fossum,
Revista Cubana de Física, vol. 29-1E, 59-61 (2012)

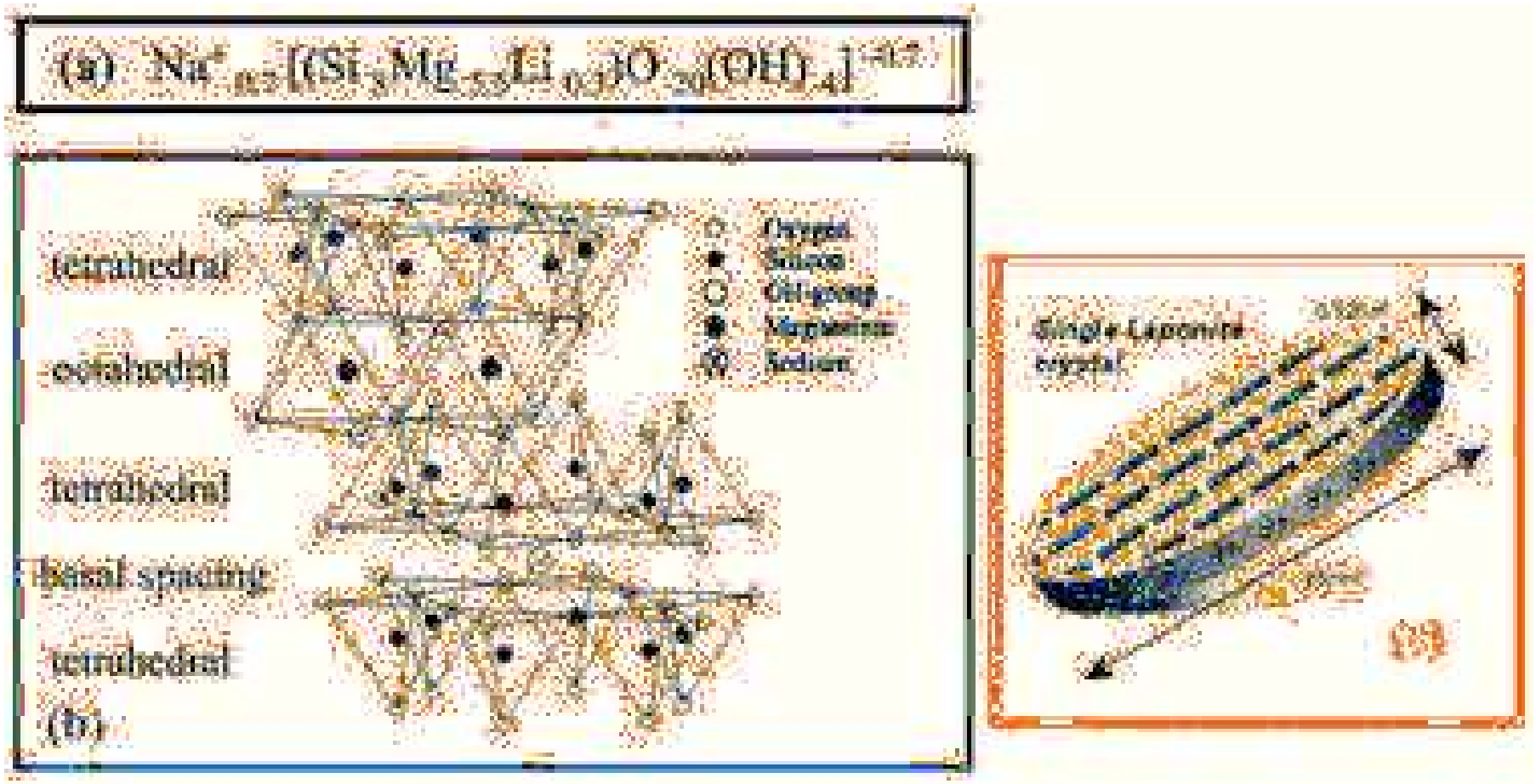




Orientalional order in a glass of charged platelets with a concentration gradient, Elisabeth Lindbo Hansen, Sara Jabbari-Farouji, Henrik Mauroy, Tomás S. Plivelic, Daniel Bonn and Jon Otto Fossum *Soft Matter*, 9, 9999-10004 (2013)



The most common and most used synthetic clay: Laponite



Colloidal gels: **Clay goes patchy**,
W. K. Kegel & H. N. W. Lekkerkerker,
Nature Materials 10, 5–6 (2011)

Observation of empty liquids and **equilibrium gels in a colloidal clay**,
B. Ruzicka, E. Zaccarelli, L. Zulian, R. Angelini, M. Sztucki, A. Moussaïd,
T. Narayanan and F. Sciortino, **Nature Materials 10, 56-60 (2011)**

Nonergodic states of charged colloidal suspensions: Repulsive and attractive glasses and gels

Hajime Tanaka,¹ Jacques Meunier,² and Daniel Bonn^{2,3}

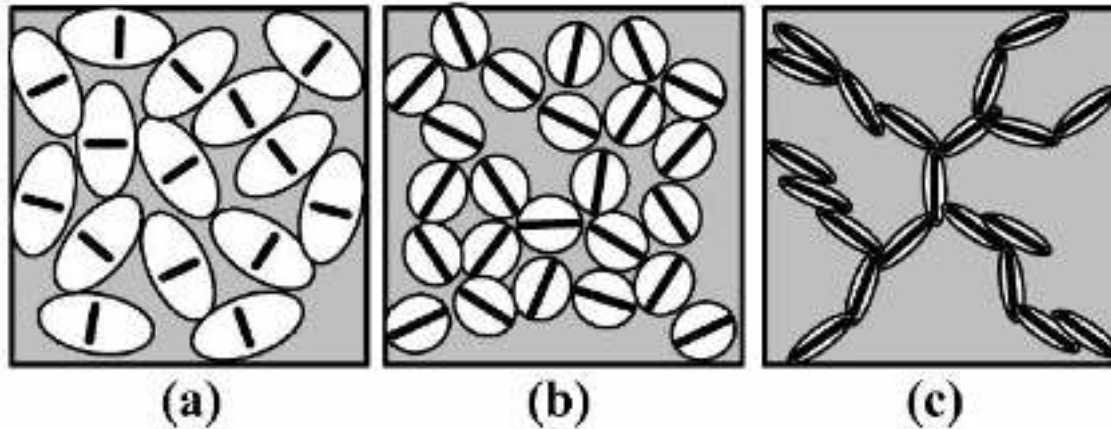
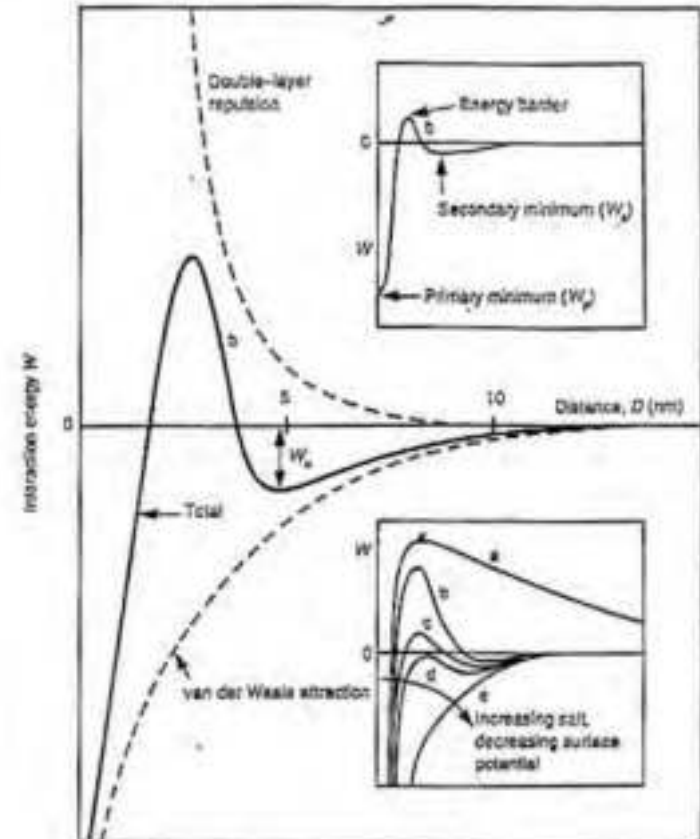


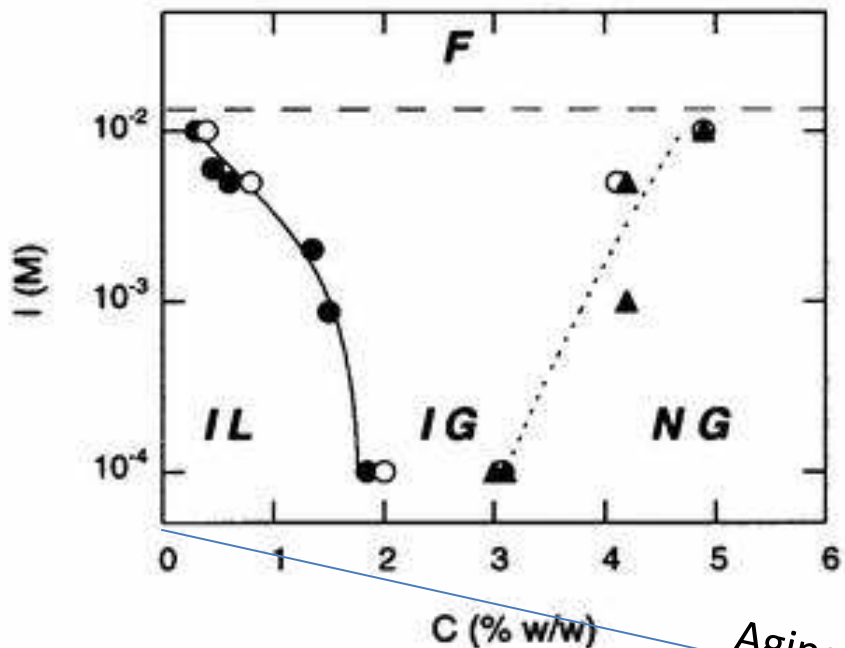
FIG. 1. Schematic figures representing repulsive “Wigner” colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions: (a), long-range electrostatic repulsions dominate. (b), attractive interactions affect the spatial distribution but repulsive interactions still play the predominant role in the slow dynamics of the system. (c), attractive interactions play a dominant role; a percolated network forms, which gives the system its elasticity and higher yield stress.

DLVO Theory: vdW + Screened Electrostatic Rep.



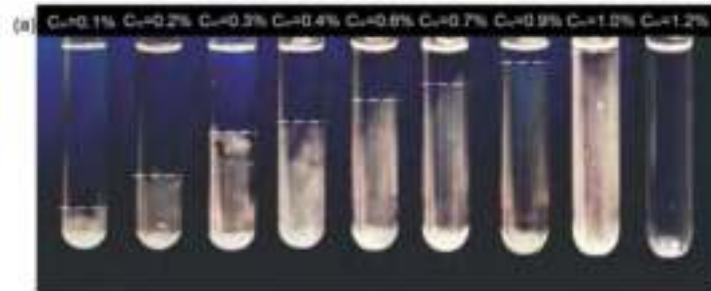
On Viscoelastic, Birefringent, and Swelling Properties of Laponite Clay Suspensions: Revisited Phase Diagram

A. Mourchid,* E. Lécolier, H. Van Damme, and P. Levitz*



Aging time \rightarrow

One sample for each point



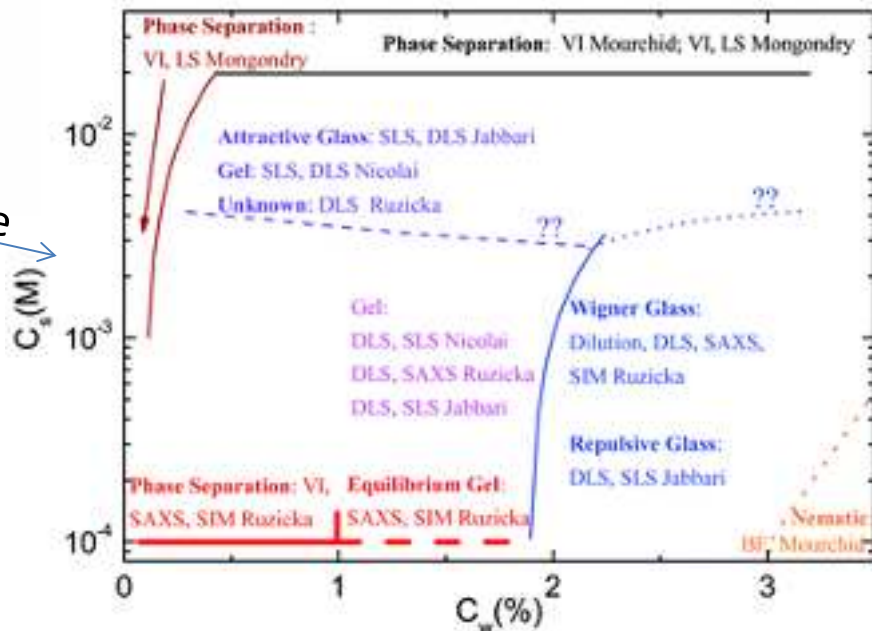
Soft Matter

Cite this: *Soft Matter*, 2011, 7, 1268

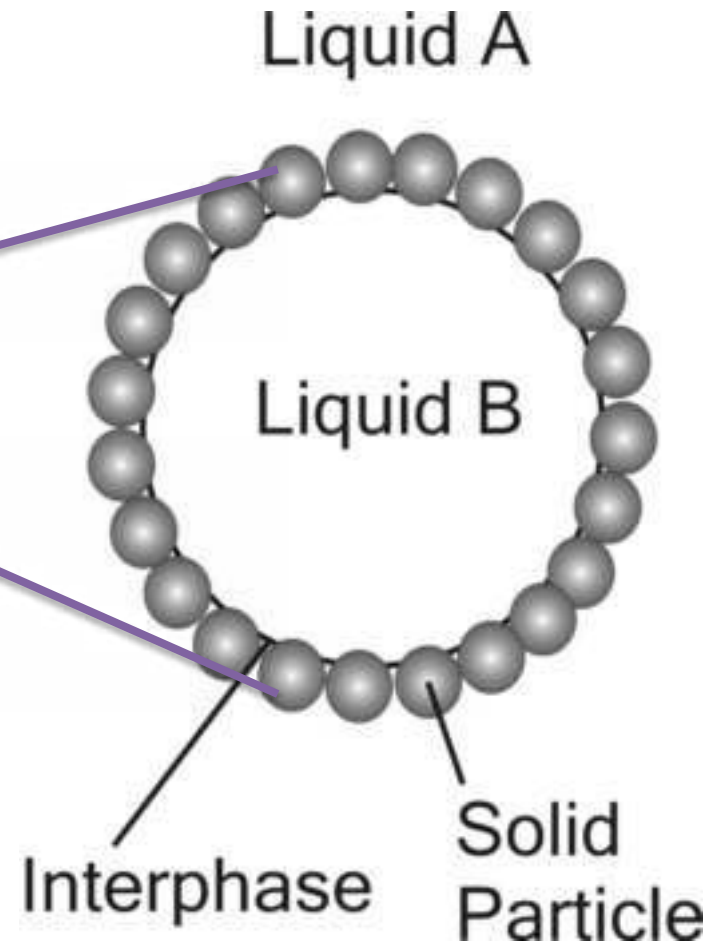
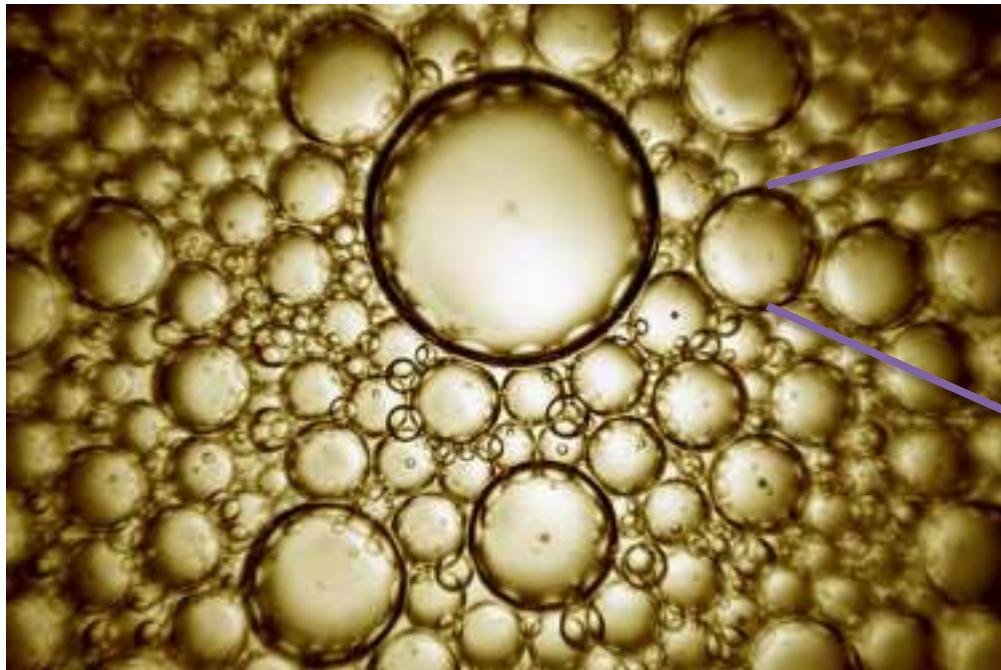
www.rsc.org/softmatter

A fresh look at the Laponite phase diagram

Barbara Ruzicka^{1,2} and Emanuela Zaccarelli^{1,3}



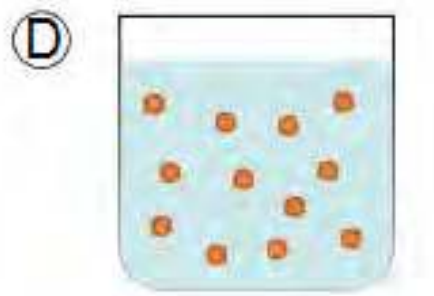
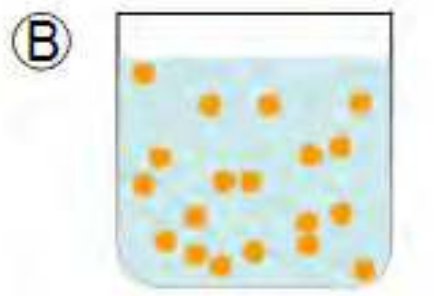
Clay particles as emulsion stabilizers: Pickering («physical») emulsions






Emulsions (= Systems of MANY drops) are important in many every day and industrial contexts such as:

- in **foods**,
- in the **paint, dyeing and tanning industries**,
- in the manufacture of **synthetic rubber and plastics**,
- in the preparation of **cosmetics** such as shampoos,
- in salves and **pharmaceutical products** for drug delivery,
- in the **petroleum industry** for certain drilling muds, for enhanced oil recovery, in oil refining and oil separation (de-emulsification) and oil&gas transport.

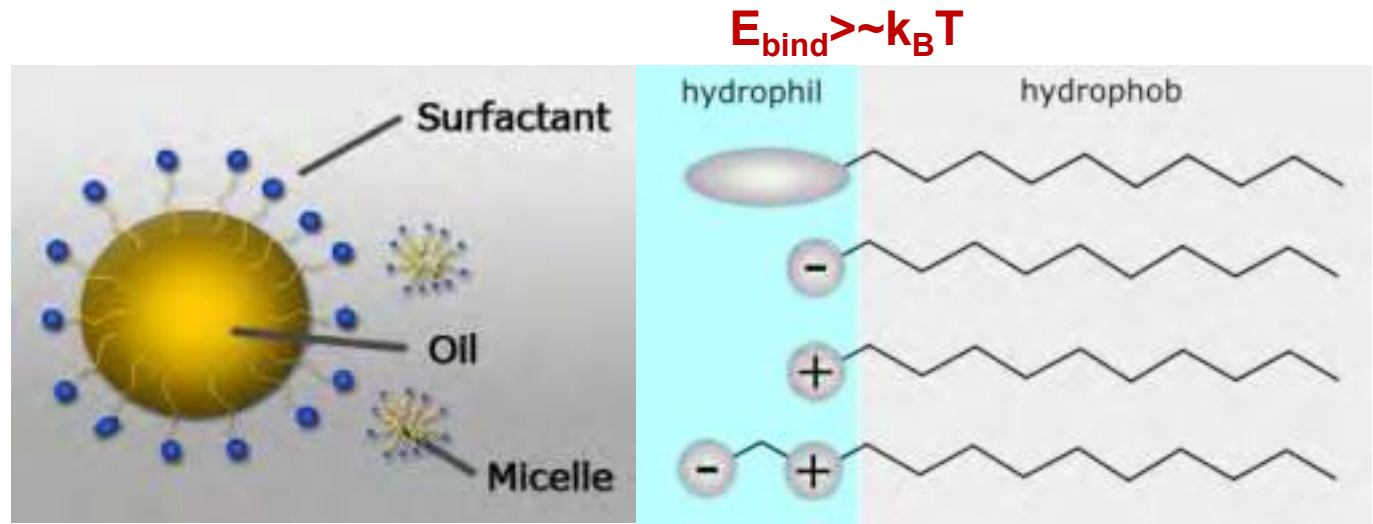
«Classical» («chemical») emulsions



Legend

-  Phase I
-  Phase II
-  Surfactant

- A. Two immiscible liquids, not emulsified
- B. Emulsion of Phase II dispersed in Phase I
- C. The unstable emulsion progressively separates
- D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion



«Classical» («chemical») emulsions



"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Congelation). — Preliminary Account." By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. GOTCH, F.R.S. Received June 8,—Read June 18, 1903.

J. Chem. Soc., Trans., 1907,91, 2001-2021

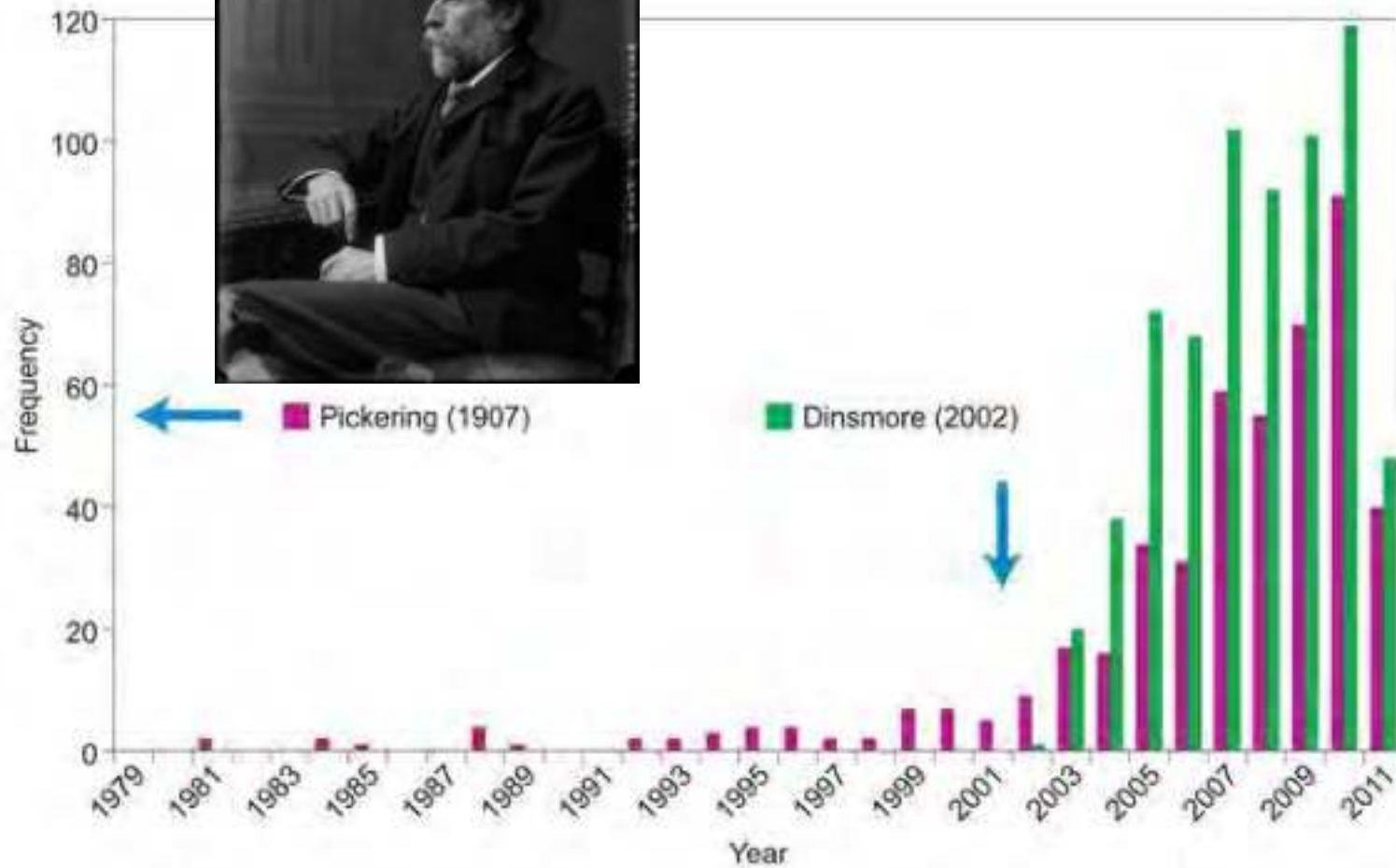
CXCVI.—*Emulsions.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Percival Spencer Umfreville Pickering (1858 –1920)

