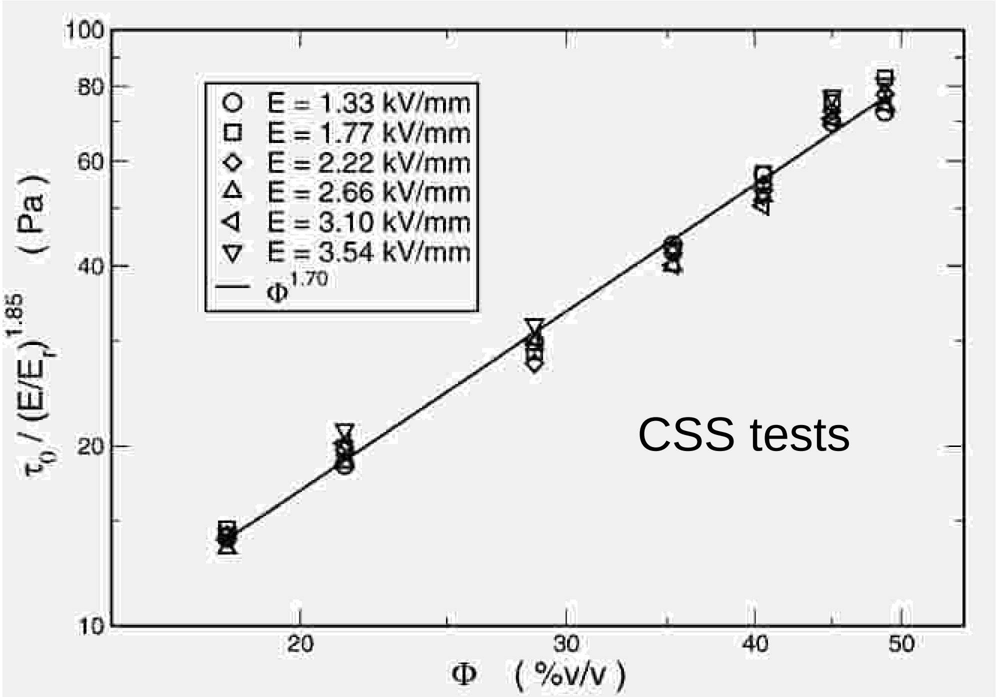
Yield stress:

Theories predict:

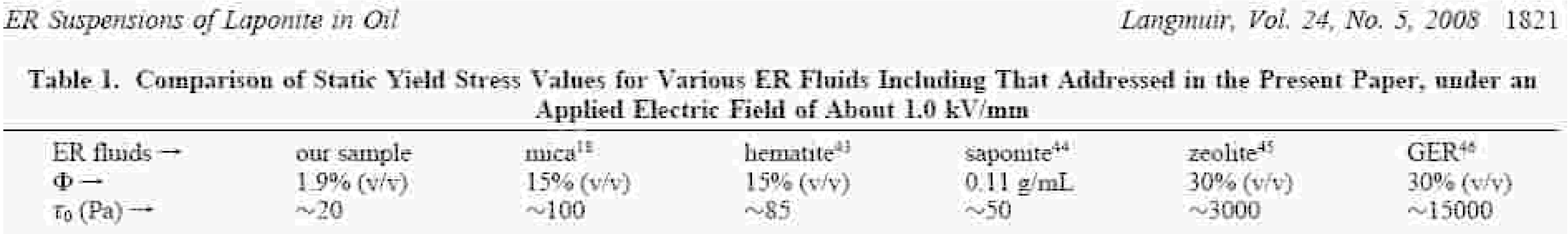
$$\tau \propto E^{\alpha}\,\Phi^{\beta}$$



CSS tests

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 β ≈ 1.70 fits to the whole dataset..

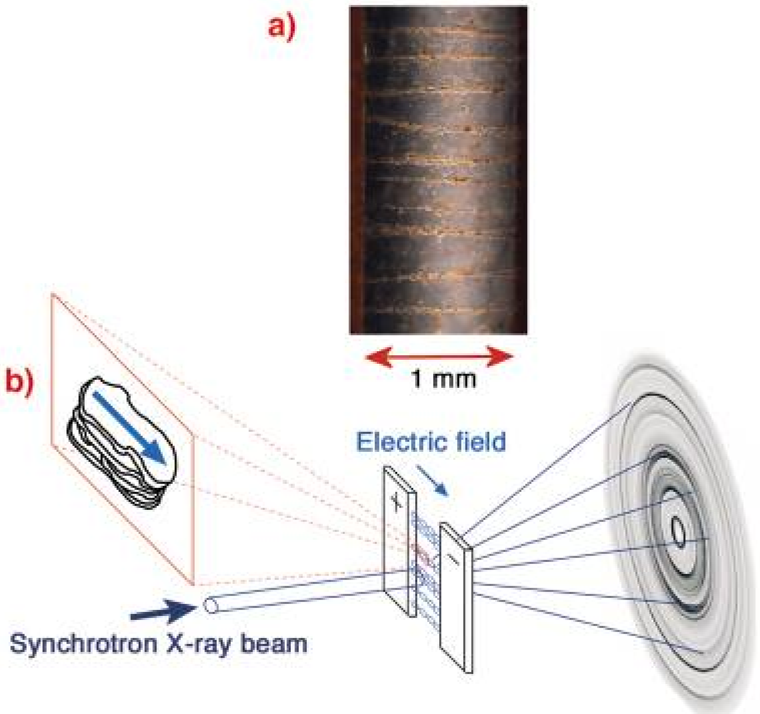


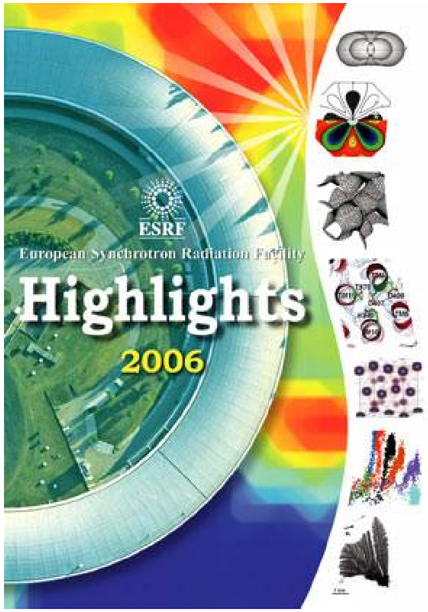
ER Suspensions of Laponite in Oil *Langmuir, Vol. 24, No. 5, 2008* 1821

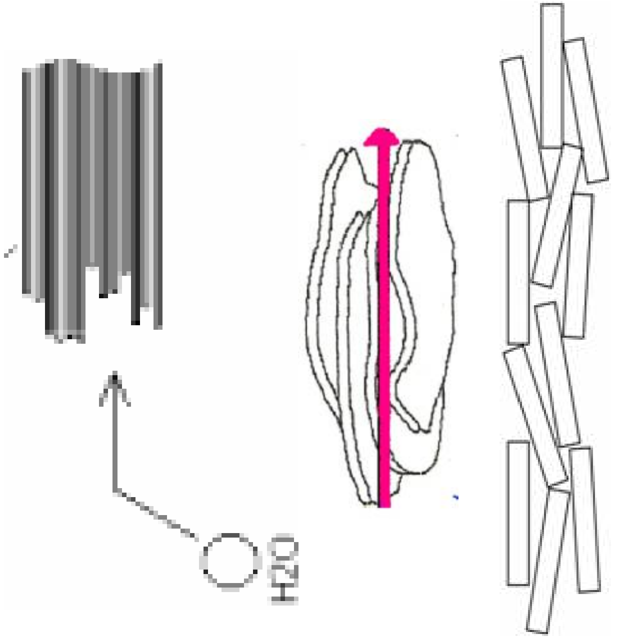
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

ER fluids →	our sample	mica[18]	hematite[43]	saponite[44]	zeolite[45]	GER[46]
Φ →	1.9% (v/v)	15% (v/v)	15% (v/v)	0.11 g/mL	30% (v/v)	30% (v/v)
τ_0 (Pa) →	~20	~100	~85	~50	~3000	~15000

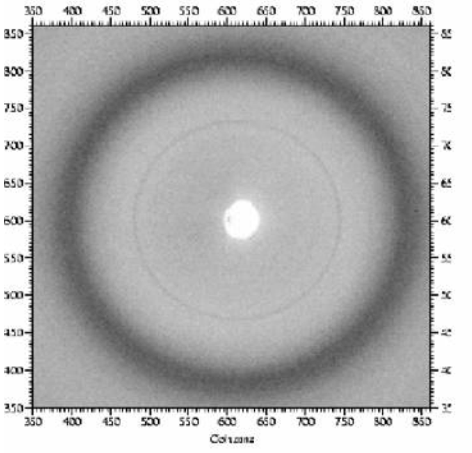
Experiments at ESRF, Grenoble:
In ESRF Scientific Highlights 2006