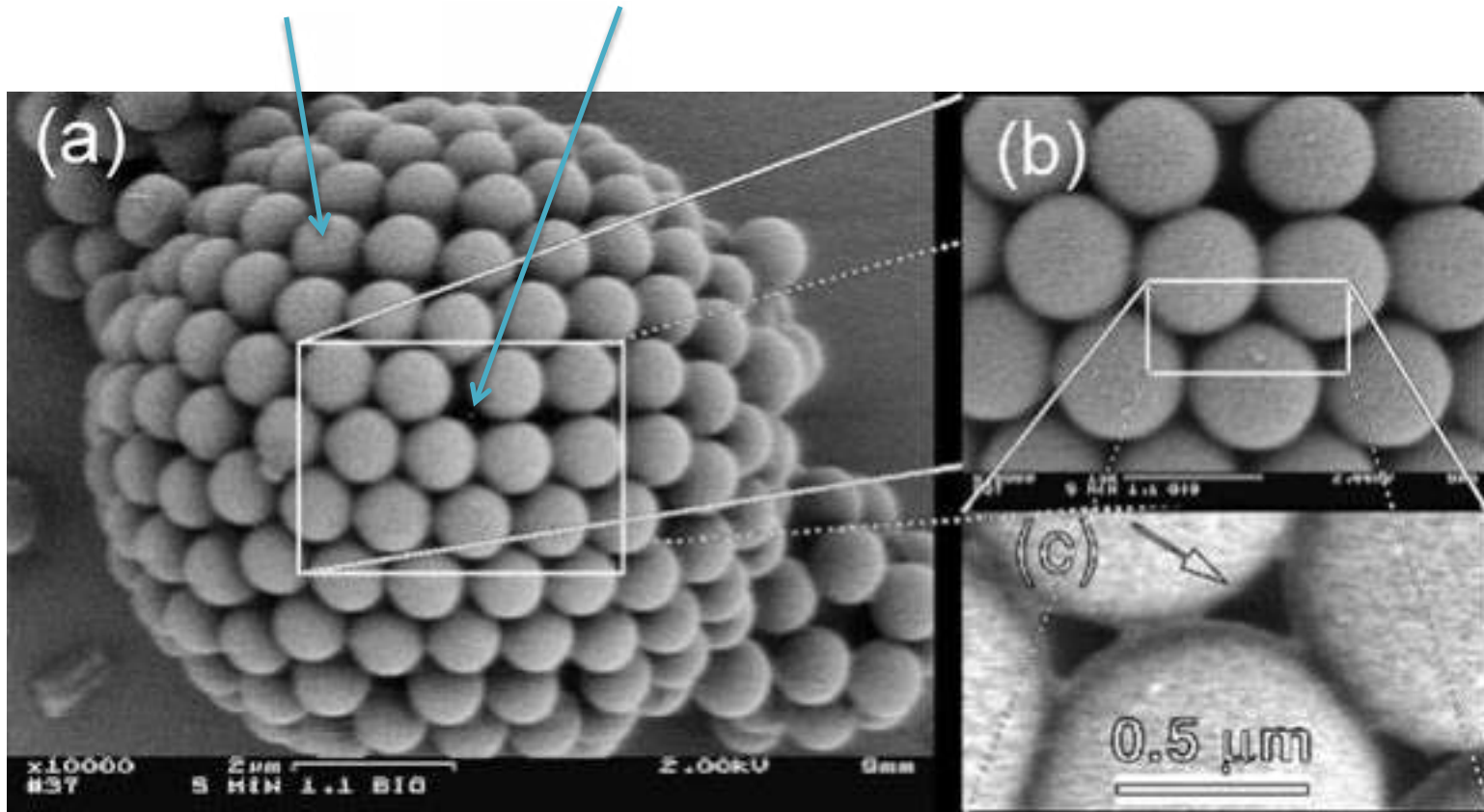
Percival Spencer Umfreville Pickering (1858–1920)



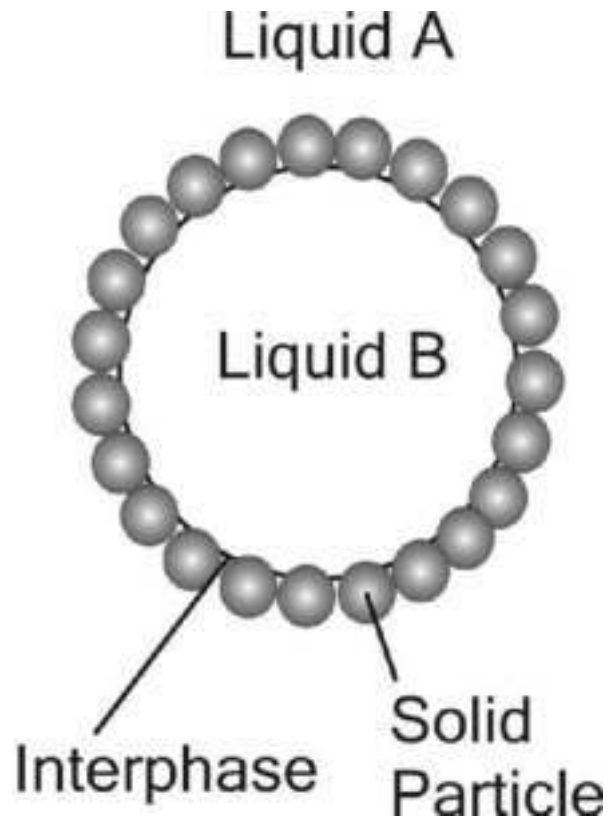
Lost history versus good science, Qian Wang, & Chris Toumey,
Nature Chemistry 3, 832–833, doi:10.1038/nchem.1179 (2011)

Colloidosomes

Composition and permeability



A.D. Dinsmore et. Al., Science, **298**, 1006 (2002); David Weitz group: Harvard Univ.



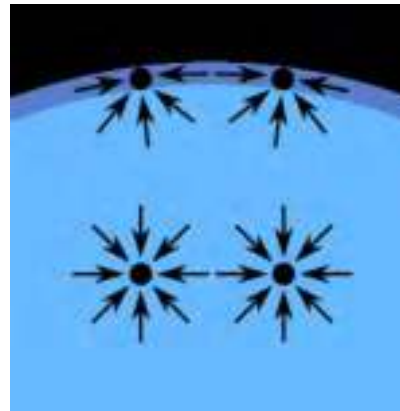
Surface Energy: $E = \gamma A$

A = Surface area $\gamma_{WA} = 0.0073 \text{ N/m}$

Capillary binding: A particle at the interface is trapped in a capillary barrier with a substantial energy cost of moving to either side of the liquid interface.

Origin of capillary binding:
Surface tension:

The forces on molecules of a liquid:

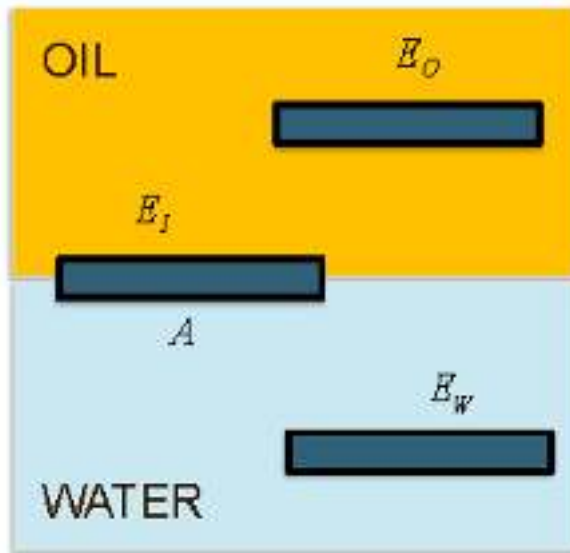


Surface tension preventing a paper clip from submerging



Capillary binding

Capillary binding of a flat solid particle at a liquid interface



Particle surface energy :

$$E_O = 2A\gamma_{SO}$$

$$E_W = 2A\gamma_{SW}$$

$$E_I = A\gamma_{SO} + A\gamma_{SW} - A\gamma_{OW}$$

Energy gain :

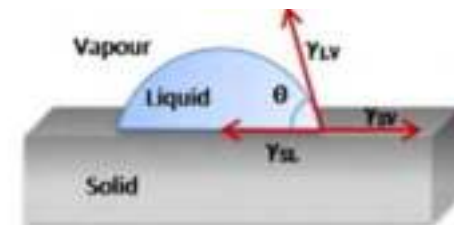
$$E_I - E_O = -A\gamma_{OW}(1 + \cos \theta)$$

$$E_I - E_W = -A\gamma_{OW}(1 - \cos \theta)$$

Wetting angle Young's relation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW} \cos \theta$$

Energetically favorable to adsorb particles at the interface.

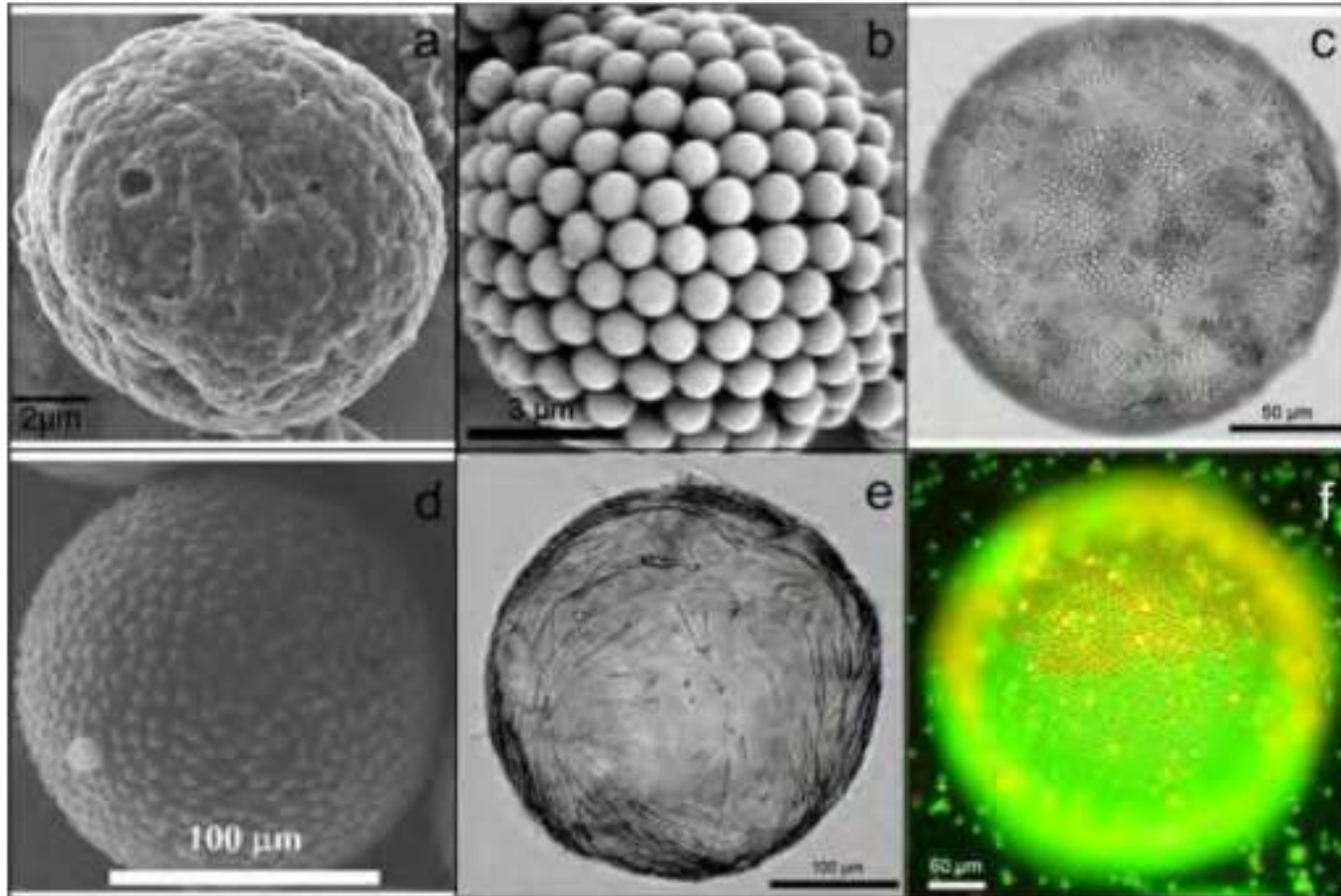


Typically:

$A_p\gamma_{OW} \sim 10000 \text{ kT}$ for microparticles

Pickering (1907) : Emulsions

Dinsmore et al. Science (2002): "Colloidosomes"



Dinsmore et.al.

Article | OPEN

Transition from glass- to gel-like states in clay at a liquid interface

A. Gholamipour-Shirazi, M. S. Carvalho, M. F. G. Huila, K. Araki, P. Dommersnes & J. O. Fossum

Scientific Reports 6,

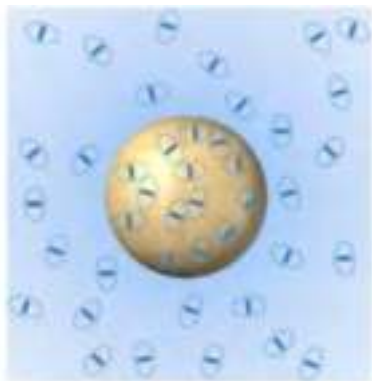
Article number: 37239 (2016)

doi:10.1038/srep37239

Received: 01 April 2016

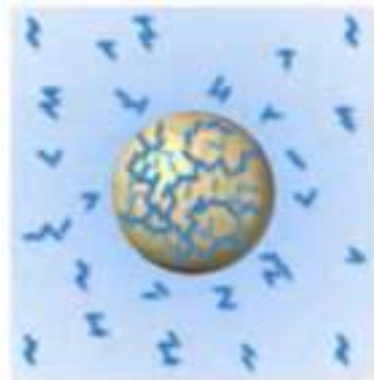
Accepted: 18 October 2016

Published online: 24 November 2016



No salt:

Pickering film not observable by Raman microscopy. Observable surface tension.



With salt:

~ 4 μm Pickering film. Increased surface tension.



The European Physical Journal Special Topics

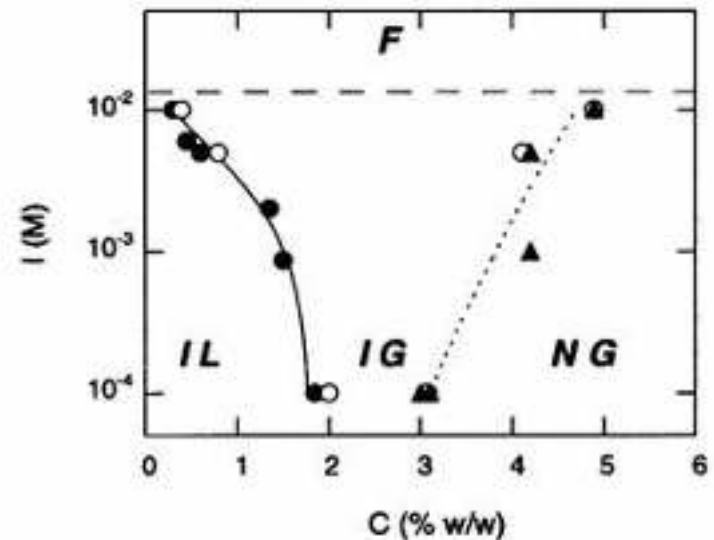
July 2016, Volume 225, Issue 4, pp 757–765

Controlled microfluidic emulsification of oil in a clay nanofluid: Role of salt for Pickering stabilization

Authors

Authors and affiliations

A. Gholamipour-Shirazi, M.S. Carvalho, J.O. Fossum



RELEVANCE OF CLAYS

Clay avalanches



Clay avalanches: Rissa Norway 1978

Simple analog landslide experiments

Quick clay and Landslides of Clayey Soils,

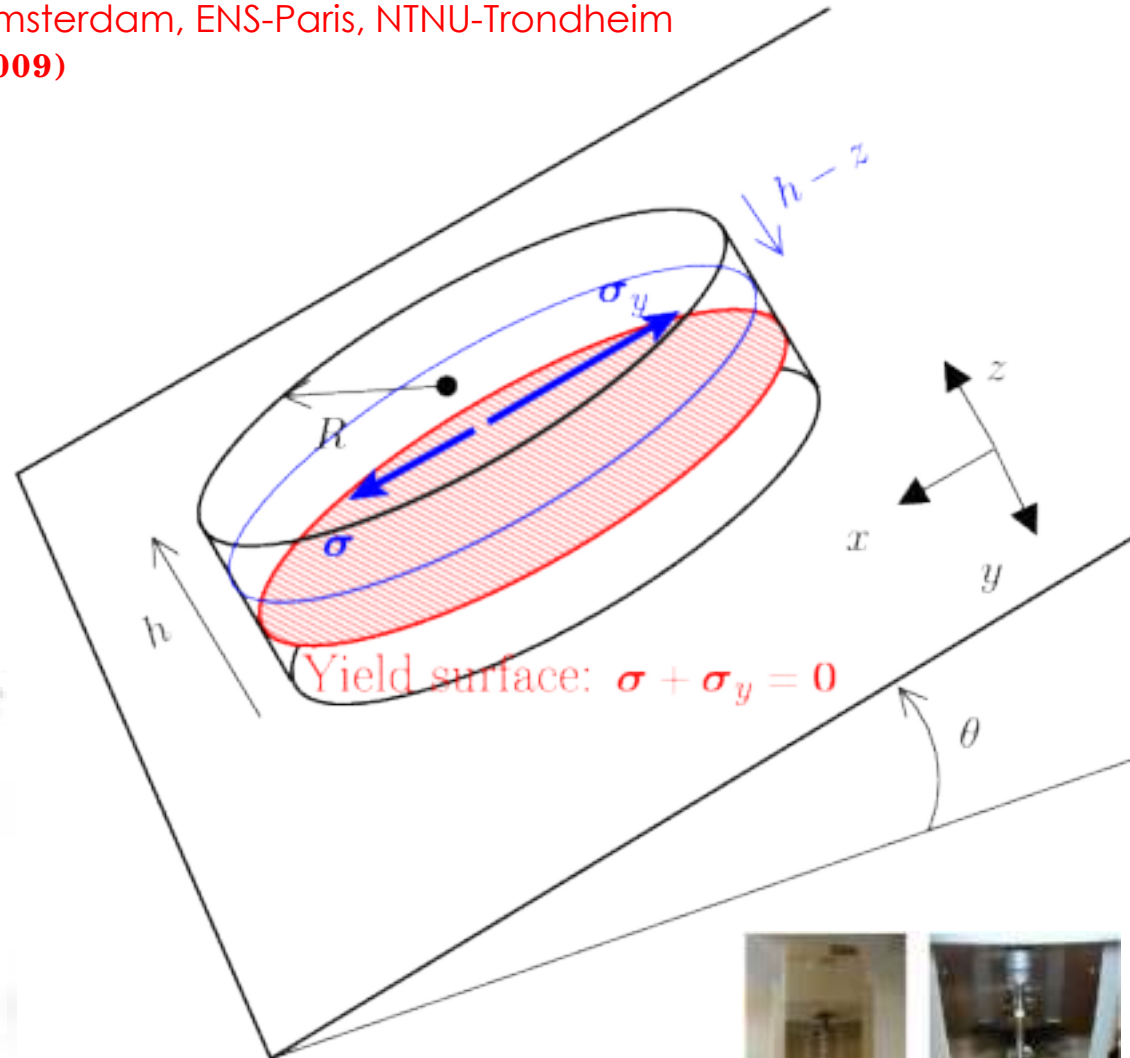
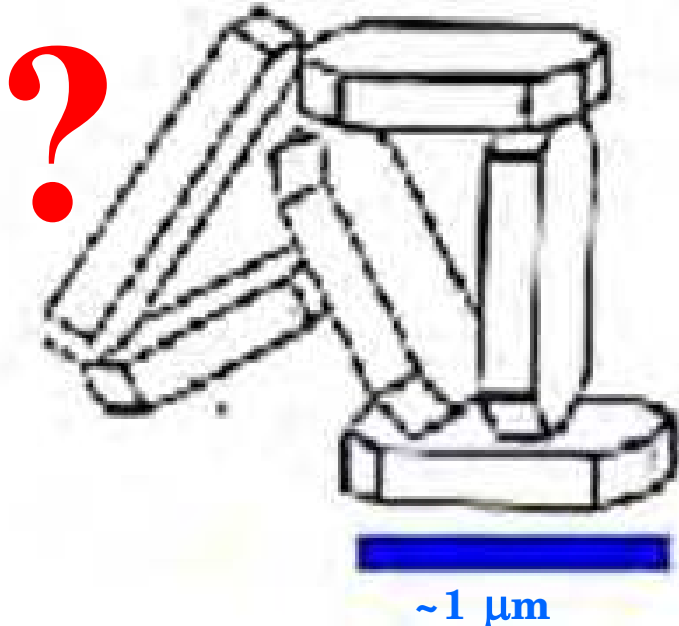
A.Khaldoun, P.Moller, A. Fall, G.Wegdam, B. De Leeuw, Y. Meheust, J.O. Fossum, D. Bonn, Géosciences Rennes 1, University of Amsterdam, ENS-Paris, NTNU-Trondheim

Physical Review Letters 103, 188301 (2009)

$$\sigma(z) = \rho g (h - z) \sin \theta$$

(null at the free surface)

All material above the yield surface is expected to flow



Clays in ENERGY and Environment

Part geological formation
Drilling muds
Oil refining



Clays in SOFT NANOTECHNOLOGY

Clays are shear-thinning materials, like for example ketchup or toothpaste

Elastic behavior below threshold stress

Newtonian (or non-Newtonian) flow above threshold stress

Striped toothpaste:



The colors do not mix because there are clay nanoplatelet particles mixed into each color? Is it true?



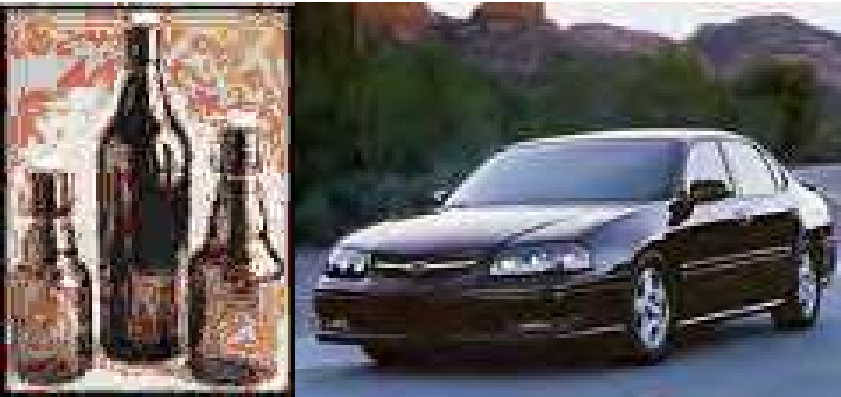
Clays in Advanced MATERIALS

Polymer Nanocomposite Materials:

Adding nanoparticle (clays) to polymer matrix:

Central issues:

- Dispersion
- Selfassembly, and alignment of clay platelet particles
- Liquid Crystalline like ordering



Clays in BIONANOTECHNOLOGY

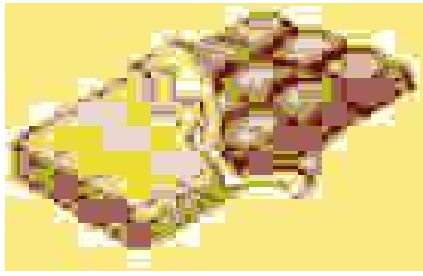
Parrots of the Amazones:

Parrots of the Amazon eat clay at riverbanks for breakfast in order to prevent stomach-ache from alkaloid poisons of the seeds in the fruits they eat for lunch.

Shows that clays may be interesting drug delivery systems



Other "places" where clays are important:



CLAY MINERALS AND THE ORIGIN OF LIFE

Edited by

A. G. GAIRNS-SMITH

*Department of Chemistry,
University of Glasgow*

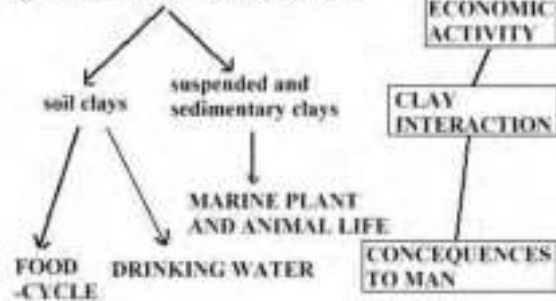
and

H. HARTMAN

*Department of Earth and
Planetary Sciences,
Massachusetts Institute of Technology*



agricultural and industrial chemicals



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Melbourne Sydney



PHYSICS:

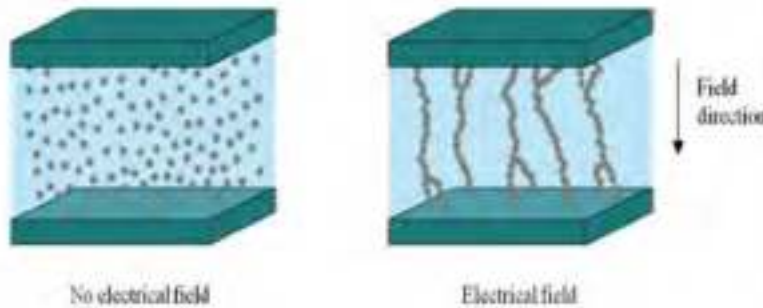
CLAYS IN OIL



NTNU – Trondheim
Norwegian University of
Science and Technology

Electro-rheological fluids

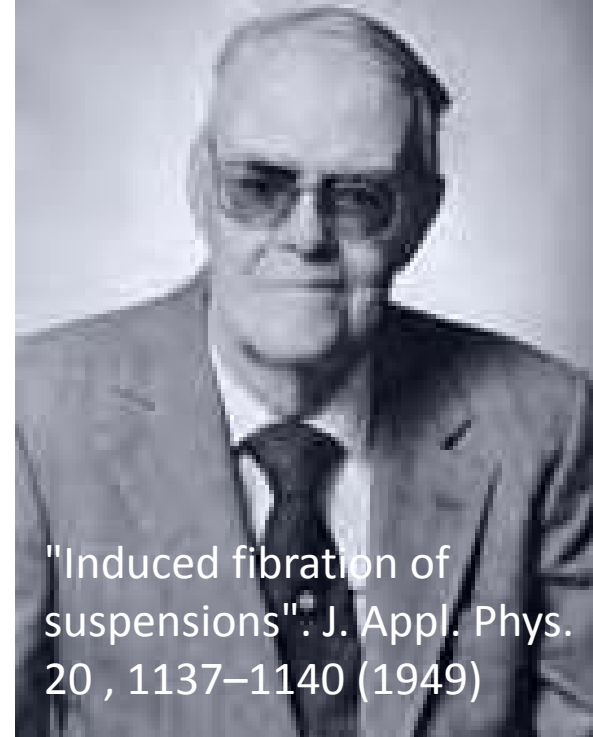
Winslow effect:



Viscosity can increase by a factor 100 000 in response to an electric field!