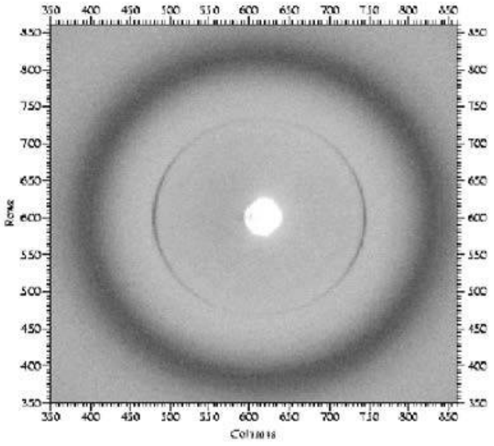


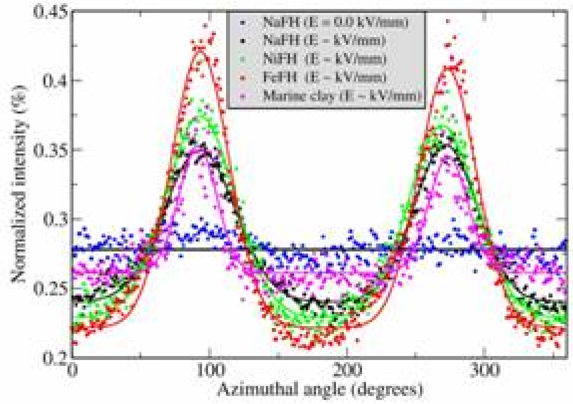


Before: 0 V/mm



After: 500 V/mm





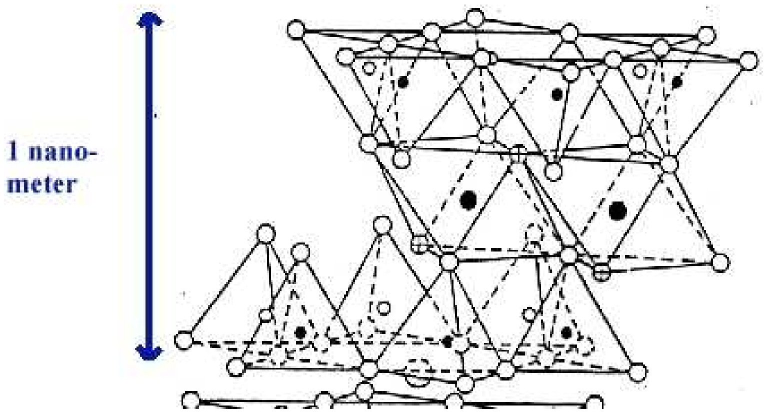
Angular distribution function
$= S_2 = ½\langle 3\cos^2\theta - 1\rangle$

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?**

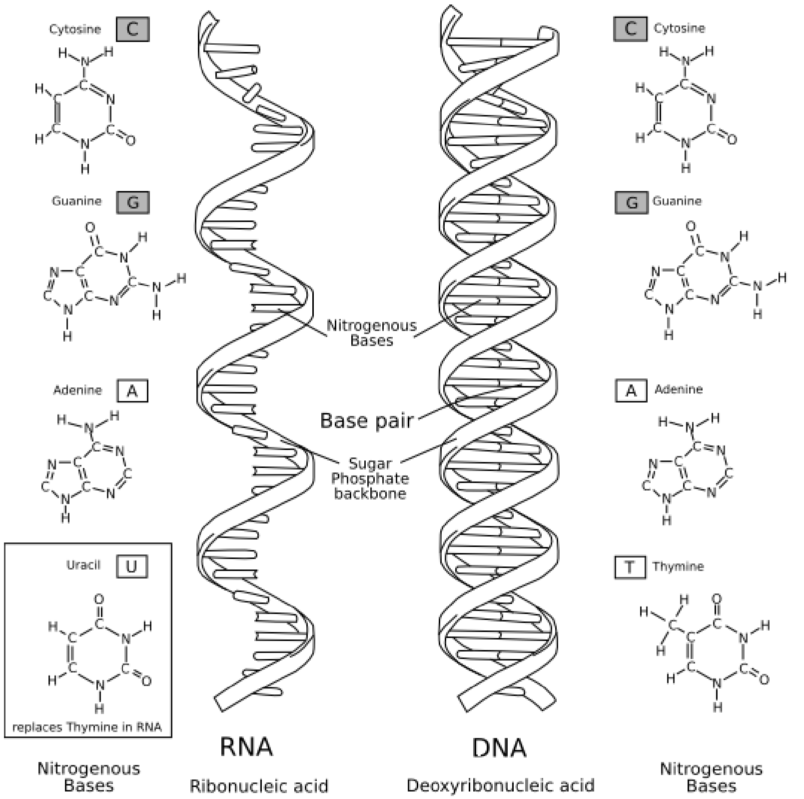


Bernal (1951), first suggested that clay minerals played a key role in chemical evolution and the origins of life because of their ability to take up, protect (against ultraviolet radiation), concentrate, and catalyze the polymerization of, organic molecules.