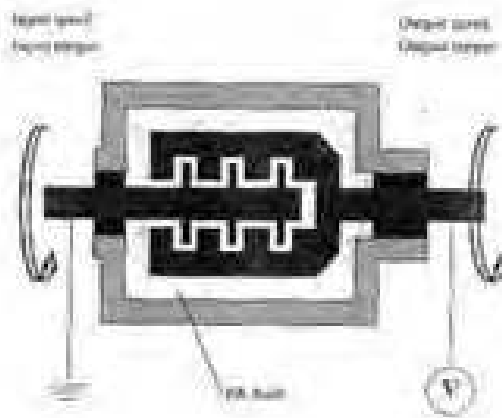
- Electric fields induce dipole attraction and chain formation
- Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)

Winslow, Willis M.



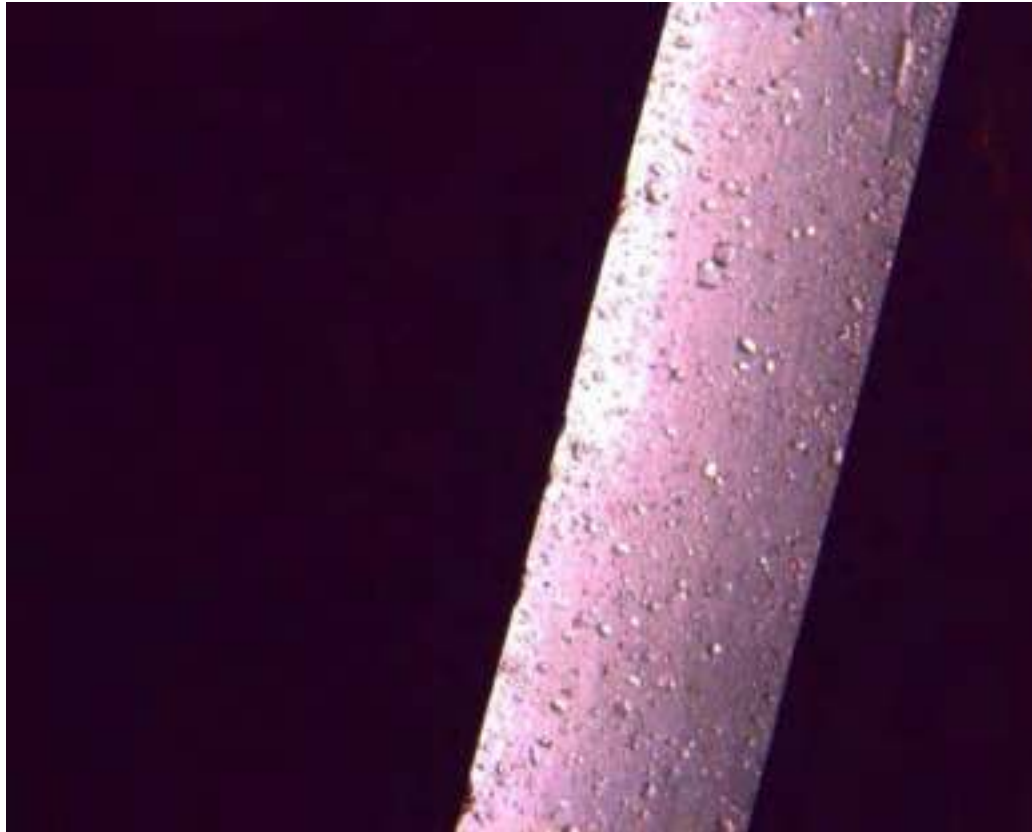
"Induced fibrillation of suspensions". J. Appl. Phys. 20 , 1137–1140 (1949)

U.S. Patent 2,417,850:
Winslow, W. M.: 'Method and means for translating electrical impulses into mechanical force', 25 March 1947



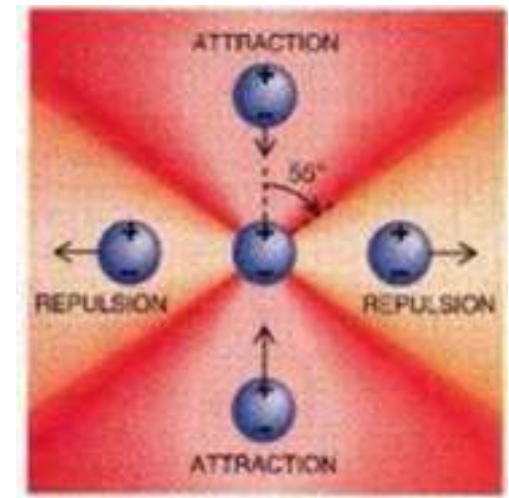
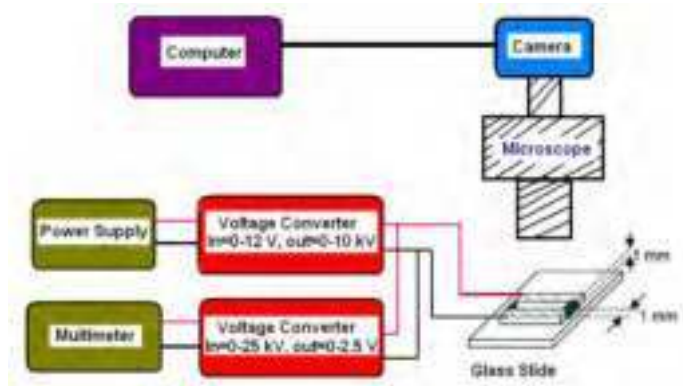
Clay particles suspended in oil:

Video microscopy (real time):



- ~500 V -

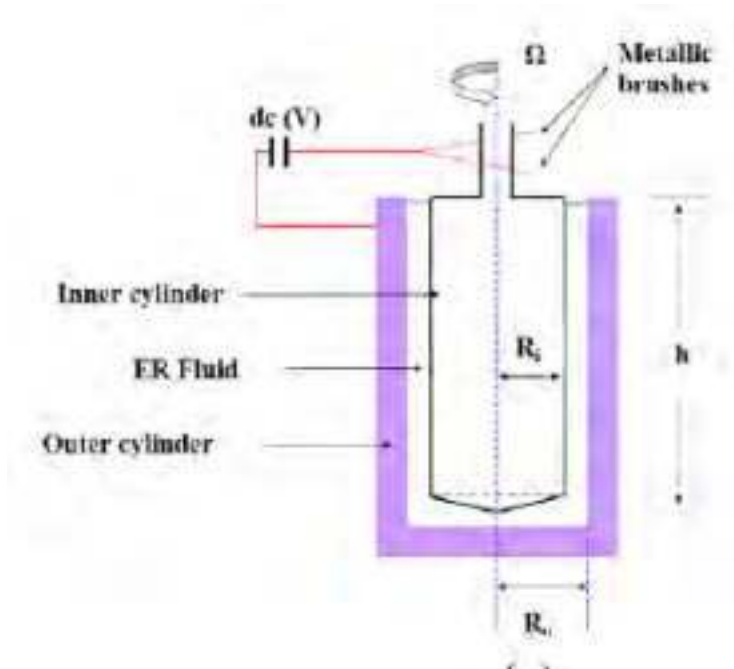
- 1 mm -



**Electrorheology:
Smart Materials**

Intercalation-enhanced electric polarization and chain formation of nano-layered particles, J.O. Fossum, Y. Méheust, K.P.S. Parmar, K.D. Knudsen, K.J. Måløy and D. M. de Fonseca, Europhys. Lett., 74, 438-444 (2006)

Our Physica MCR 300 Rheometer inl electrorheol. cell:



Langmuir 24, 1814 (2008)

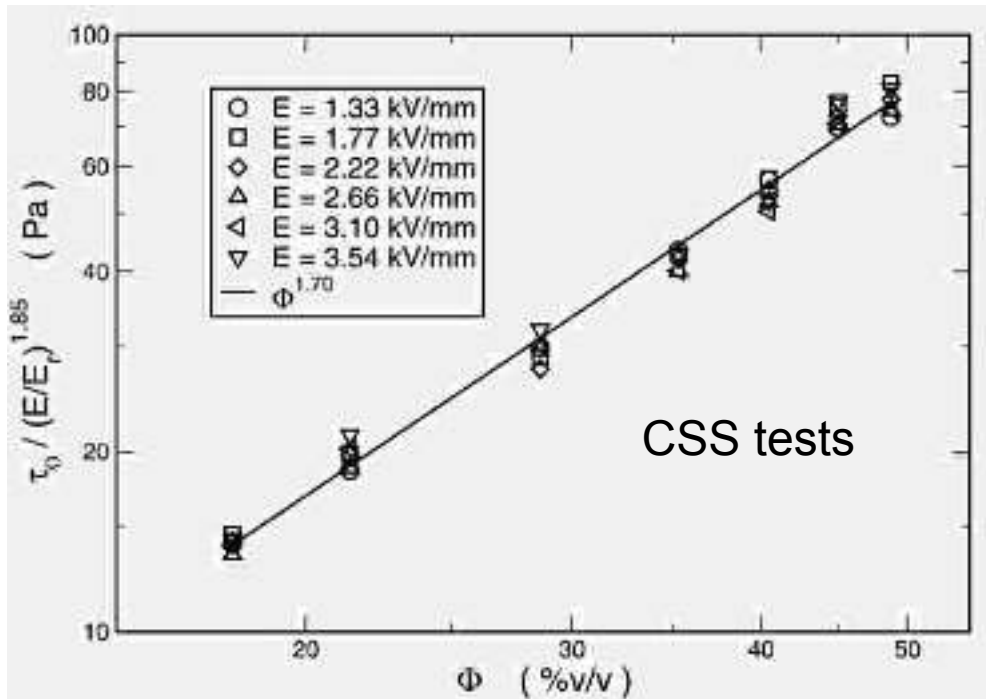
J. Phys.: Condens. Matter 22, 324104 (2010)

J. Rheol. 55, 2011 (2010)

Yield stress:

Theories predict:

$$\tau \propto E^\alpha \Phi^\beta$$



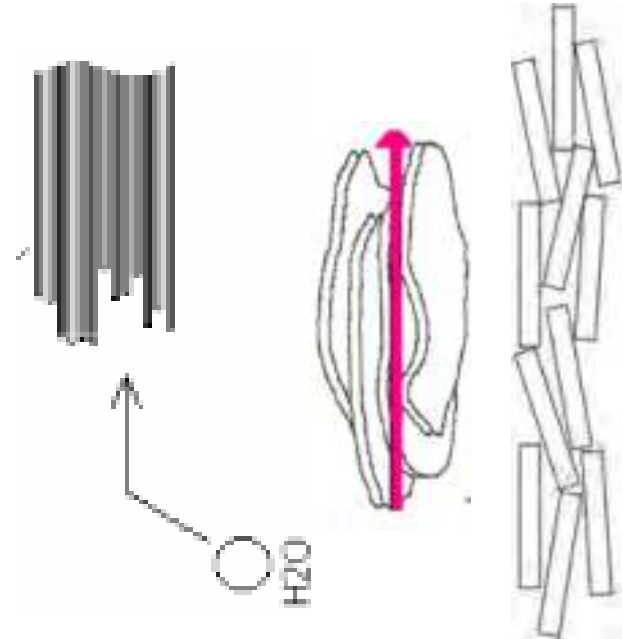
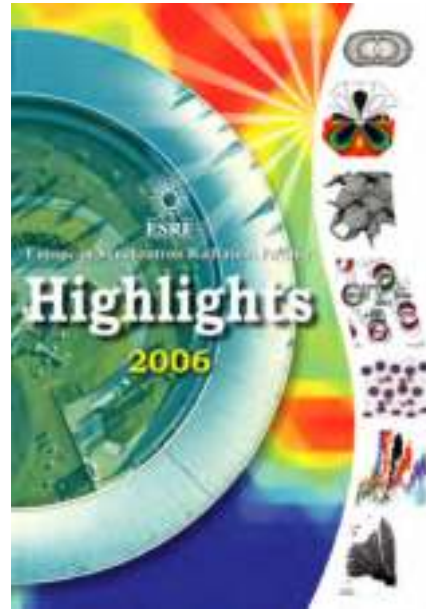
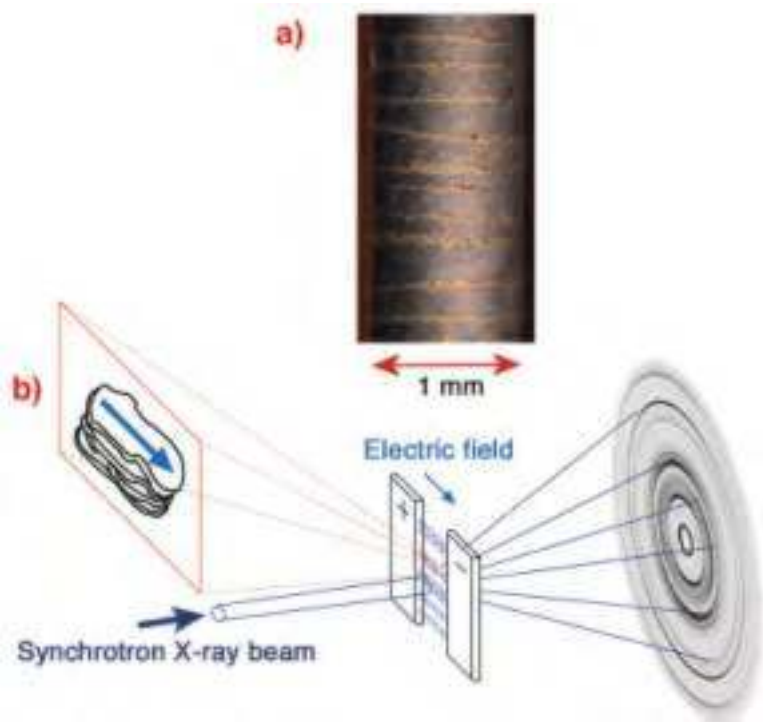
Static yield stress:
Yield stress for an
undisrupted ER fluid.

Log-log plot of the static yield stress, normalized by $E^{1.86}$, vs. the volume fraction at different strengths of the applied electric field. A power law $\beta \approx 1.70$ fits to the whole dataset..

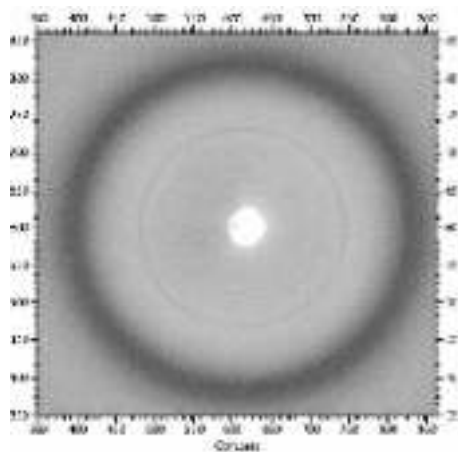
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

ER fluids \rightarrow	our sample	muca ¹²	hematite ⁴¹	saponite ⁴⁴	zeolite ⁴⁵	GER ⁴⁶
$\Phi \rightarrow$	1.9% (v/v)	15% (v/v)	15% (v/v)	0.11 g/mL	30% (v/v)	30% (v/v)
τ_0 (Pa) \rightarrow	~ 20	~ 100	~ 85	~ 50	~ 3000	~ 15000

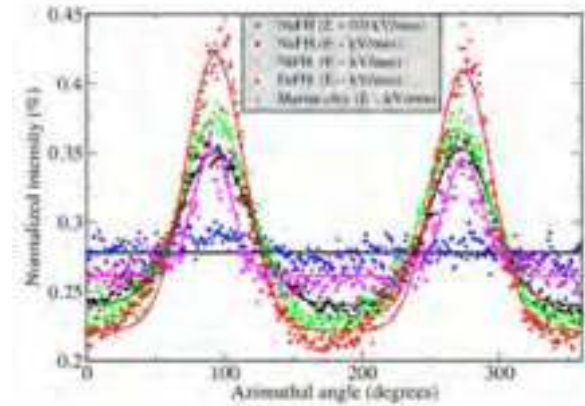
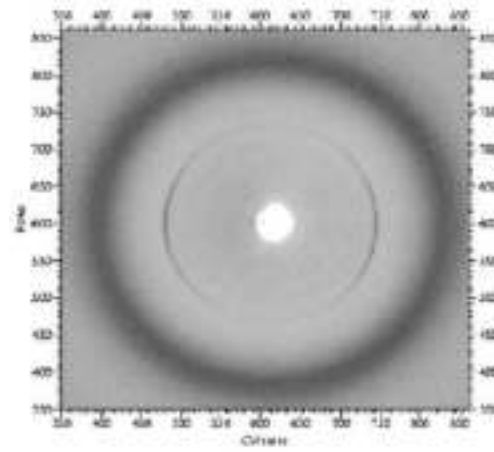
Experiments at ESRF, Grenoble: In ESRF Scientific Highlights 2006



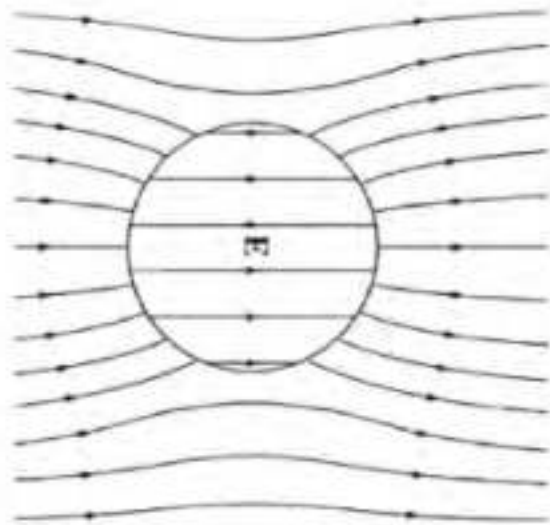
Before: 0 V/mm



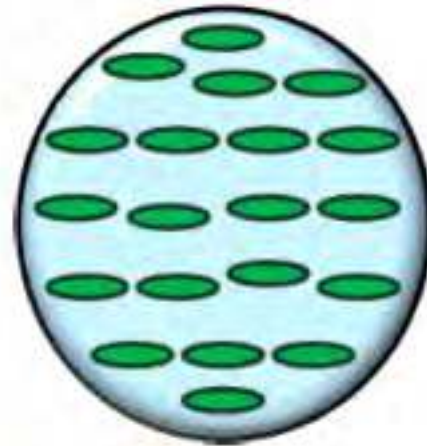
After: 500 V/mm



Angular distribution function
= $S_2 = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle$



Electric field

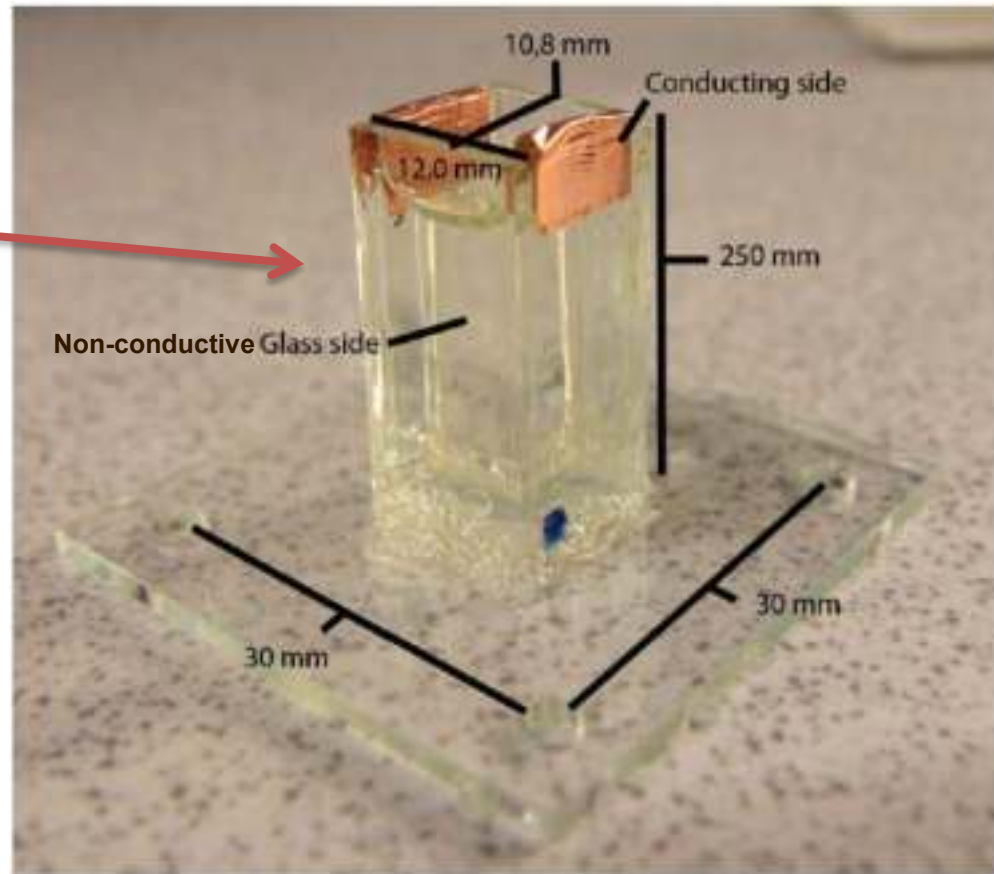


Chain formation inside a drop?

Electrorheological droplets for microfluidics
Electrorheological emulsions

Is it possible to make electrorheological drops?

Sample cell



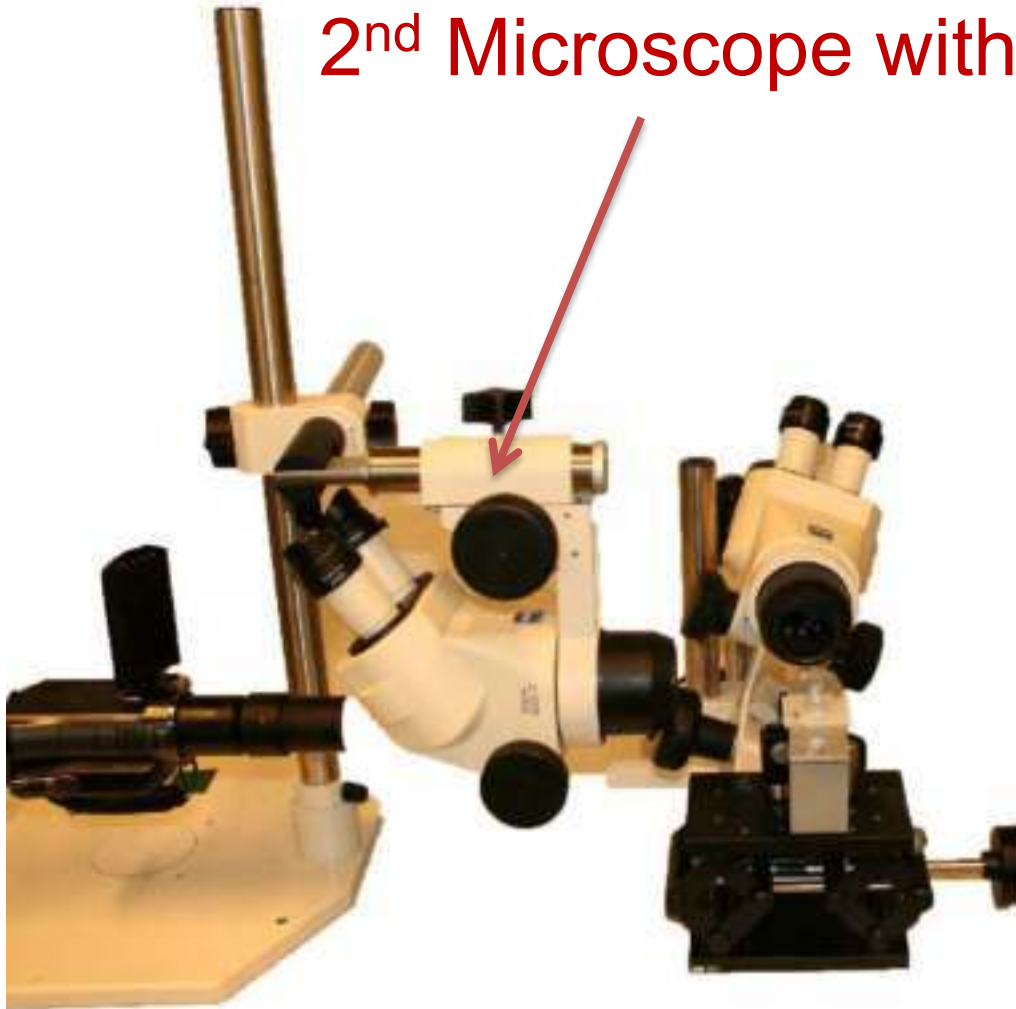
Experimental setup at NTNU Trondheim

1st Microscope with camera

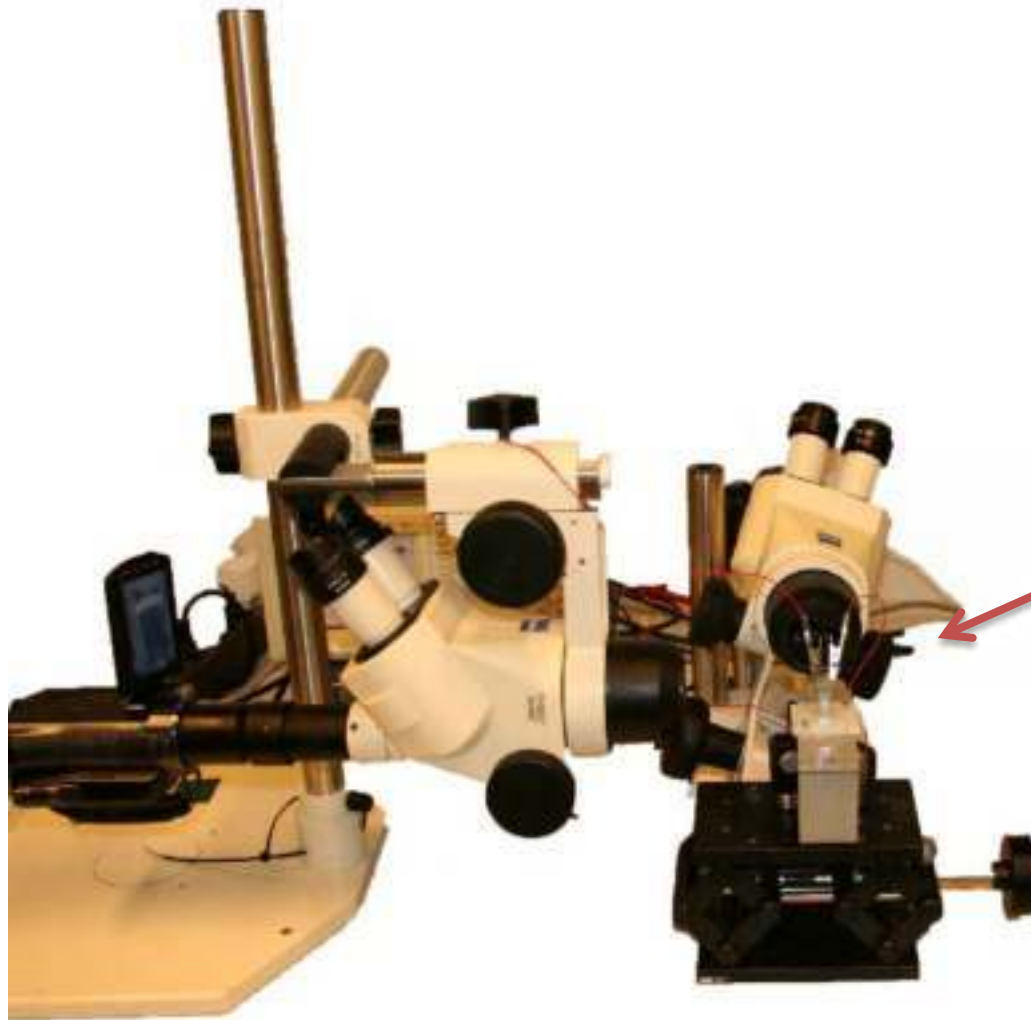


Experimental setup at NTNU Trondheim

2nd Microscope with camera

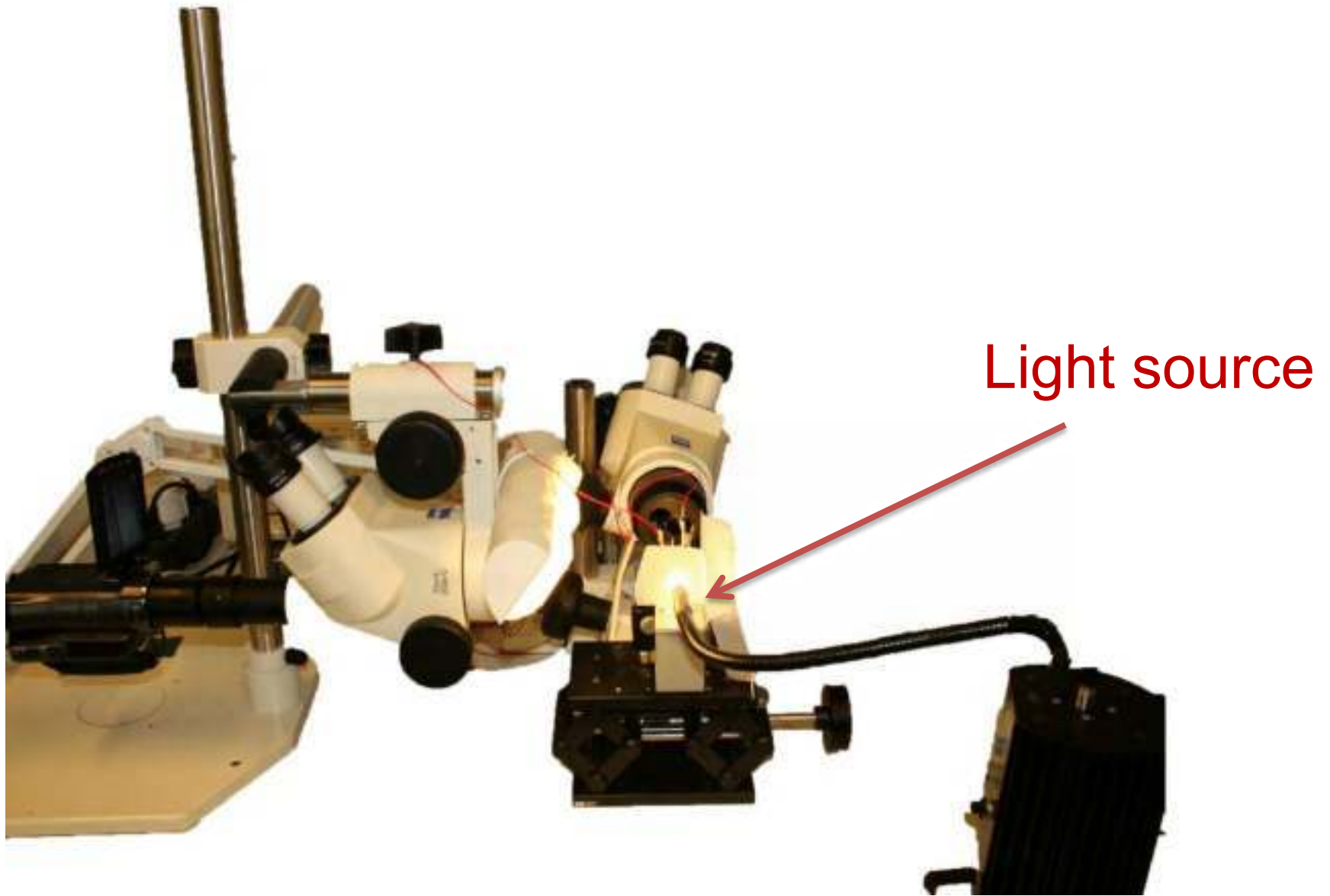


Experimental setup at NTNU Trondheim



Electrodes

Experimental setup at NTNU Trondheim

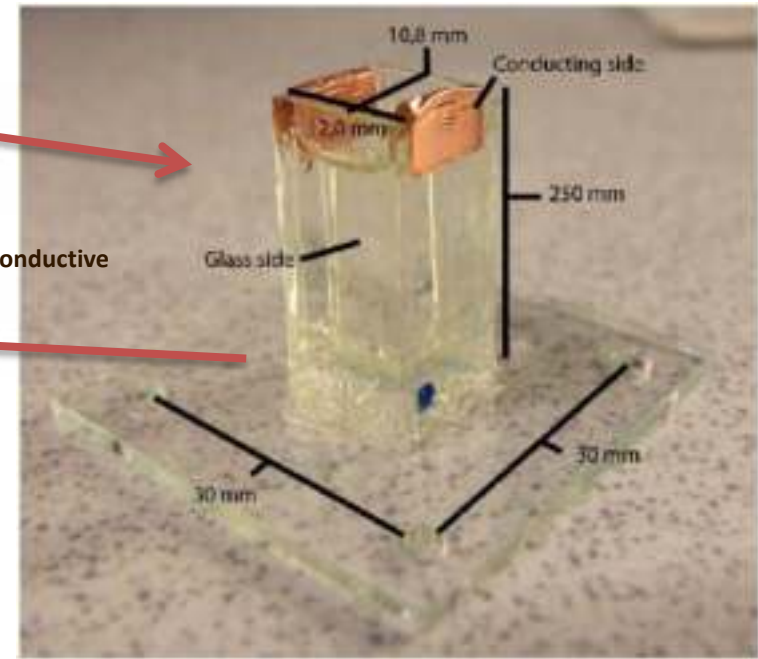


Experimental setup at NTNU Trondheim

Sample cell

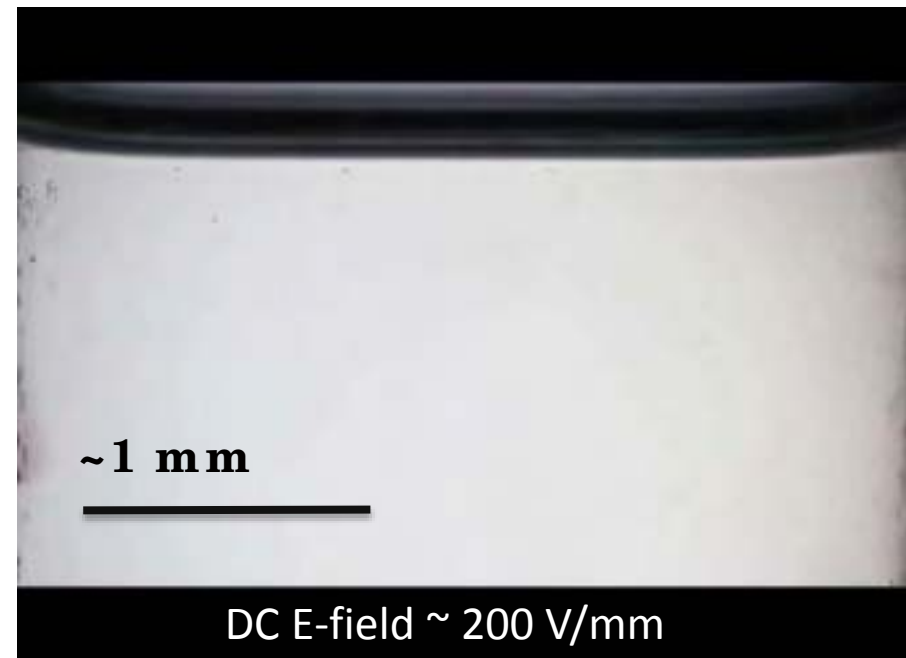
2x ITO transparent electrodes

2x glass walls

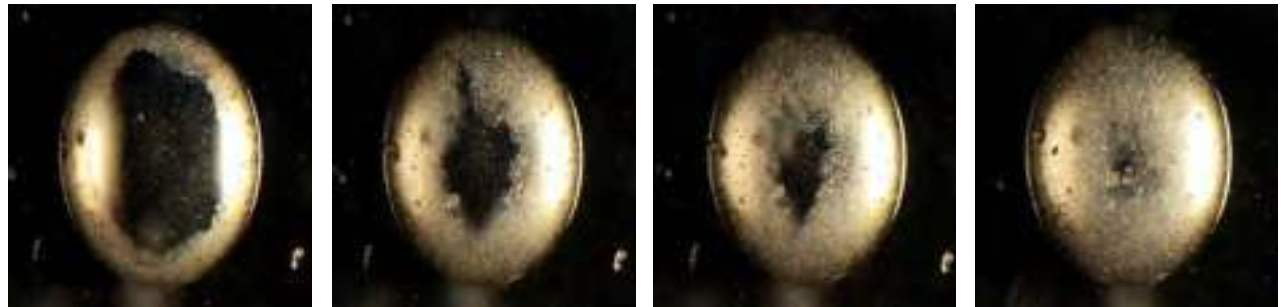


Clay in silicone oil dispersion
(~ 1 mm diameter drop)

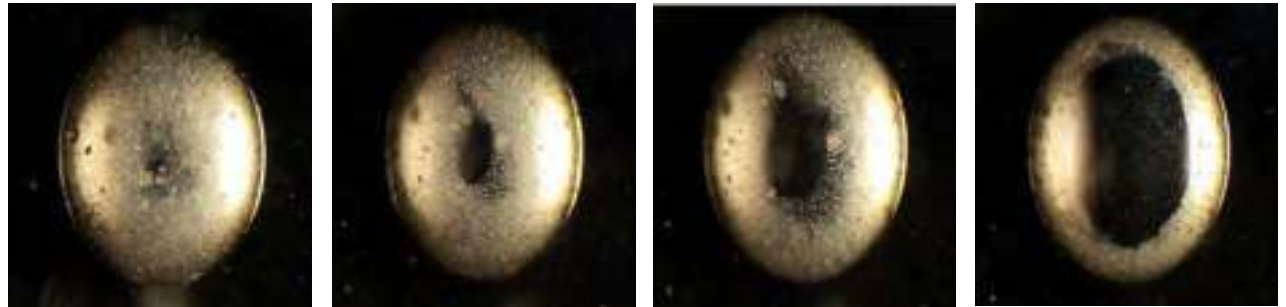
Castor oil
(continuous phase)



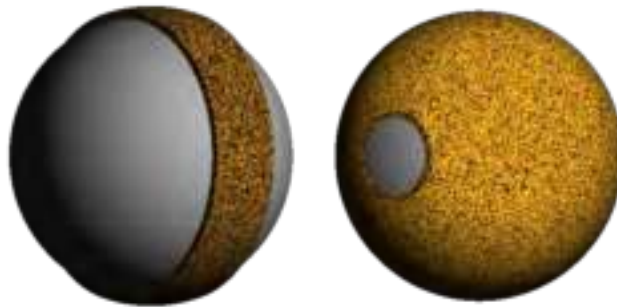
200 \longrightarrow 500 V/mm



200 \longleftarrow 500 V/mm



Electro-hydrodynamic flow



Dipole-dipole interactions

Active pupil-like colloidal shell (opening - closing)

Active structuring of colloidal armour on liquid drops

Paul Dommersnes^{1,2,3,4,*}, Zbigniew Rozynek^{1,*}, Alexander Mikkelsen¹, Rene Castberg², Knut Kjerstad¹, Kjetil Hersvik³ & Jon Otto Fossum^{1,4,*}

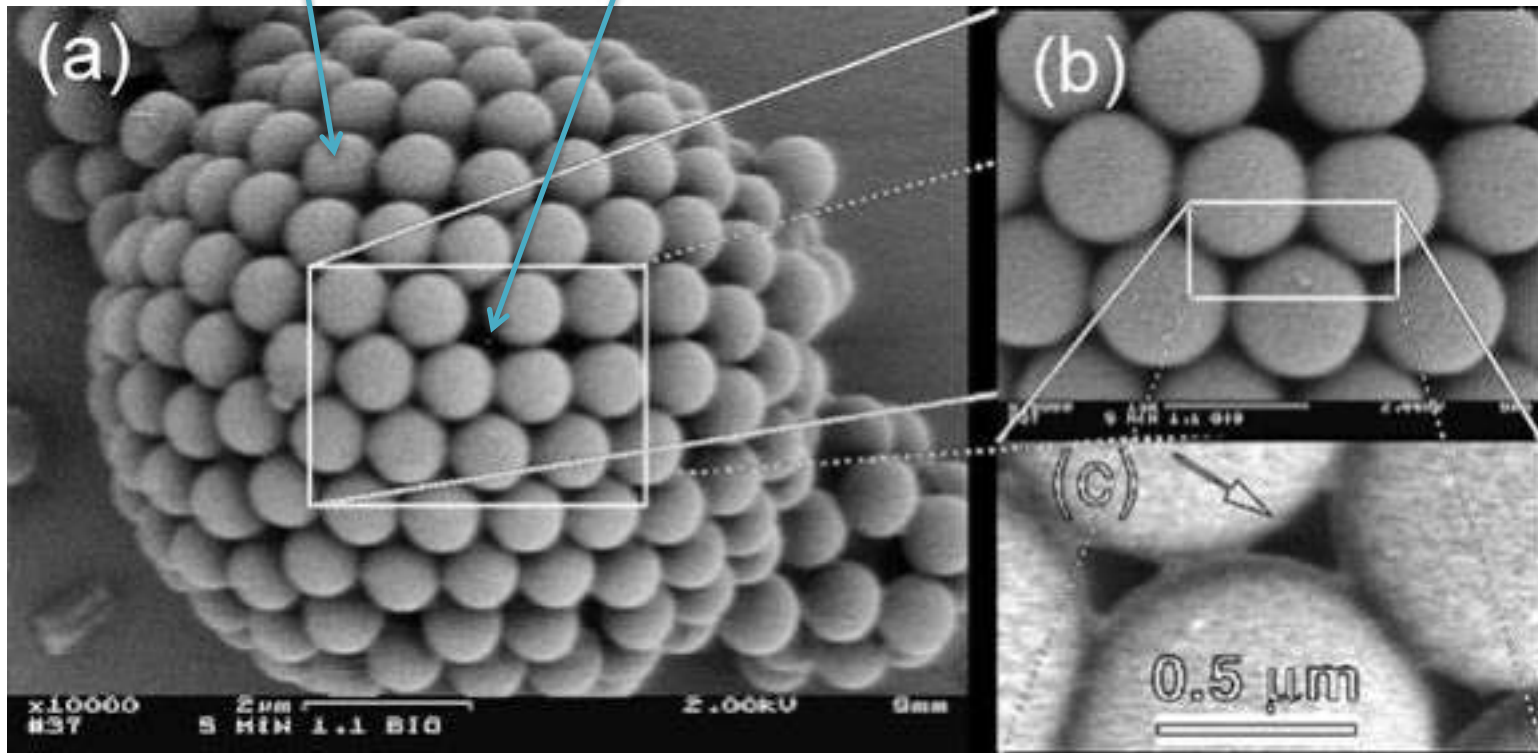
NATURE COMMUNICATIONS | 4:2066 | DOI: 10.1038/ncomms3066



Active pupil-like colloidal shell (opening - closing)

Dynamic Colloidosome

Composition and permeability

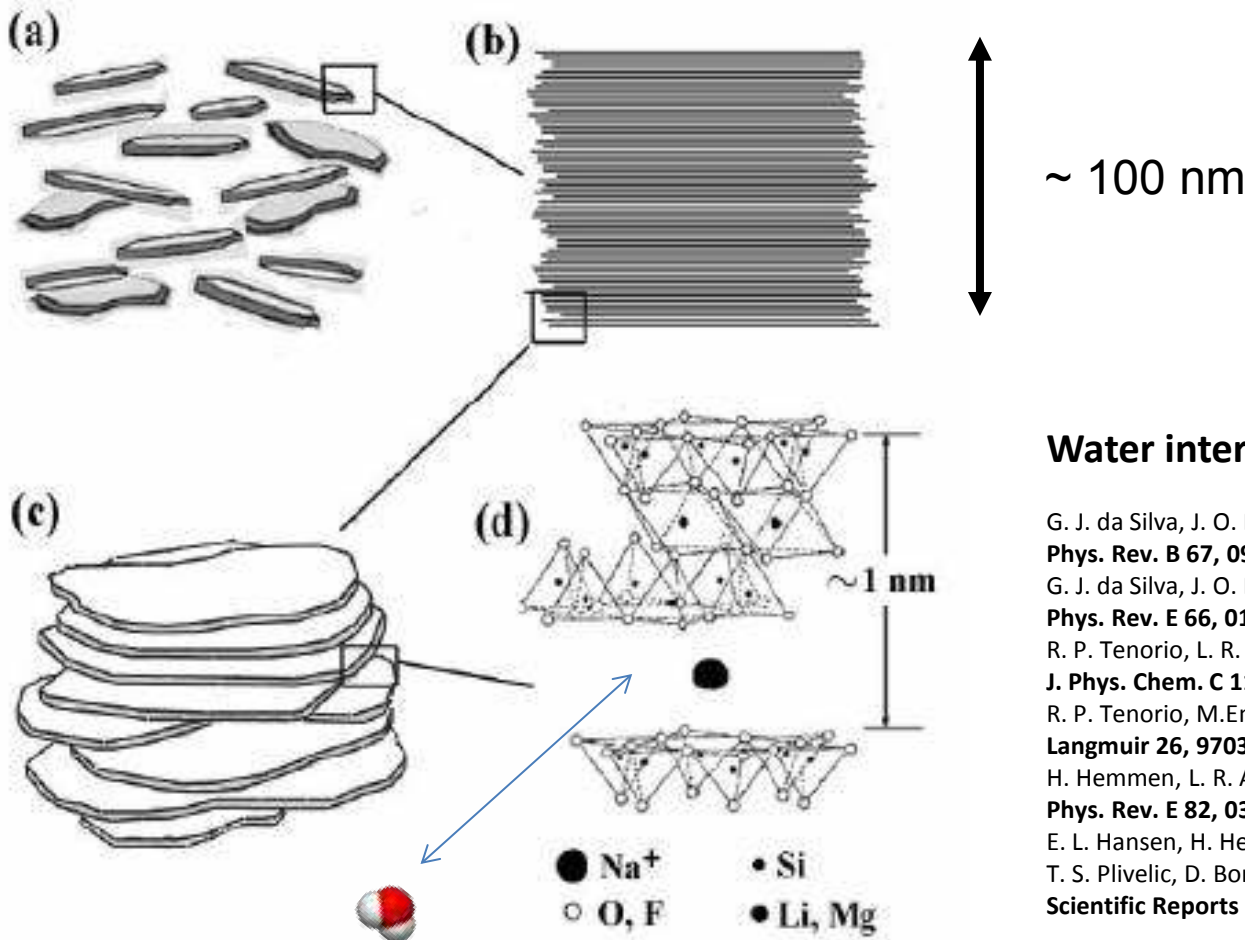


MOLECULAR INTERACTIONS WITH CLAYS: H₂O, CO₂, DRUGS,.....



Our clay experimental model system:

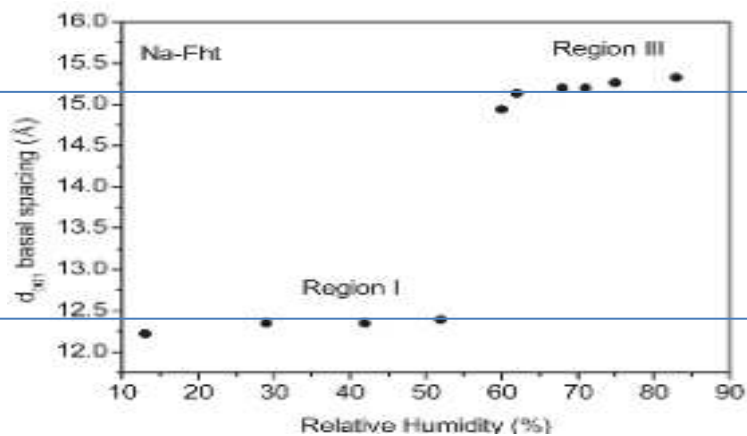
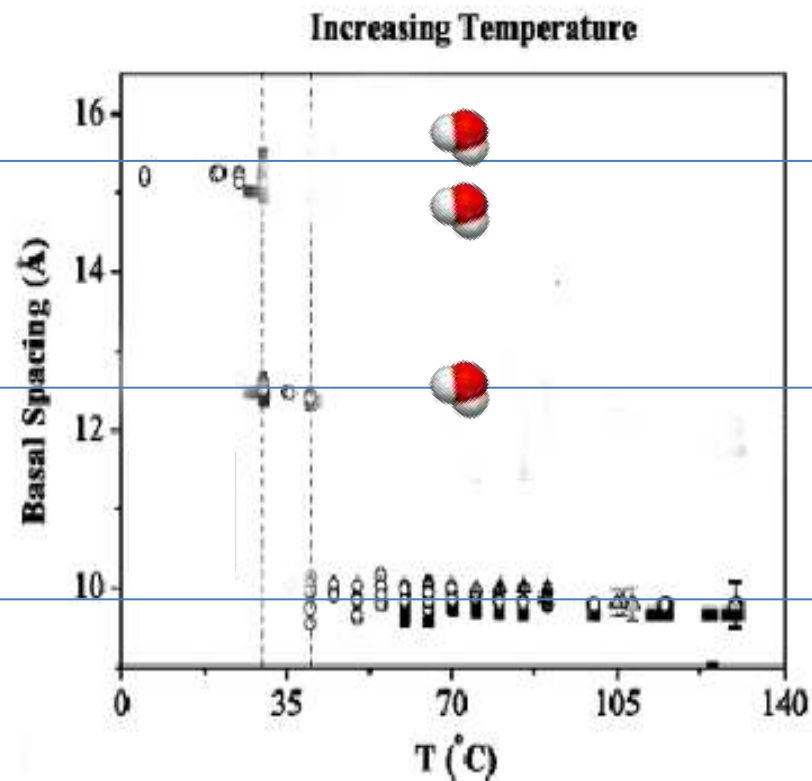
Q-fluorohectorite synthetic clay: $Q_x-(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+ , Li^+ , Ni^{2+} , Fe^{3+} , etc)



Water intercalation:

- G. J. da Silva, J. O. Fossum, E. DiMasi, and K. J. Maloy, **Phys. Rev. B** **67**, 094114 2003.
- G. J. da Silva, J. O. Fossum, E. DiMasi, K. J. Maloy, and S. B. Lutnaes, **Phys. Rev. E** **66**, 011303 2002.
- R. P. Tenorio, L. R. Alme, M. Engelsberg, J. O. Fossum, and F. Hallwass, **J. Phys. Chem. C** **112**, 575 2008.
- R. P. Tenorio, M. Engelsberg, J. O. Fossum, and G. J. da Silva, **Langmuir** **26**, 9703 2010.
- H. Hemmen, L. R. Alme, J. O. Fossum and Y. Meheust, **Phys. Rev. E** **82**, 036315 2010.
- E. L. Hansen, H. Hemmen, D. M. Fonseca, C. Coutant, K. D. Knudsen, T. S. Plivelic, D. Bonn, J. O. Fossum, **Scientific Reports** **2**, 618 2012

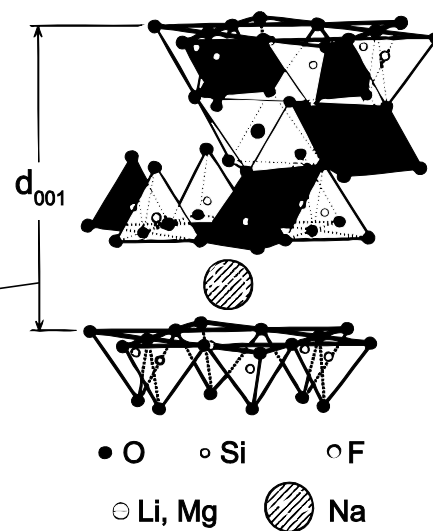
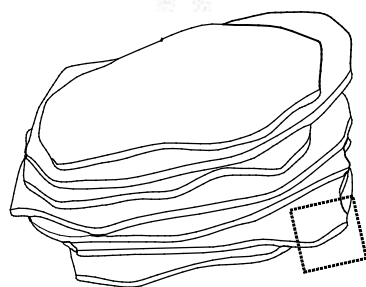
H₂O intercalation controlled by T/RH of sample environment: Na-fluorohectorite powder in humid air



2 wl

1 wl

0 wl



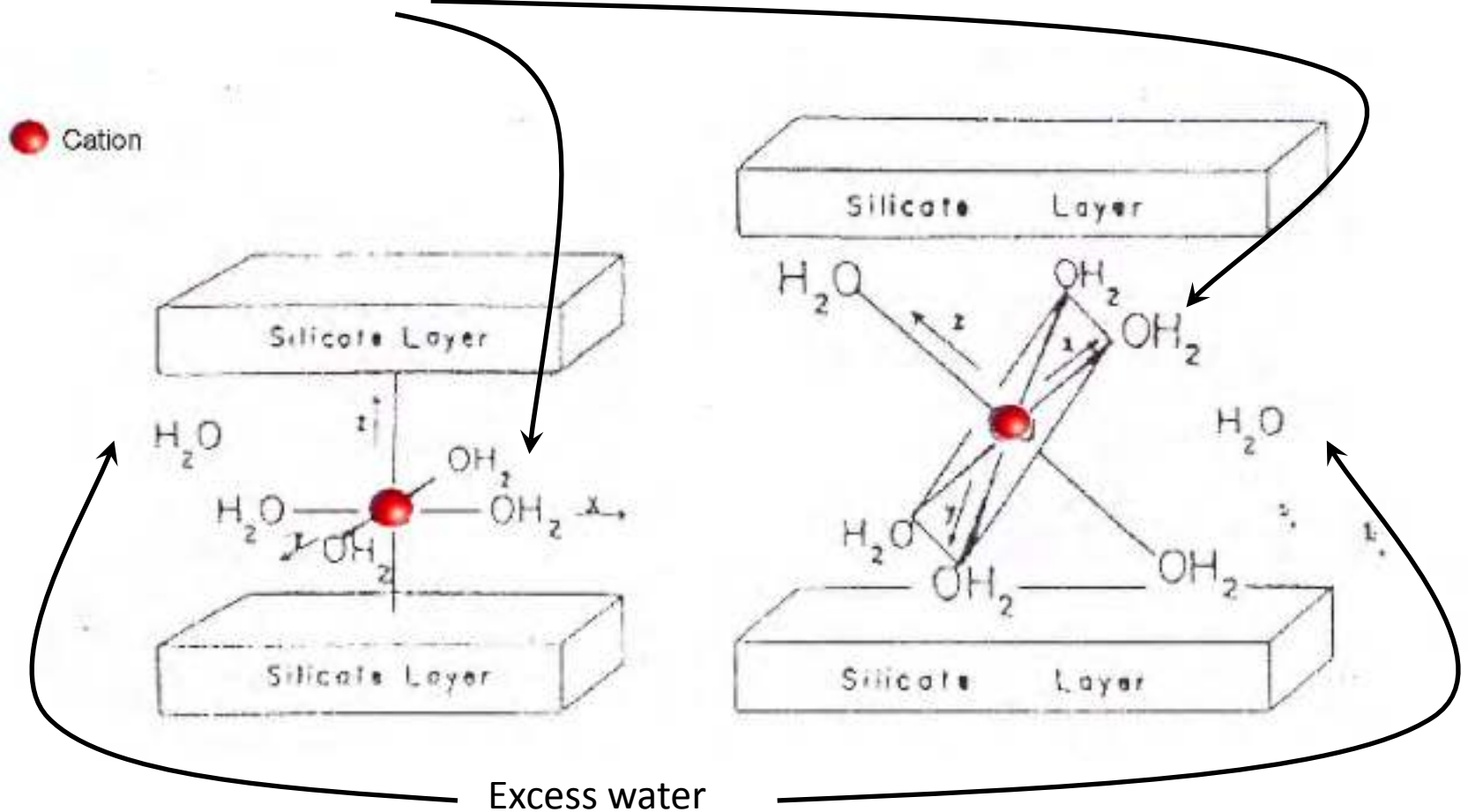
NMR spectroscopy:

R. P. Tenorio, L. R. Alme, M. Engelsberg, J. O. Fossum, and F. Hallwass, *J. Phys. Chem. C* **112**, 575 2008.

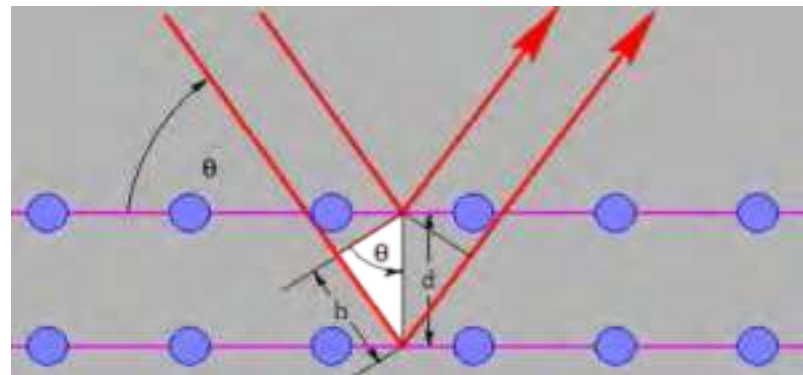
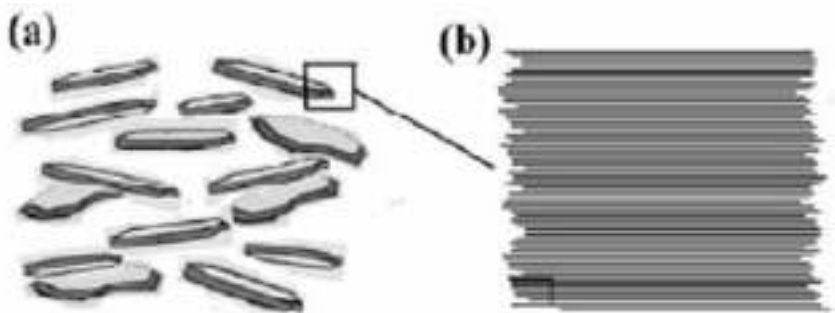
R. P. Tenorio, M. Engelsberg, J. O. Fossum, and G. J. da Silva, *Langmuir* **26**, 9703 2010.

Two kinds of intercalated water:

Water "bound" in ion complexes

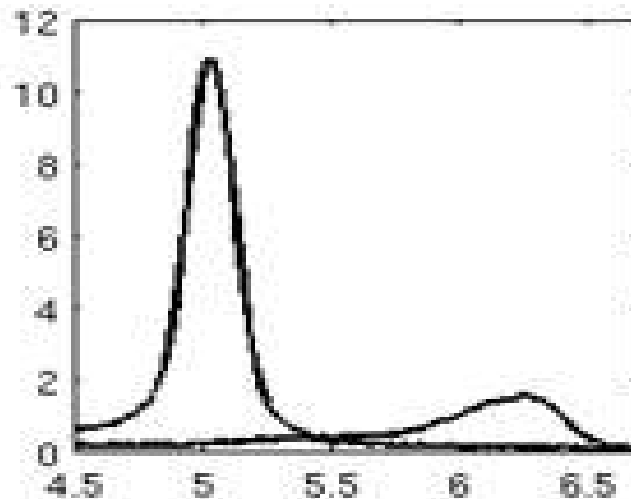
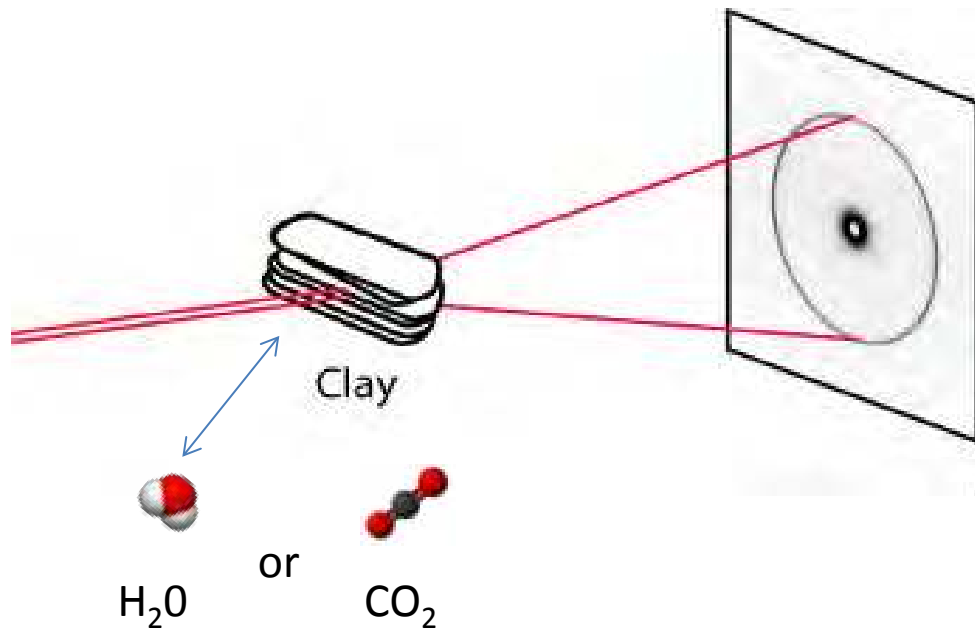


Scattering of X-rays: Bragg's law:



Constructive interference when

$$2h = 2d \sin \theta = n \lambda$$



↑ q (nm⁻¹)

1.25 nm
1 layer H₂O intercalated

↑

1 nm
Dry clay

Before 2012:

**J. J. Fripiat, M. I. Cruz,
B. F. Bohor, J. Thomas.**
*Interlamellar adsorption
of carbon dioxide by
smectites Clays Clay
Miner. 22, 23, (1974).*

*The evidence presented in
this study clearly shows
that CO₂ at about -70 °C
penetrates (intercalates)
the smectite structure to a
degree dependent upon the
nature of the replaceable
interlayer cation.*

Langmuir Letter

dx.doi.org/10.1021/la204164q | *Langmuir* 2012, 28, 1678–1682

**X-ray Studies of Carbon Dioxide Intercalation in Na-Fluorohectorite
Clay at Near-Ambient Conditions**

Henrik Hemmen,^{*†} Erlend G. Rolseth,[‡] Davi M. Fonseca,^{†||} Elisabeth L. Hansen,[†] Jon Otto Fossum,^{*†,§}
and Tomás S. Pivčević[‡]

[†]Department of Physics, Norwegian University of Science and Technology, Høgskoleingen 5, N-7491 Trondheim, Norway

[‡]Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters, Drammensveien 78, N-0271 Oslo, Norway

[§]MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden

^{||}Department of Cancer Research and Molecular Medicine, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

**2012 and later: Large number of publications have
appeared on clays + CO₂**

SCIENTIFIC REPORTS nature.com

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SCIENTIFIC REPORTS | ARTICLE **OPEN**

**Intercalation and Retention of Carbon Dioxide in a
Smectite Clay promoted by Interlayer Cations**

L. Michels, J. O. Fossum, Z. Rozynek, H. Hemmen, K. Rustenberg, P. A. Sobas, G. N.
Kalantzopoulos, K. D. Knudsen, M. Janek, T. S. Pivčević & G. J. da Silva

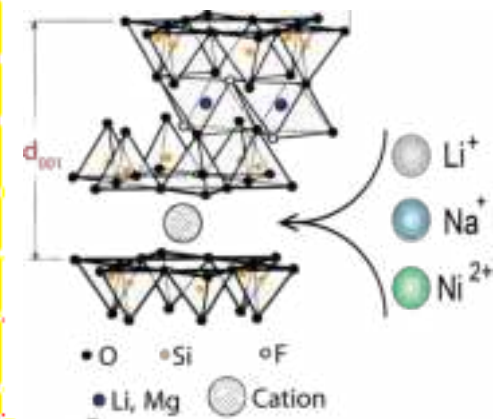
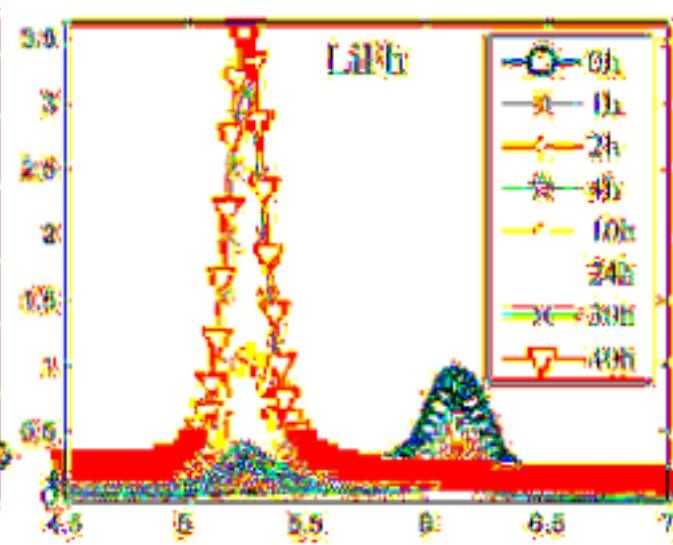
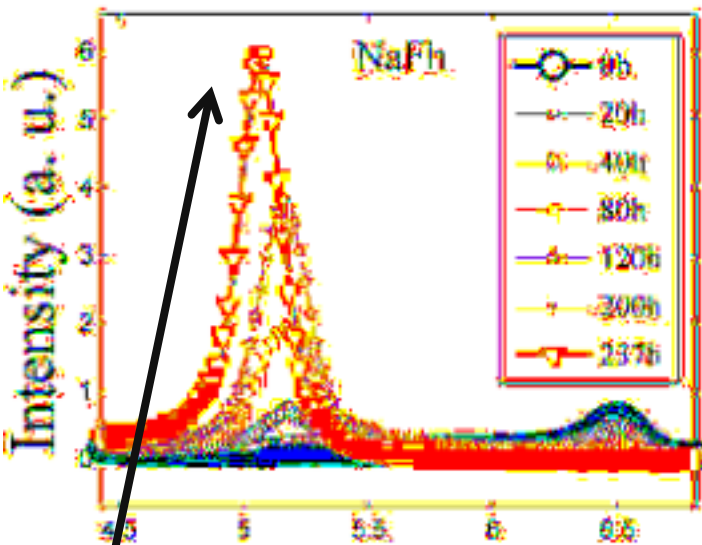
Affiliations | Contributions | Corresponding authors

Scientific Reports 5, Article number: 8775 | doi:10.1038/srep08775
Received 12 November 2014 | Accepted 29 January 2015 | Published 05 March 2015

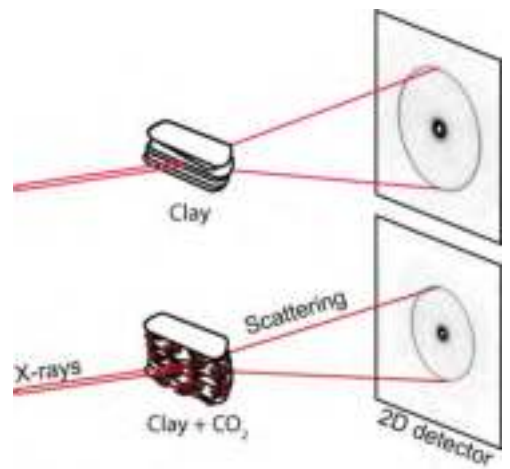
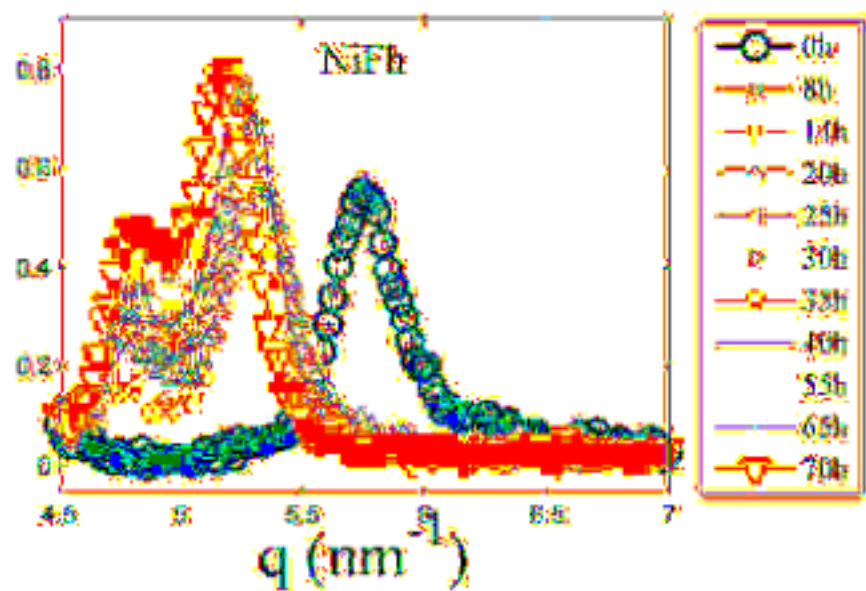
CO₂ intercalation

$P = 20 \text{ bar}$

$T = -20^\circ\text{C}$

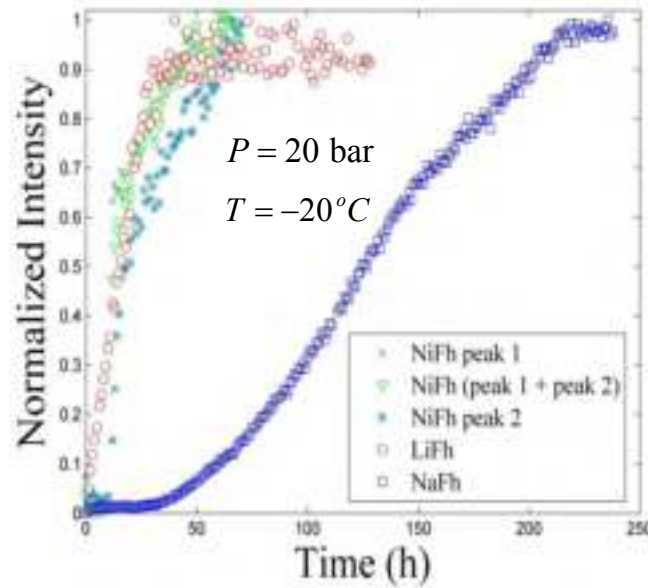
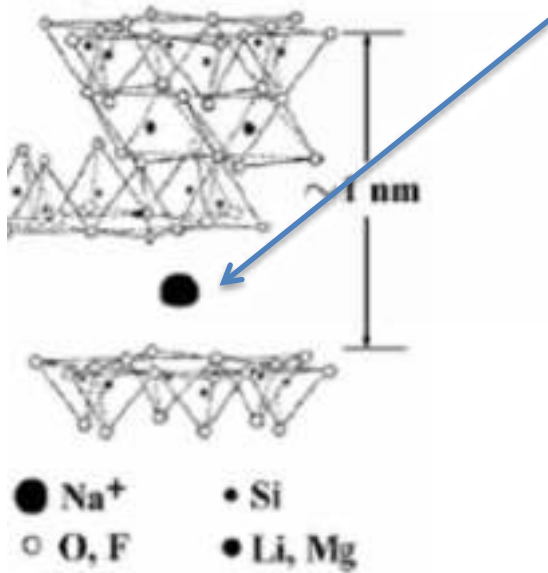


Na-Fh
with
CO₂



Powders are completely dehydrated before exposed to CO₂: Blue data points above

Cation dependence

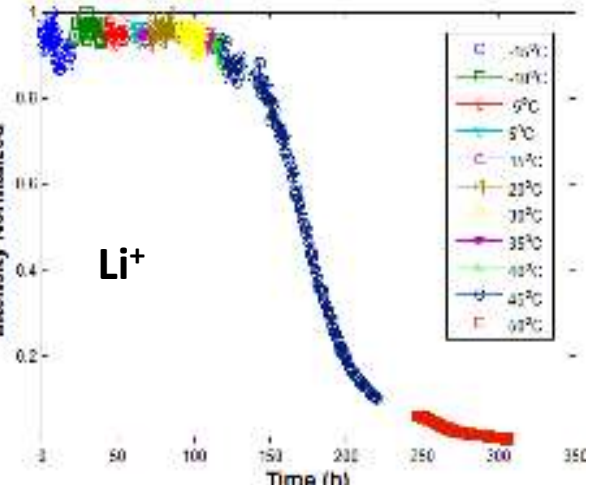
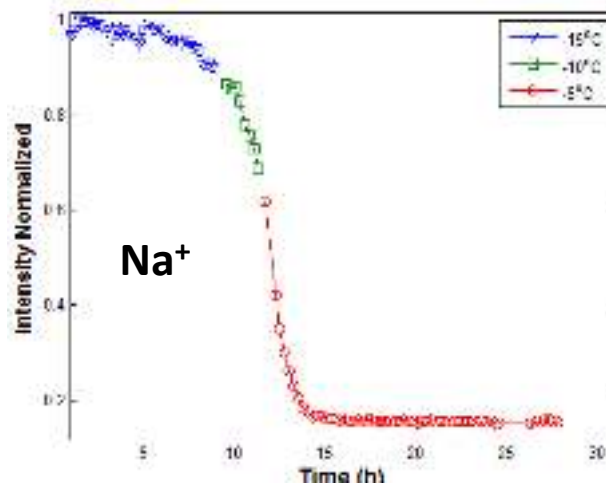


CO₂ Capture:

Faster uptake for:
Lower T or higher p

CO₂ Retention:

- N₂ flushing
- Increasing temperature

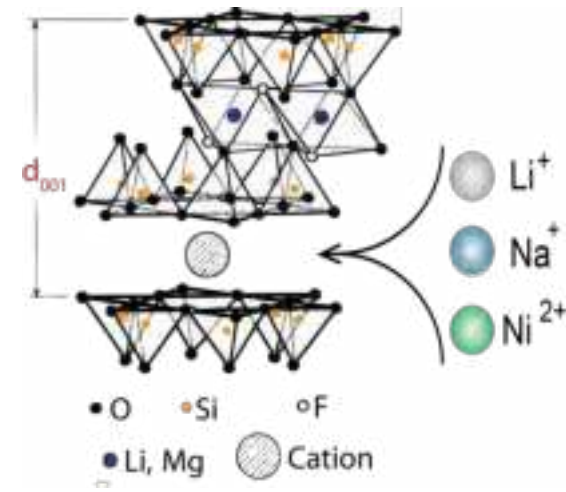


CO₂ polarisibility by Li⁺ vs Na⁺ ??

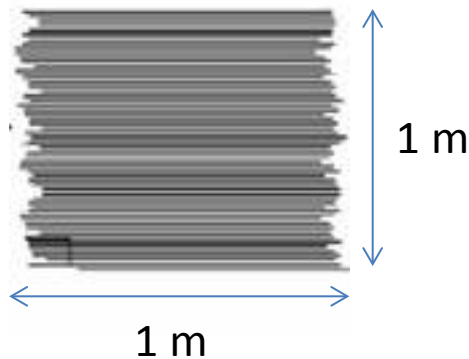
Simplest interpretation:

The clays provide a large surface area available for CO₂ capture.

The cations control capture and release of CO₂ (sometimes modified by clay swelling specifics).



How much CO₂ is captured?



In 1 m³ of compactly packed clay the total clay surface $2 \times 10^9 \text{ m}^2 = 2000 \text{ (km)}^2$.

The typical packing density of our clay powder is 0.6, so **the total clay surface area available in 1 m³ of clay powder is $0.6 \times 2000 \text{ (km)}^2 \sim 1200 \text{ (km)}^2$.**

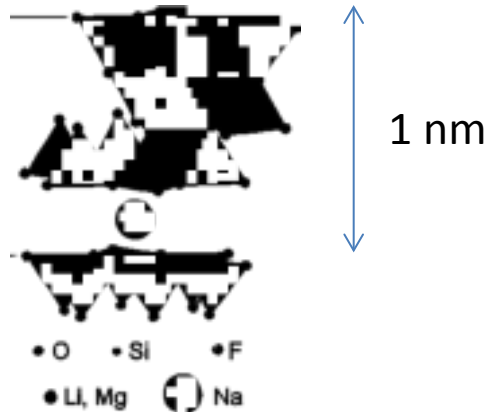
The lateral unit cell size is $\sim < 1 \text{ (nm)}^2$, and there is about 1.2 monovalent charge compensating monovalent cations per unit cell area in fluorohectorite, i.e.

$\sim 1 \text{ cation per (nm)}^2$.

Assumption:

$\sim 2 \text{ CO}_2 \text{ molecules captured per cation}$, (NMR: ~ 2 water molecules complexed per cation at ambient conditions), **which corresponds to $\sim 2 \text{ CO}_2 \text{ molecules captured per (nm)}^2$.**

$\sim 14\%$ mass increase of the clay when saturated with CO₂, or $\sim 0.22 \text{ tons CO}_2/\text{m}^3 \text{ clay}$.



To check this we did:

pressure composition Temperature (pcT) experiments measure mass increase when sample is loaded with CO₂ => **15% mass increase, confirms assumption above.**

The amount of captured CO₂ for fluorohectorite clay compared with those of other materials.

<i>Material</i>	<i>Efficiency (mmol/g)</i>	<i>Density (g/cm³)</i>	<i>Captured CO₂ (ton/m³)</i>
<i>Ideal porous material: Liquid/Solid CO₂</i>			<i>0.5 (liquid) 1 (solid)</i>
<i>Benchmark Zeolite 13X</i>	<i>2.5</i>	<i>2.2</i>	<i>0.14</i>
<i>"Best"? Zeolite</i>	<i>5</i>	<i>2.2</i>	<i>0.29</i>
<i>"Best"? MOF</i>	<i>6</i>	<i>2.0</i>	<i>0.32</i>
<i>Fluorohectorite clay (our experiments)</i>	<i>3</i>	<i>2.8</i>	<i>0.22</i>

The density of liquid CO₂ is 0.77 ton/m³ at 56 atm and 20 °C (the density of solid CO₂ is about twice of this) suggesting that ~1 ton CO₂ captured per m³ is near the theoretical "perfect and unachievable" upper limit for CO₂ capture by any porous material, zeolite, MOF, carbon based, clay, or other.

Our synthetic fluorohectorite clay has about twice as many cations per (nm)² as compared to natural clays like bentonite.

Price comparison: Cost of producing synthetic smectites is about 1-10 USD/kg, whereas price of producing MOFs may be about 50 USD/kg.

Clays in BIONANOTECHNOLOGY

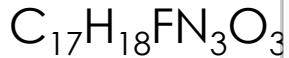
Parrots of the Amazones:

Parrots of the Amazon eat clay at riverbanks for breakfast in order to prevent stomach-ache from alkaloid poisons of the seeds in the fruits they eat for lunch.

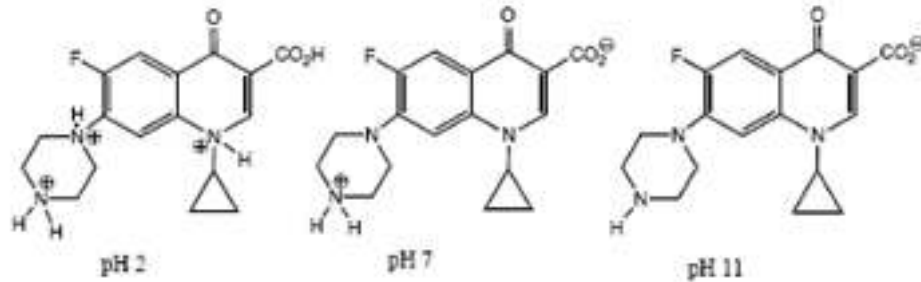
Shows that clays may be interesting drug delivery systems



Cipro (ciprofloxacin) is an antibiotic in a group of drugs called fluoroquinolones (flor-o-KWIN-o-lones). It is used to fight bacteria in the body. Cipro is used to treat different types of bacterial infections. It may also be used to prevent or slow anthrax after exposure.



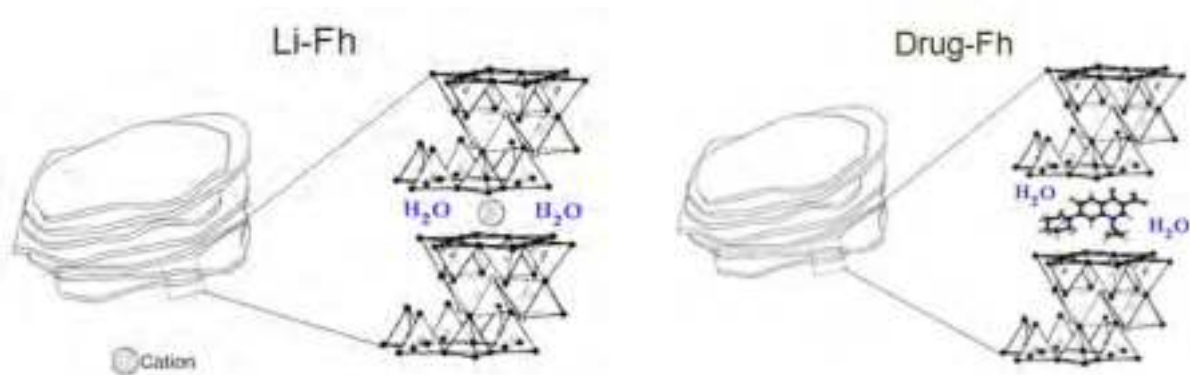
Zwitterionic



Positive

Dipole

Negative



Intercalates by far best for acid pH

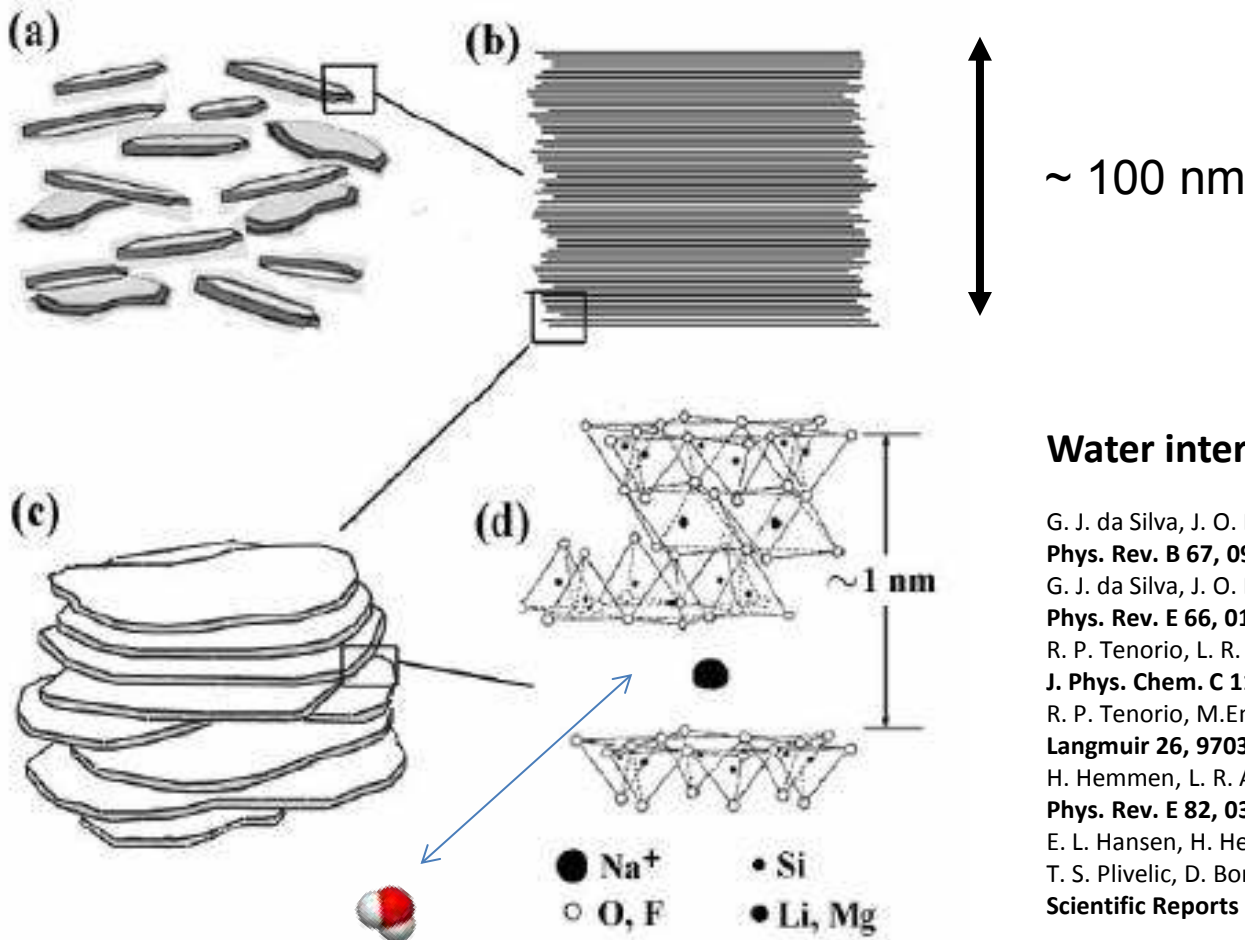
Different intercalation mechanism at pH 7?

Rapid release at basic pH

Techniques: XRD, UV-VIS Spectroscopy

Our clay experimental model system:

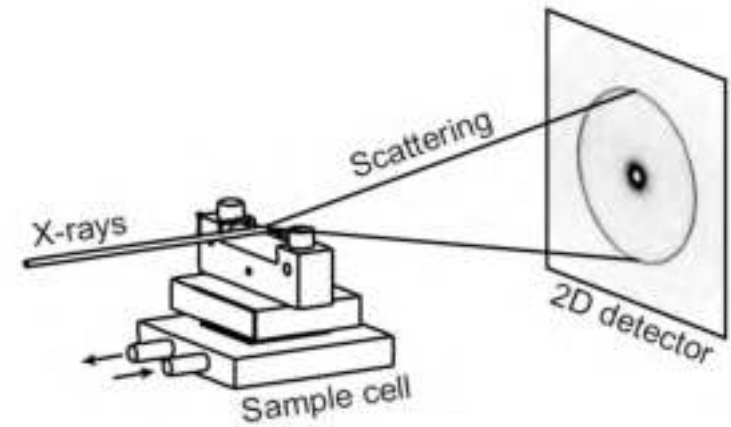
Q-fluorohectorite synthetic clay: $Q_x-(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+ , Li^+ , Ni^{2+} , Fe^{3+} , etc)



Water intercalation:

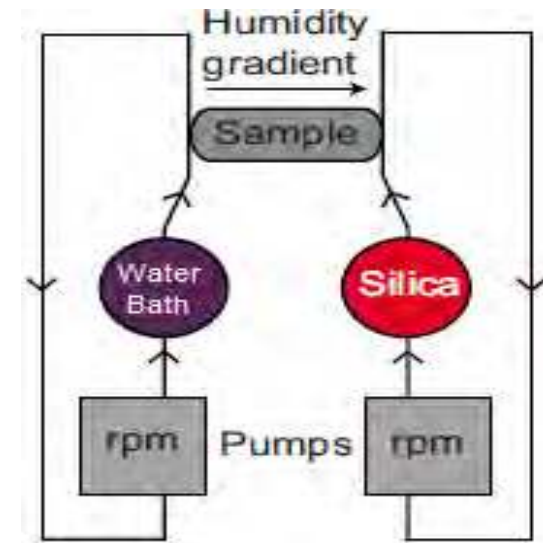
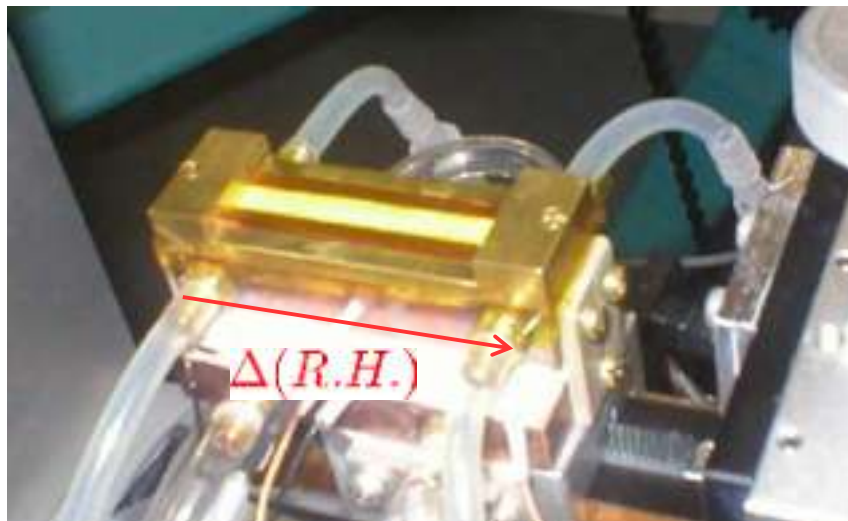
- G. J. da Silva, J. O. Fossum, E. DiMasi, and K. J. Maloy, **Phys. Rev. B** **67**, 094114 2003.
- G. J. da Silva, J. O. Fossum, E. DiMasi, K. J. Maloy, and S. B. Lutnaes, **Phys. Rev. E** **66**, 011303 2002.
- R. P. Tenorio, L. R. Alme, M. Engelsberg, J. O. Fossum, and F. Hallwass, **J. Phys. Chem. C** **112**, 575 2008.
- R. P. Tenorio, M. Engelsberg, J. O. Fossum, and G. J. da Silva, **Langmuir** **26**, 9703 2010.
- H. Hemmen, L. R. Alme, J. O. Fossum and Y. Meheust, **Phys. Rev. E** **82**, 036315 2010.
- E. L. Hansen, H. Hemmen, D. M. Fonseca, C. Coutant, K. D. Knudsen, T. S. Plivelic, D. Bonn, J. O. Fossum, **Scientific Reports** **2**, 618 2012

Water Transport Experiment



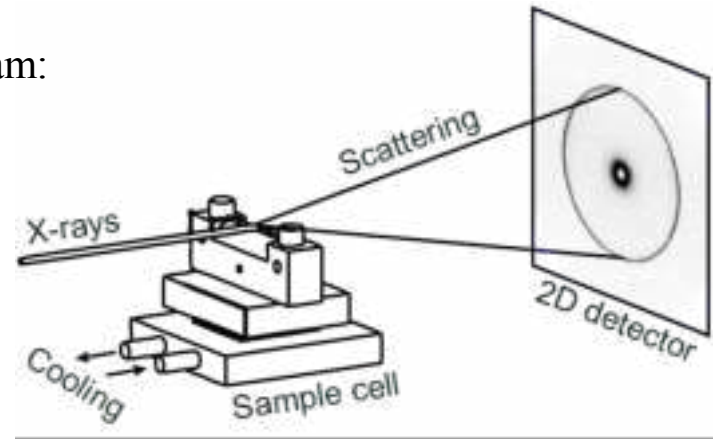
Only 2 cm of the capillary was observed using x-rays

→ Diffusive transport

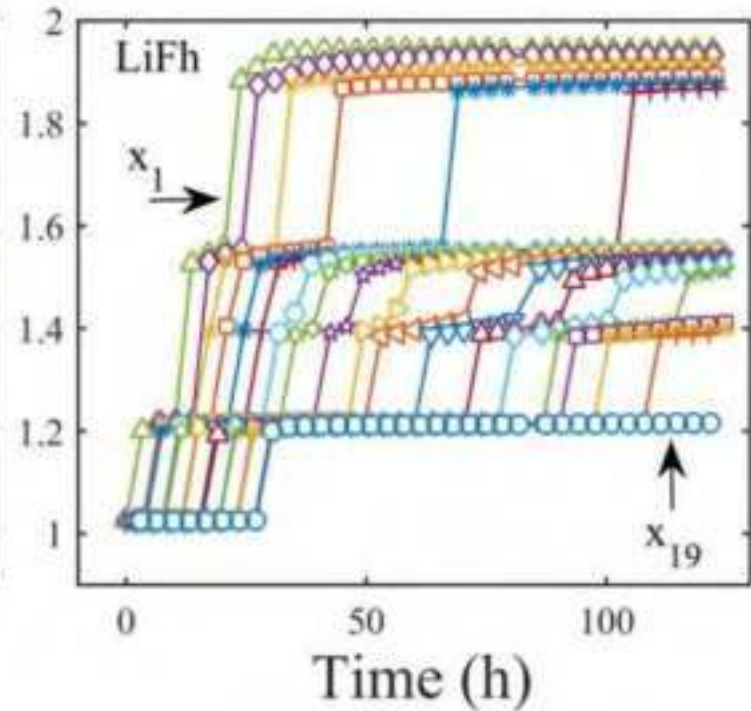
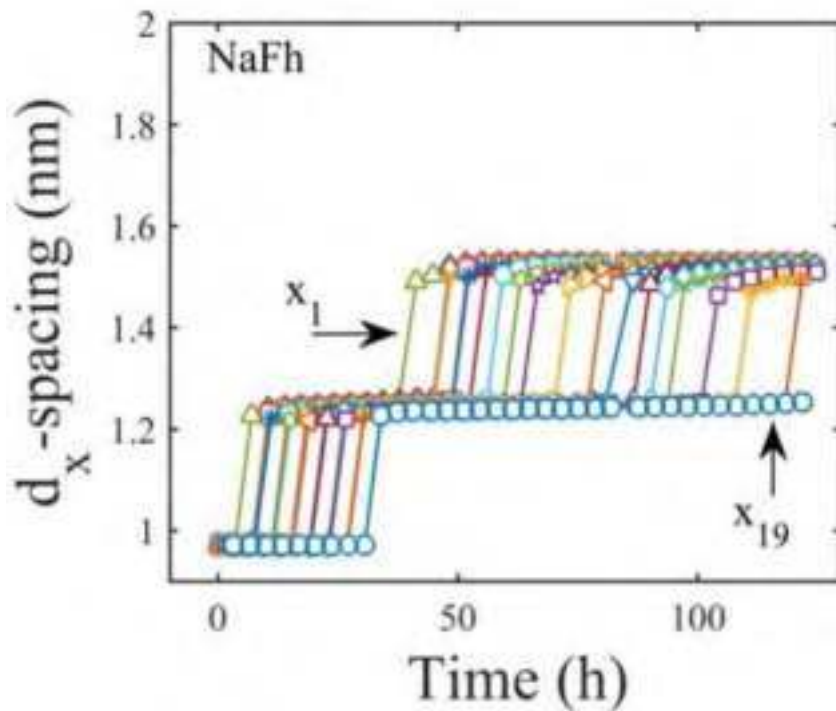


The Fluorohectorite was placed in 1 mm glass capillaries open in both ends, one end exposed to high relative water humidity (96%), the other end exposed to dry air (0.4%)

The sample is scanned forth and back in front of the X-ray beam:

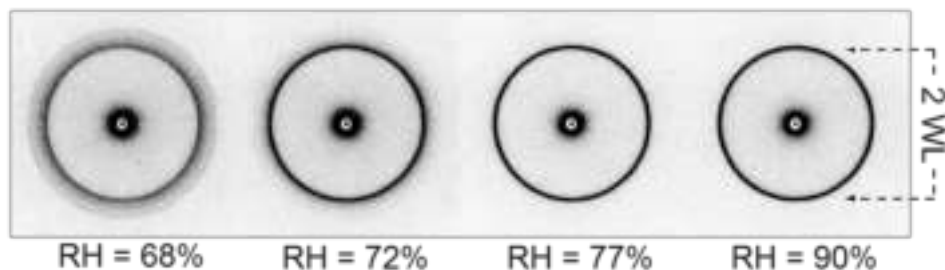
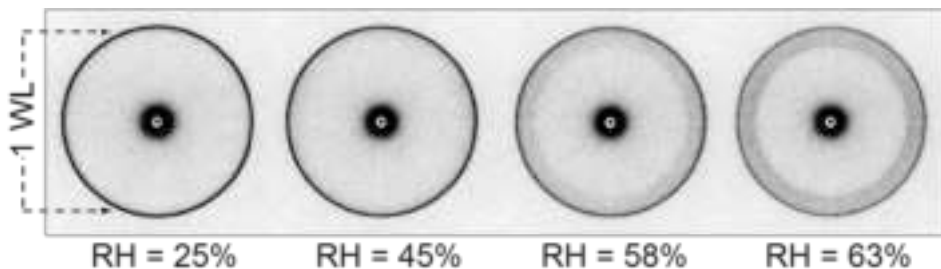


The hydration state is monitored at regular positions x as a function of time:



The sample is scanned forth and back in front of the X-ray beam:

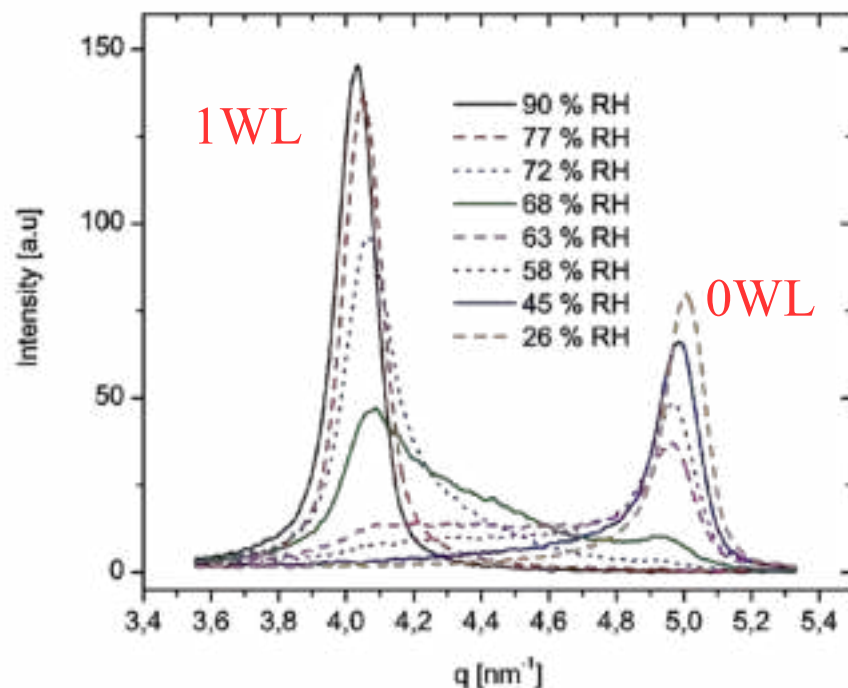
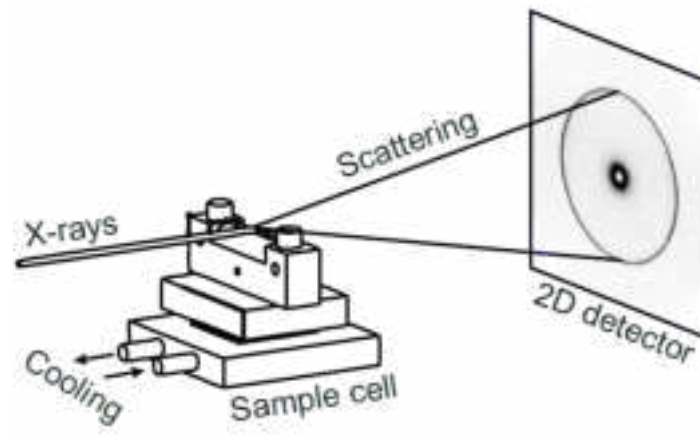
- The quasi-isotropic clay powder diffracts the beam,
- resulting in circular high-intensity rings that denote
- the **structural d-spacing** d_{001} :



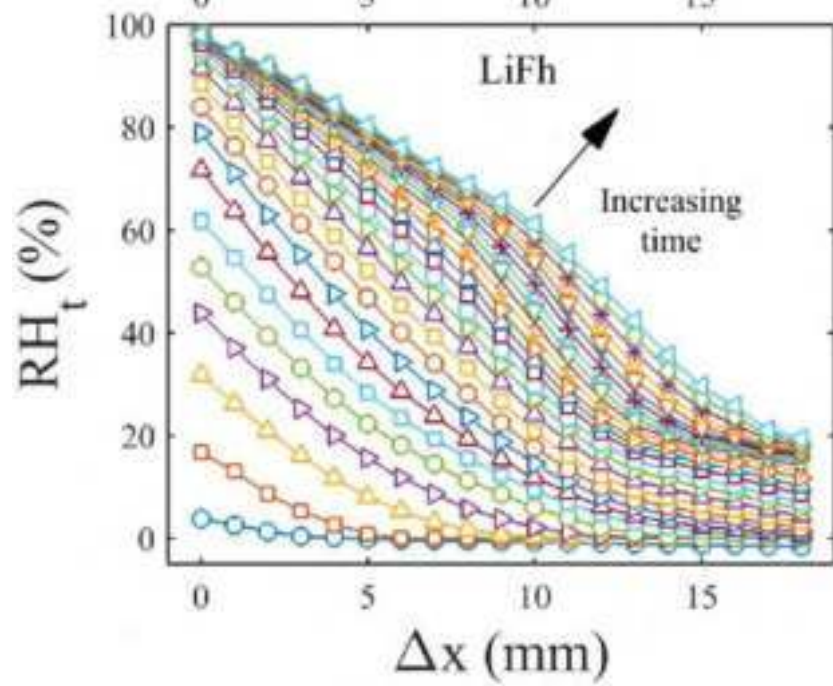
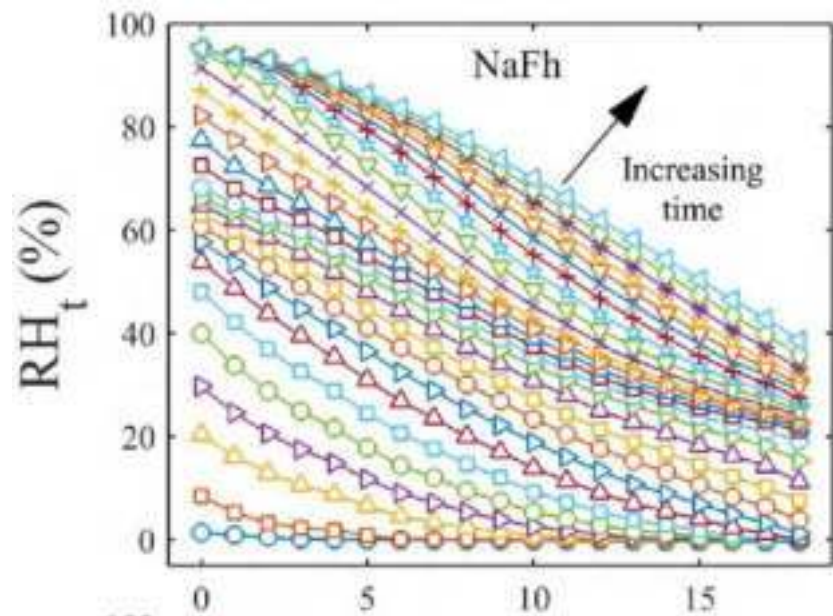
- Azimuthal integration of the rings provides 1D
- diffraction spectra

- The position of the peak is related to d_{001} :

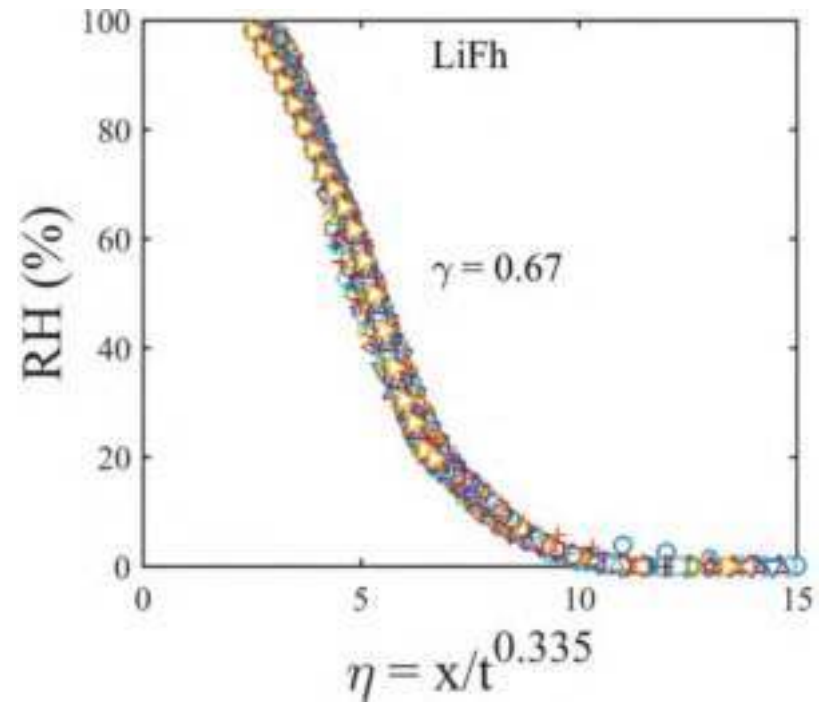
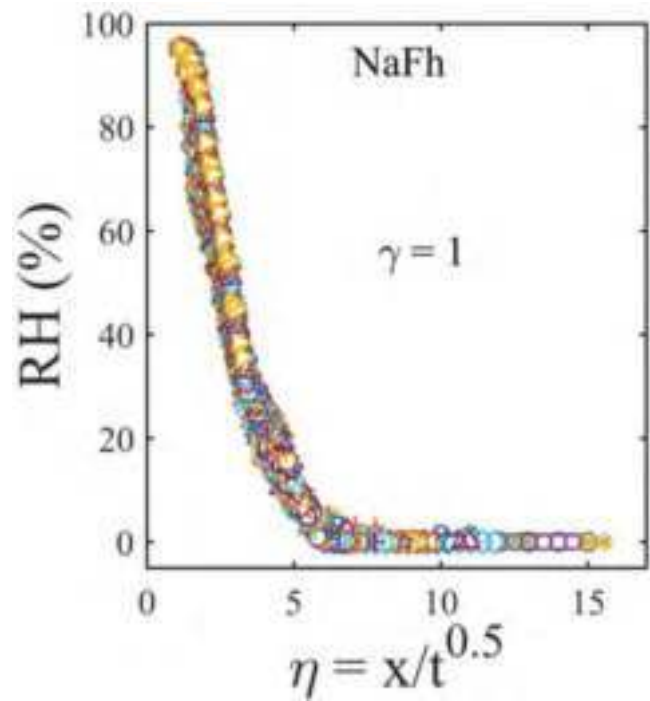
$$q = \frac{2\pi}{d} \quad (\text{Bragg's law})$$



$$q = (4\pi/\lambda) \sin\theta$$



Using the values γ values inferred from the scaling of the intercalation fronts:

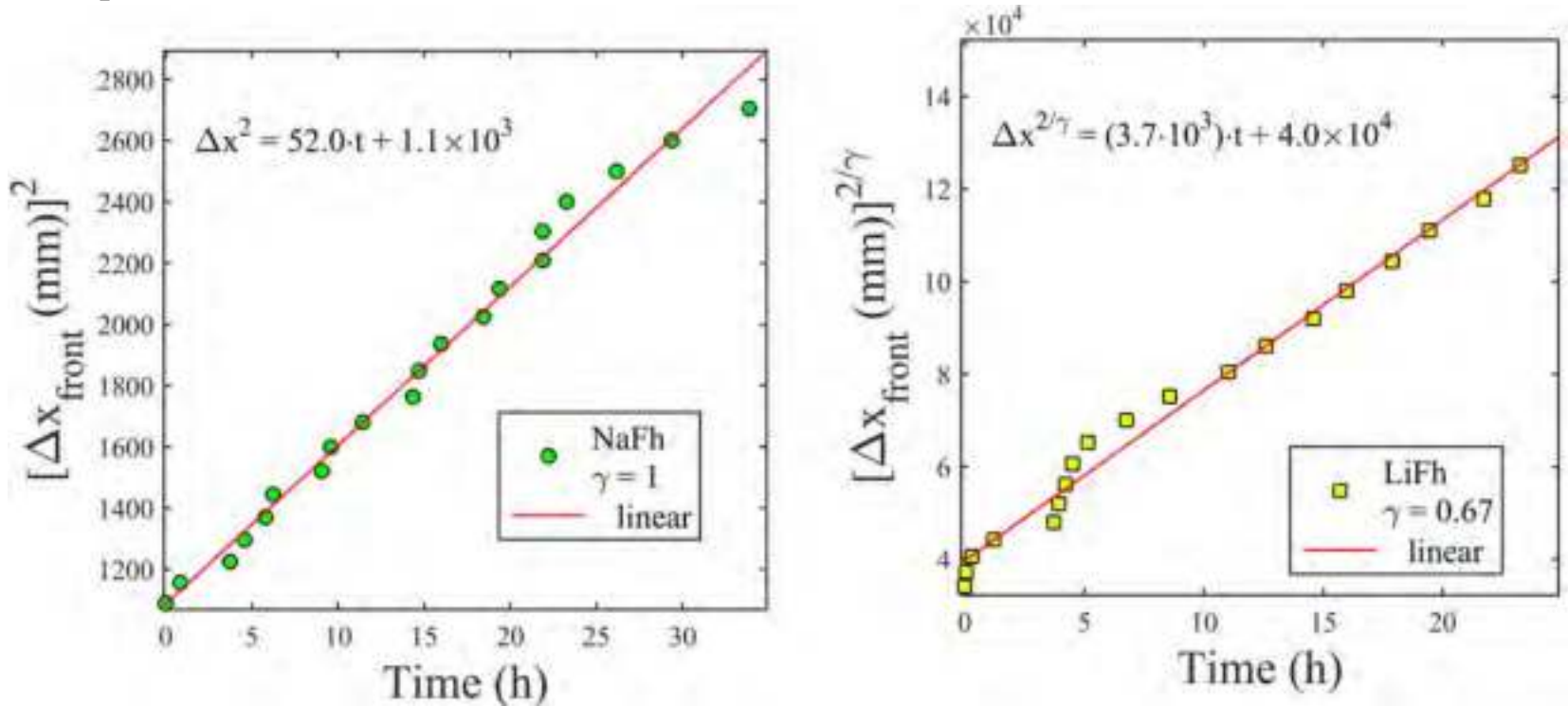


- Suggests [anomalous transport for LiFh](#), normal transport for NaFh
- We now need to consider the concentration field in the mesoporous space

The longitudinal position of the hydration front is monitored as a function of time:



The position of the intercalation front is monitored as a function of time



- Suggests **anomalous transport for LiFh**, normal transport for NaFh
- We now need to consider the concentration field in the mesoporous space

Time it takes to diffuse 1 m:

NaFh: $t_{1\text{meter}} \approx 26 \text{ hours} / (2600 \cdot 10^{-6}) \approx 10^4 \text{ hours} \approx \mathbf{1 \text{ year}}$

LiFh: $t_{1\text{meter}} \approx 24 \text{ hours} / (12 \cdot 10^4 \cdot 10^{-9}) \approx 2 \cdot 10^5 \text{ hours} \approx \mathbf{20 \text{ years}}$

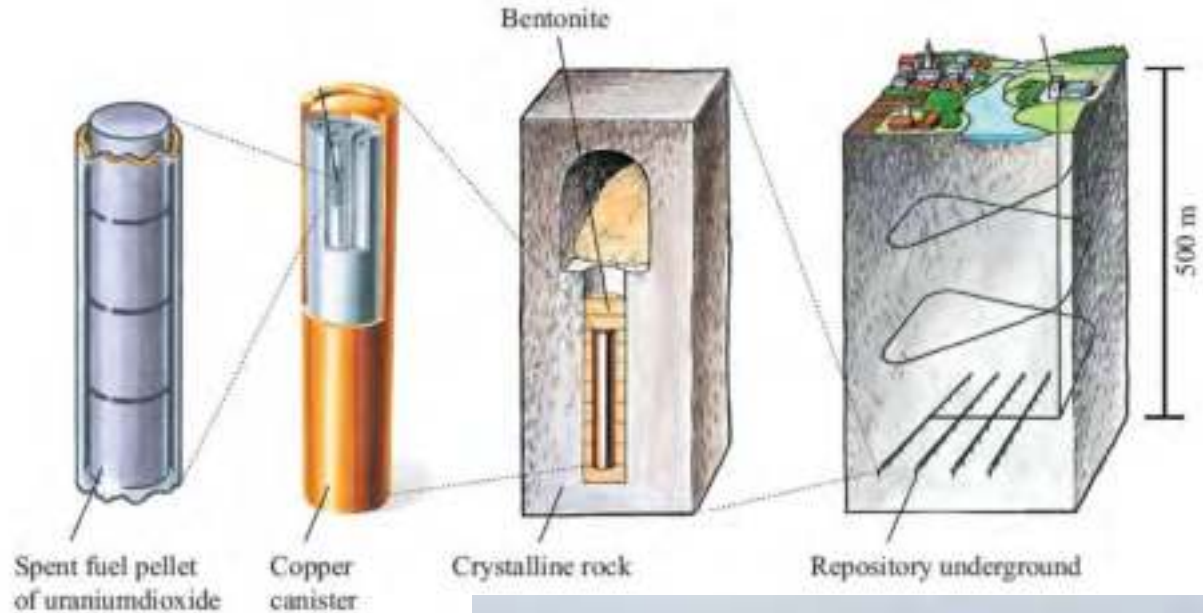
Permanent and safe storage of nuclear waste

Swedish Nuclear Fuel and Waste Management Company (Svensk Kärnbränslehantering Aktiebolag, abbreviated **SKB**):
Swedish demand for clays as nuclear waste barriers amounts to about one shipload per year.

The Bentonite Barrier

Swelling properties, redox chemistry and mineral evolution

P. Daniel Svensson



DOCTORAL DISSERTATION

by due permission of the Faculty of Engineering, Lund University, Sweden.

To be defended in public at the Center for Chemistry and Chemical Engineering,
Lecture Hall K:C, on March 9, 2015, at 13:15.

Faculty opponent

Prof. Jon Otto Fossum, Norwegian University of Science and Technology

Synthetic clays?



New development of, or enhancing existing, forestry or agriculture for CO₂ capture and improved living conditions



Trees or agriculture in Sahara or similar dry environments? For large scale CO₂ capture?

www.desertcontrol.com

Kristian P. Olesen

CEO

Patent Holder



Cover the sand with a layer of clay aqueous suspension and add fertilizer in order to capture the evaporating otherwise escaping ground water? (www.desertcontrol.com)



Sinai Desert test site: Before and after soil treatment with NanoClay

Clay based electronics:



NATURE | LETTER

日本語要約

Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance

Michael Ghidju, Maria R. Lukatskaya, Meng-Qiang Zhao, Yury Gogotsi & Michel W. Barsoum

Department of Materials Science and Engineering, and A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania 19104, USA

Nature 516, 76–81 (04 December 2014) | doi:10.1038/nature13970

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Quasi-Solid Electrolytes for High Temperature Lithium Ion Batteries

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¹ Department of Materials Science and Nano Engineering, Rice University, Houston, Texas 77005, United States

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ACS Appl. Mater. Interfaces 2015, 7 (46), pp 25777–25783

DOI: 10.1021/acsami.5b07636

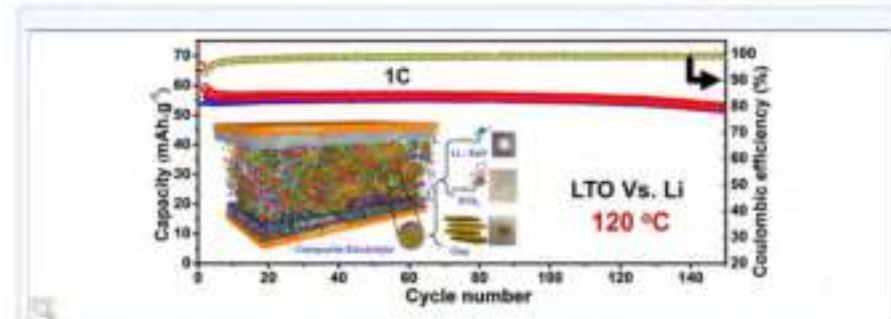
Publication Date (Web): November 4, 2015

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*E-mail: ajayan@rice.edu; *E-mail: leela.arava@rice.edu

Abstract

Jump to a section



Rechargeable batteries capable of operating at high temperatures have significant use in various targeted applications. Expanding the thermal stability of current lithium ion batteries requires replacing the electrolyte and separators with stable alternatives. Since solid-state electrolytes do not have a good electrode interface, we report here the development of a new class of quasi-solid-state electrolytes, which have the structural stability of a solid and the wettability of a liquid. Microflakes of clay particles drenched in a solution of lithiated room-temperature ionic liquid forming a quasi-solid system has been demonstrated to have structural stability until 355 °C. With an ionic conductivity of $\sim 3.35 \text{ mS cm}^{-1}$, the composite electrolyte has been shown to deliver stable electrochemical performance at 120 °C, and a rechargeable lithium battery with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode has been tested to deliver reliable capacity for over several cycles of charge-discharge.

Keywords: high temperature energy devices, quasi-solid electrolytes, lithium ion battery, ionic liquids, clay composites, lithium titanate

Clay based electronics?

Nanolayered materials beyond graphene: Heterostructures and metamaterials

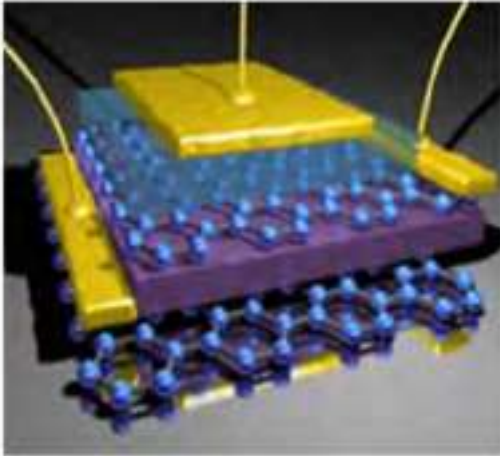


Figure 1:

Principal sketch of our graphene-clay electronic device, manually assembled at Univ. Manchester in Prof. Novoselov's group, using manual exfoliation techniques developed in that laboratory.

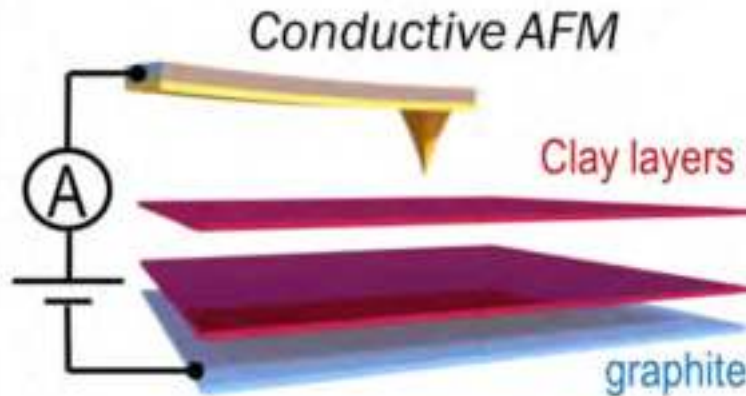


Figure 2:

Principle sketch of experimental set-up for measurements of IV-characteristic of our prototype graphene-clay device. The experiments were performed at Univ. Manchester in Prof. Novoselov's group.

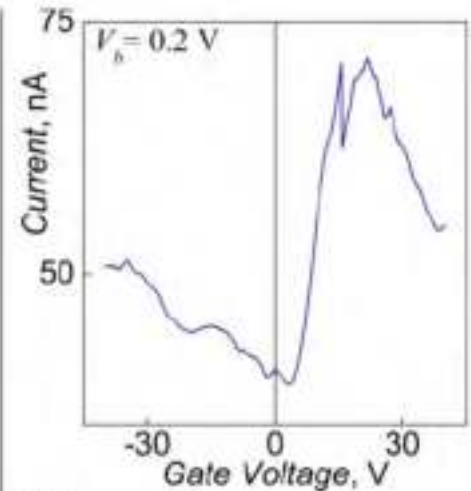
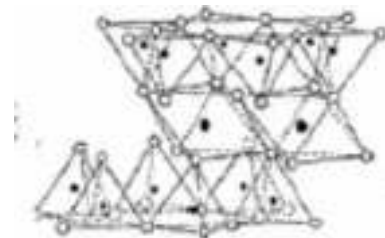


Figure 3:

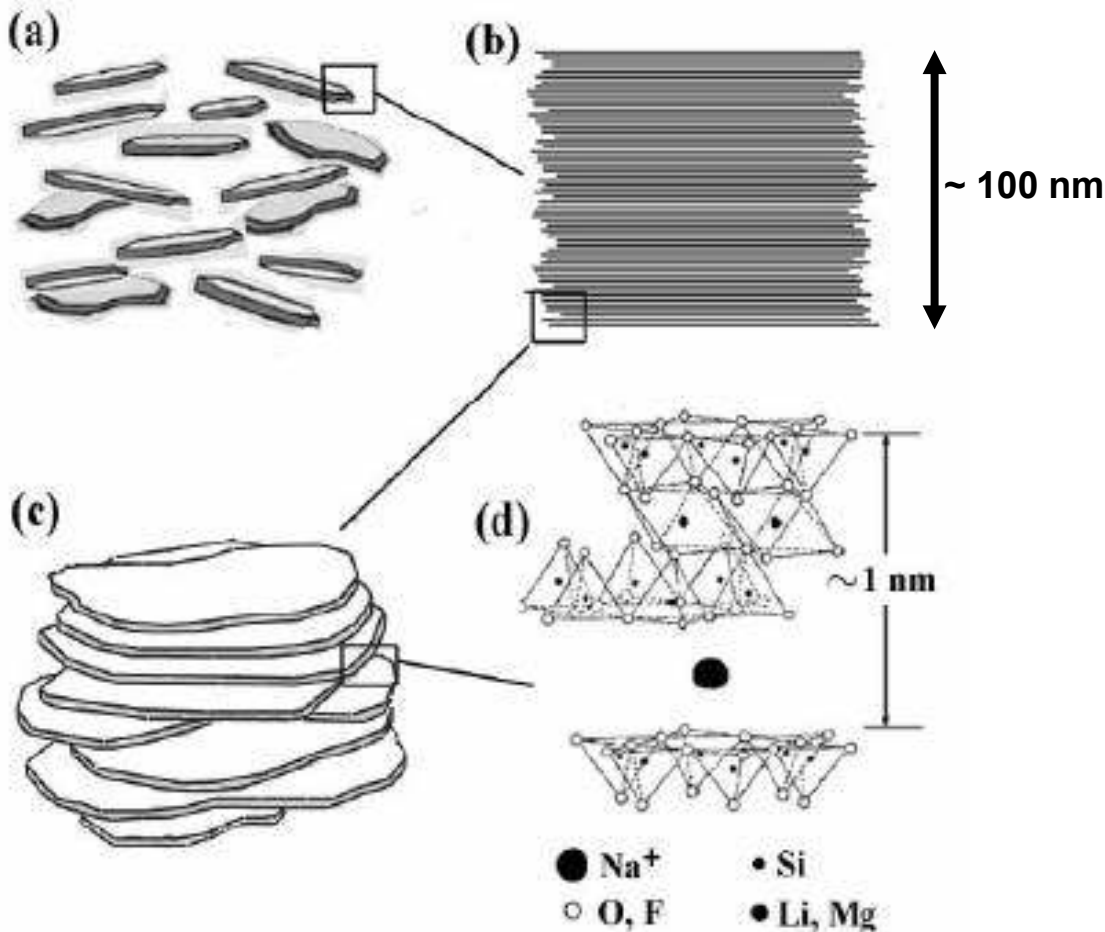
Preliminary tunneling I-V characteristics for our prototype graphene-clay device. The experiments were performed at Univ. Manchester.

Electronic and magnetic properties along or perpendicular to the clay sheets etc.



Our clay experimental model system:

Q-fluorohectorite synthetic clay: $Q_x-(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+ , Li^+ , Ni^{2+} , Fe^{3+} , etc)



Sources of fluorohectorite:

Corning Inc.

$x \approx 0.6 \pm 0.05$

Lateral $\sim 0.5-10 \mu m$

(incl. 20% known impurities)

Inorg. Chem.

Univ. Bayreuth, Germany

Prof. Josef Breu

$x = (0.2 \leftrightarrow 0.6) \pm 0.005$

Lateral $> 100 \mu m$

(pure)



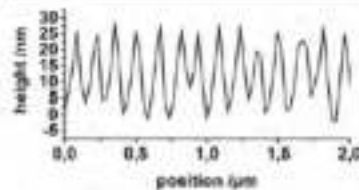
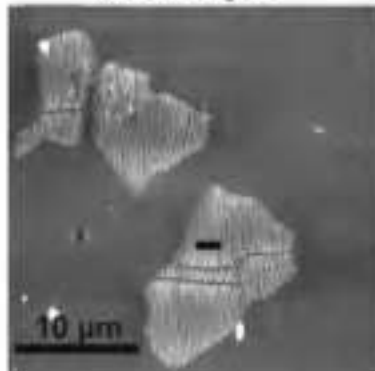
Nanomechanics – Wrinkling



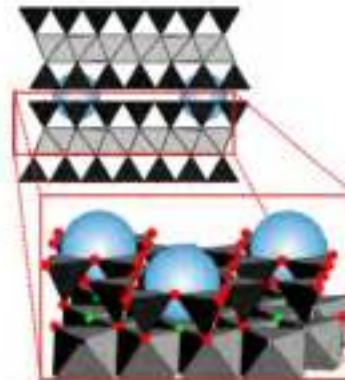
$$E_p = \frac{3E_s(1-\nu_p^2)}{(1-\nu_s^2)} \left(\frac{\lambda}{2\pi h} \right)^3$$



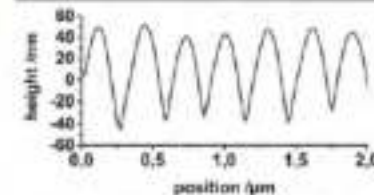
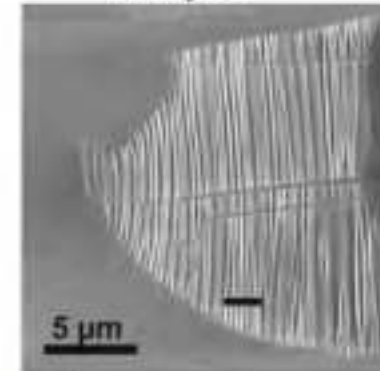
Monolayer



wavelength: 145 ± 7 nm
In-plane modulus: 0.15 ± 0.02 TPa



Bilayer



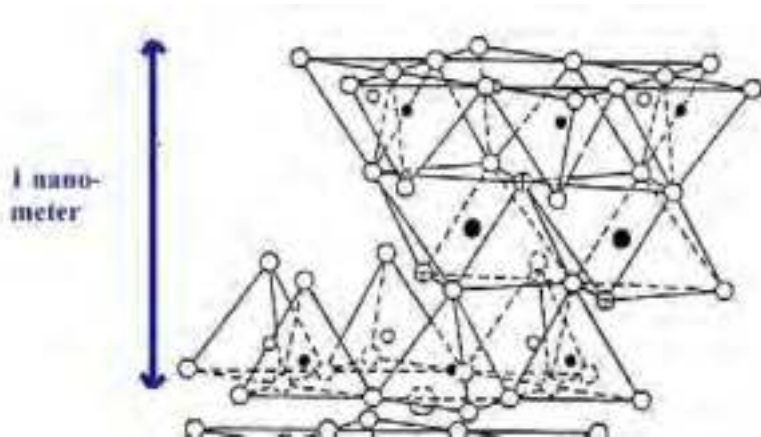
wavelength: 313 ± 10 nm
In-plane modulus: 0.17 ± 0.01 TPa

CLAY MINERALS AND THE ORIGIN OF LIFE

The confinement by cell membranes offers localized concentration and protection for biomolecules such as nucleic acids, leading to efficient biochemical reactions.

In defining the pre-cellular environment, it is important to address the following questions:

- 1) How did biomolecules encounter each other and maintain sufficient proximity to perform complicated biochemical reactions?
- 2) How did the biomolecules survive in the environment without any protection?

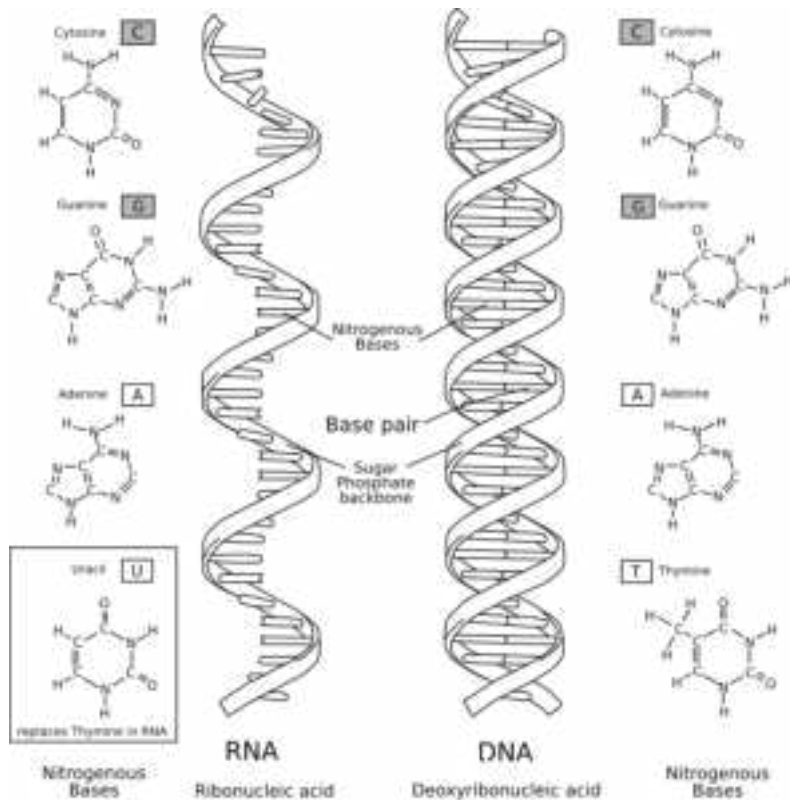


Bernal (1951), first suggested that clay minerals played a key role in chemical evolution and the origins of life because of their ability to take up, protect (against ultraviolet radiation), concentrate, and catalyze the polymerization of, organic molecules.

Clay minerals have been proposed as a likely candidate among solid materials to play roles for life evolution, due to their wide distribution, historical prevalence throughout the timeline of geological and biological events on Earth and their affinity for organic molecules.

For example, clay has been demonstrated to be capable of catalyzing the polymerization of RNA and accelerating the formation of fattyacid vesicles (a protocell model).

Clay -> Selection and Amplification of Chemistry



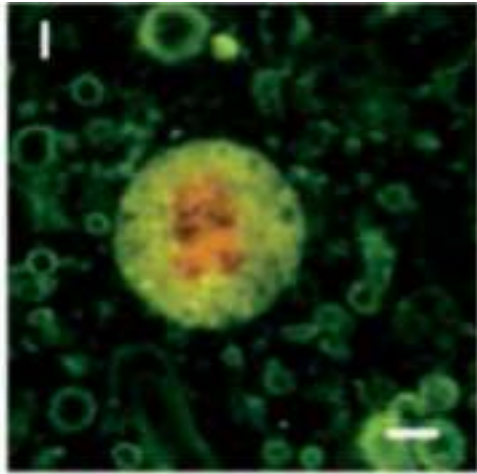
The RNA world refers to the self-replicating ribonucleic acid (RNA) molecules hypothesised to have been the precursors to all current life on Earth.

Supported by several lines of evidence including how RNA was protected on the early earth.

Eventually DNA is thought to have taken over the role RNA in data storage due to its increased stability, while proteins, through a greater variety of monomers (amino acids), replaced RNA's role in specialized biocatalysis.

Smectite clay tends to adsorb organic compounds and this contributes to its ability to catalyze a variety of organic reactions critical to scenarios of life's origins. It has been shown experimentally that RNA molecules bind efficiently to clays and that montmorillonite can catalyze the formation of longer molecules (oligomers), thus lending support to the RNA world hypothesis.

Life on Earth: Fresh clues hint at how the first living organisms arose from inanimate matter, Alonso Ricardo and **Jack W. Szostak**, Scientific American, September 2009, pp. 54-61



(I) Montmorillonite smectite clay coated with Cy3-labeled RNA (red) trapped inside dye-labeled vesicles (green).

Experimental Models of Primitive Cellular Compartments: Encapsulation, Growth, and Division

Martin M. Hanczyc,* Shelly M. Fujikawa,* Jack W. Szostak†

The clay montmorillonite is known to catalyze the polymerization of RNA from activated ribonucleotides. Here we report that montmorillonite accelerates the spontaneous conversion of fatty acid micelles into vesicles. Clay particles often become encapsulated in these vesicles, thus providing a pathway for the prebiotic encapsulation of catalytically active surfaces within membrane vesicles. In addition, RNA adsorbed to clay can be encapsulated within vesicles. Once formed, such vesicles can grow by incorporating fatty acid supplied as micelles and can divide without dilution of their contents by extrusion through small pores. These processes mediate vesicle replication through cycles of growth and division. The formation, growth, and division of the earliest cells may have occurred in response to similar interactions with mineral particles and inputs of material and energy.



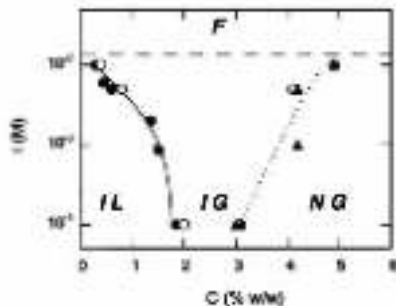
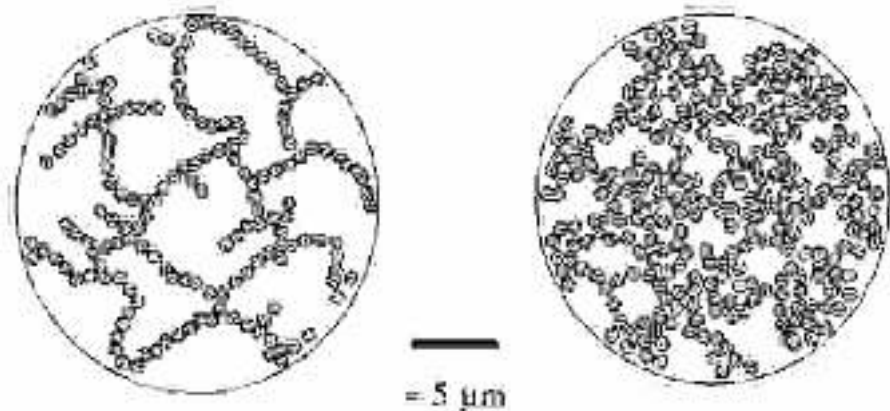
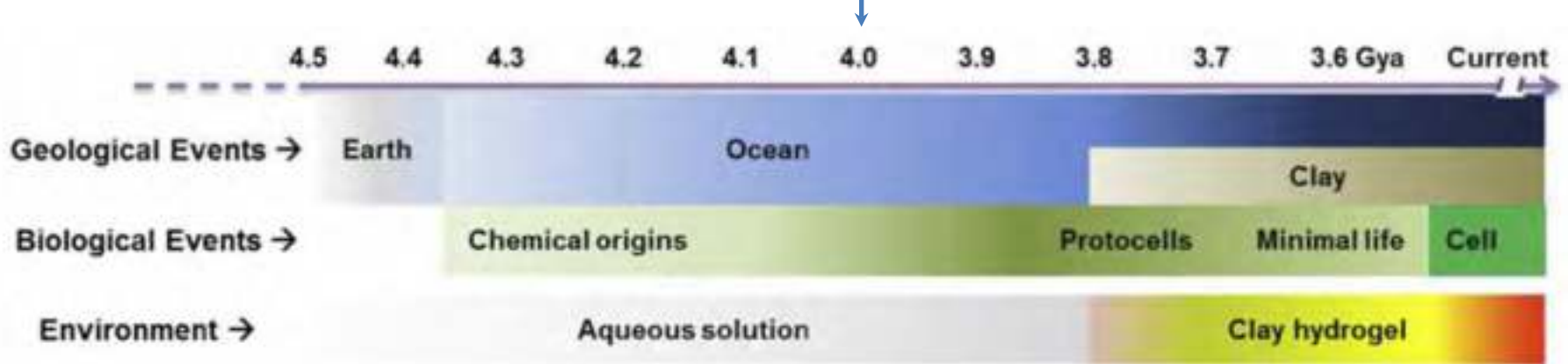
The Szostak Lab

<http://molbio.mgh.harvard.edu/szostakweb/>

Jack William Szostak : Biologist, Nobel Prize laureate Medicine 2009, Professor of Genetics at Harvard Medical School, and Alexander Rich Distinguished Investigator at Massachusetts General Hospital, Boston

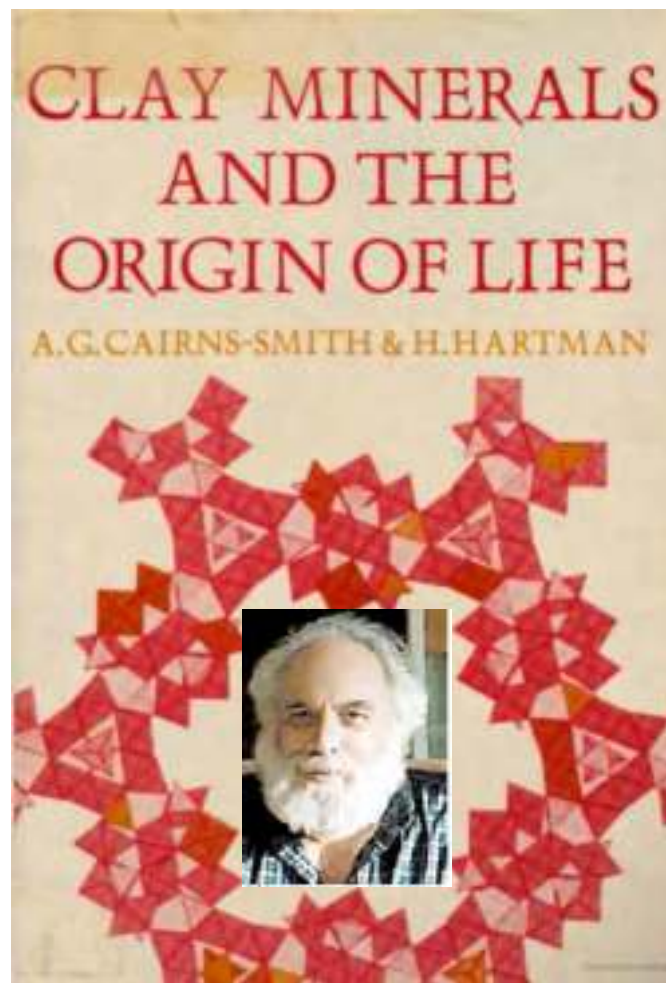
Enhanced transcription and translation in clay hydrogel and implications for early life evolution, Dayong Yang, Songming Peng, Mark R. Hartman, Tiffany Gupton-Campolongo, Edward J. Rice, Anna Kathryn Chang, Zi Gu, G. Q. (Max) Lu & Dan Luo, **SCIENTIFIC REPORTS**, 3 : 3165, DOI: 10.1038/srep03165 (2013)

~ RNA world



Confinement by clay hydrogel provide an effective environment for localized concentration and protection of nucleic acids.

Bulk-scale clay hydrogel is easily broken down by shear forces into micro-particles, which act as the confinement for biomolecules and biochemical reactions



CLAY MINERALS AND THE ORIGIN OF LIFE



Edited by

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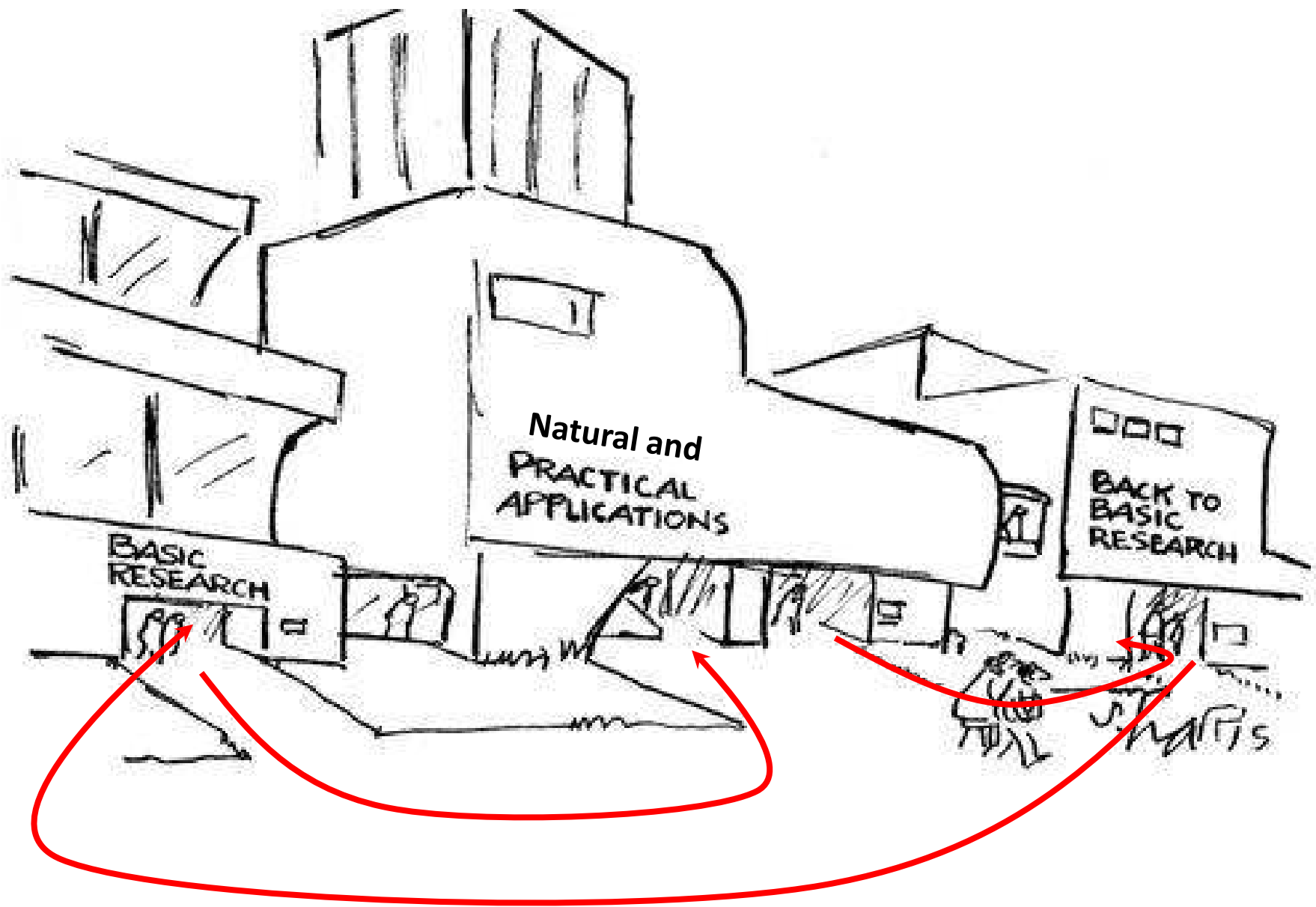
-**The physical basis of life**, **Bernal, J. D.** (Routledge & K. Paul London; 1951).

-**Mineral Catalysis and Prebiotic Synthesis: Montmorillonite-Catalyzed Formation of RNA**, James P. Ferris, *ELEMENTS* 1, 145-149 (2005)

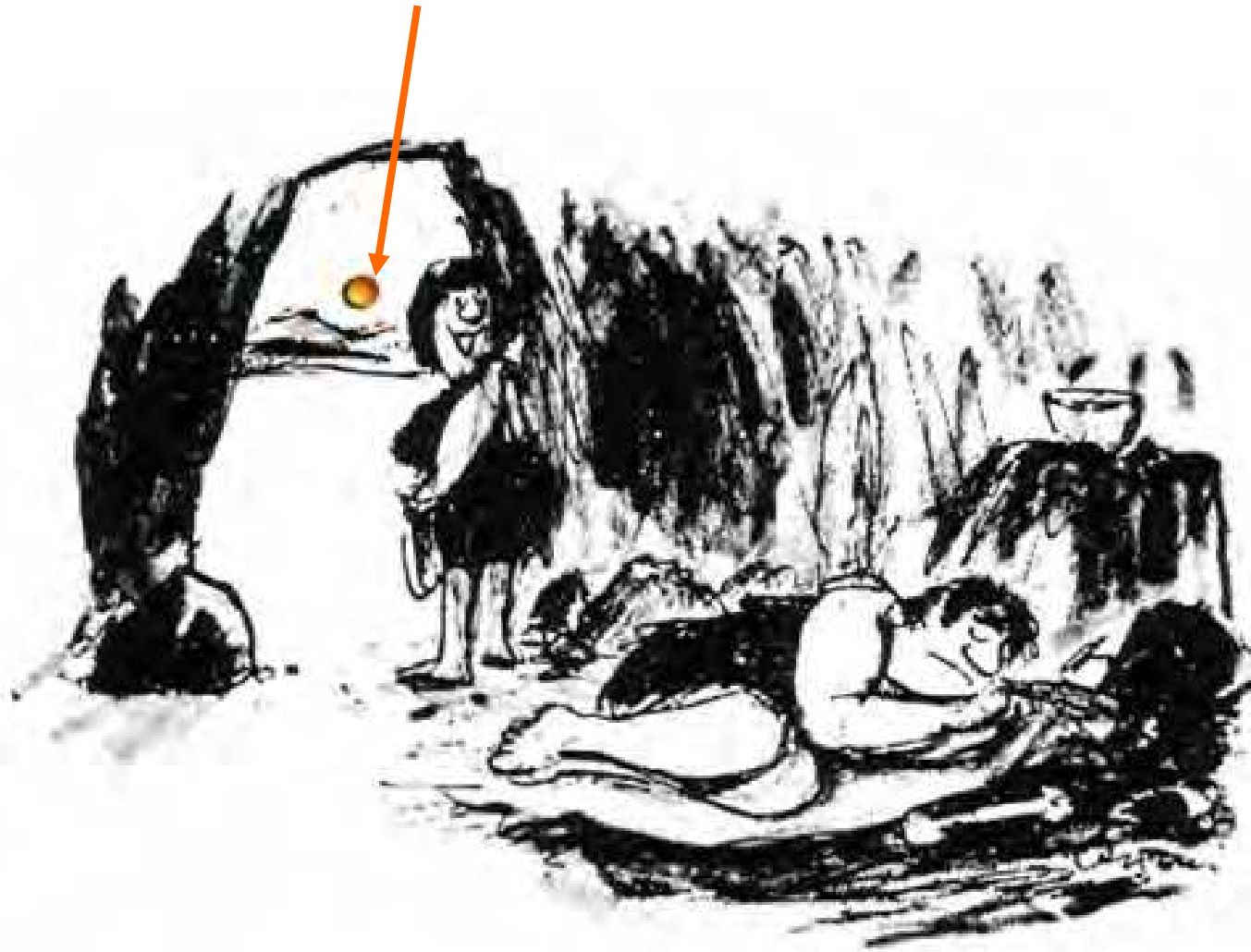
-**Role of Clay Minerals in Chemical Evolution and the Origins of Life**, Hideo Hashizume in *Earth and Planetary Sciences » Geology and Geophysics » "Clay Minerals in Nature - Their Characterization, Modification and Application"*, book edited by Marta Valašková and Gražyna Simha Martynková, ISBN 978-953-51-0738-5, Published: September 12, 2012, DOI: 10.5772/50172



Drawing by Ernesto Altshuler



We are curiosity driven. Very little industrial funding.

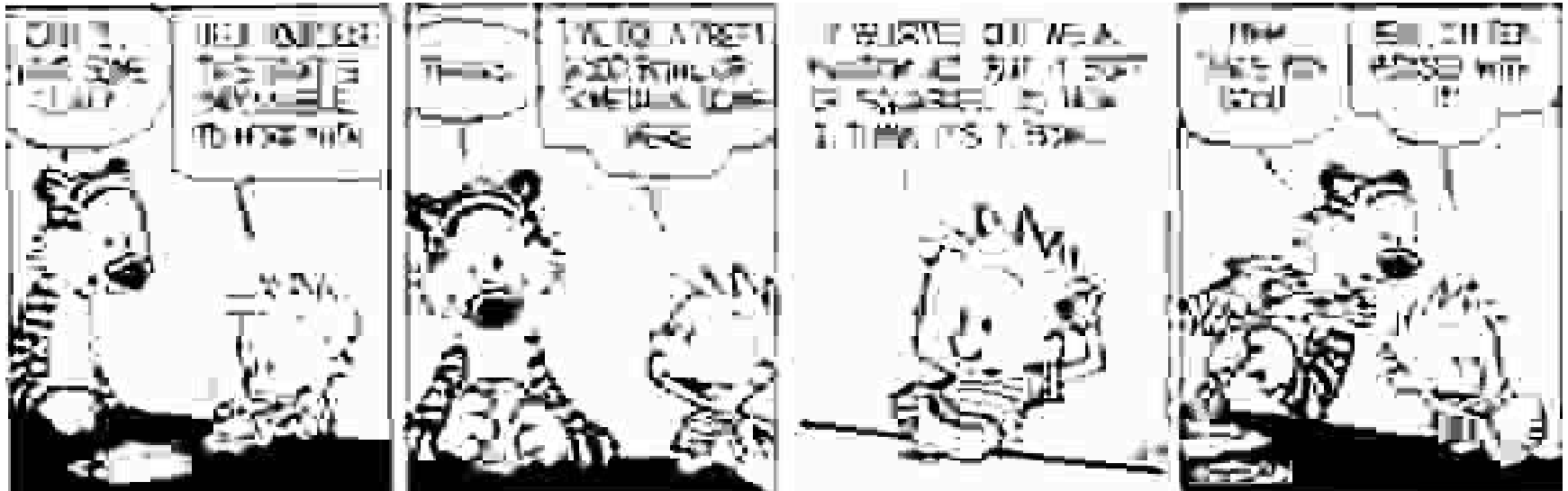


«HEY, SAM, THE BIG ROUND YELLOW THING CAME UP AGAIN»

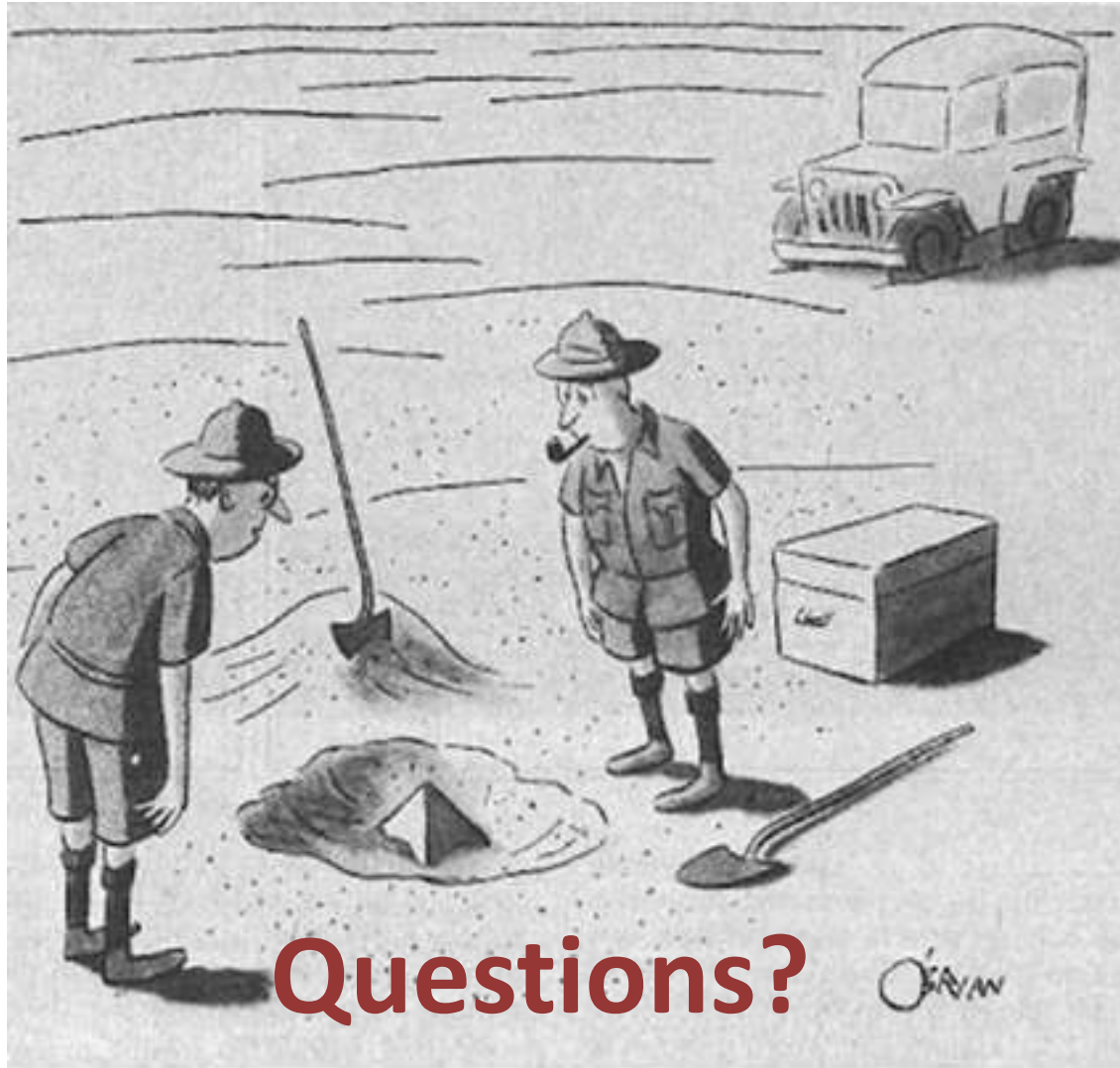
Acknowledgements to

MSc + PhD students, postdocs,
Collaborators in several countries

Clay baths will prolong your life:



Thank you for your attention!



"This could be the discovery of the century. Depending, of course, on how far down it goes."