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

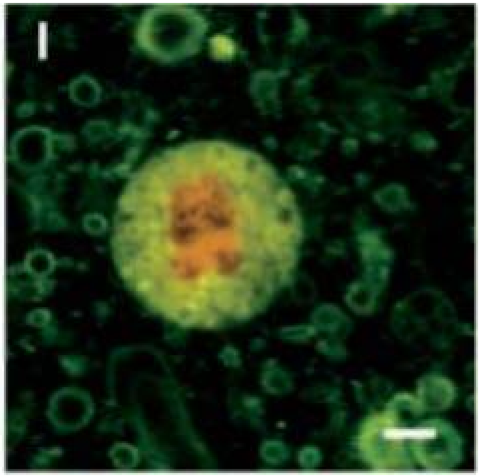


The RNA world refers to the self-replicating ribonucleic acid (RNA) molecules hypothesised to have been the precursors to all current life on Earth.

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

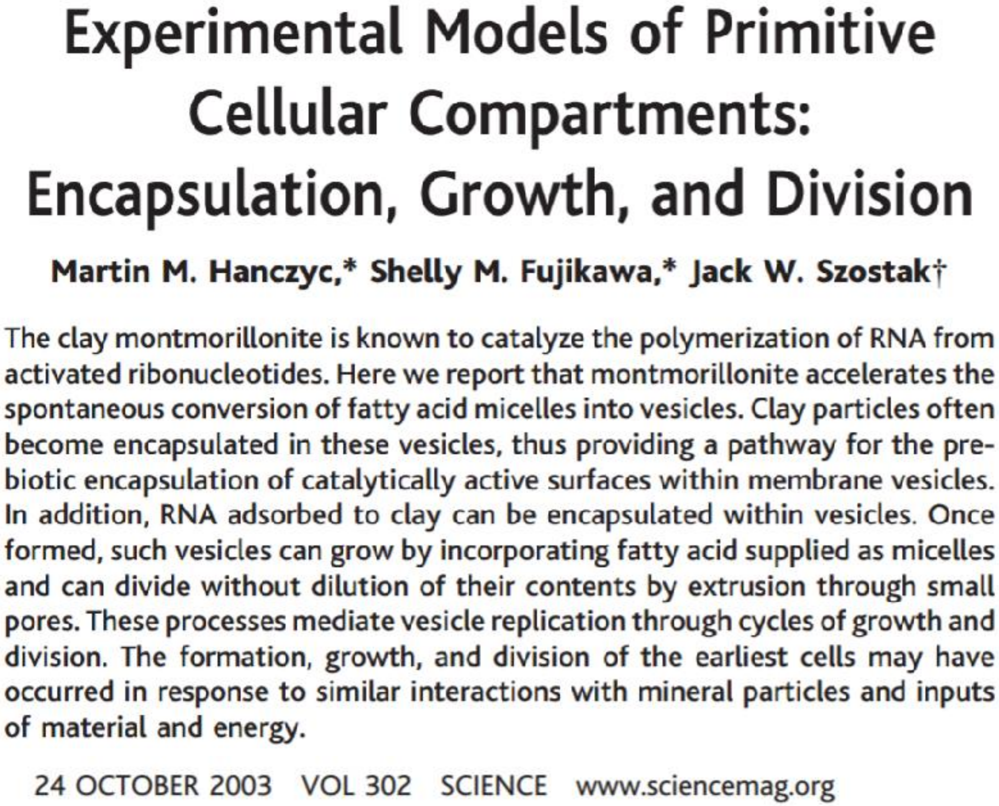
Eventually DNA is thought to have taken over the role RNA in data storage due to its increased stability, while proteins, through a greater variety of monomers (amino acids), replaced RNA's role in specialized biocatalysis.

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.

24 OCTOBER 2003 VOL 302 SCIENCE www.sciencemag.org

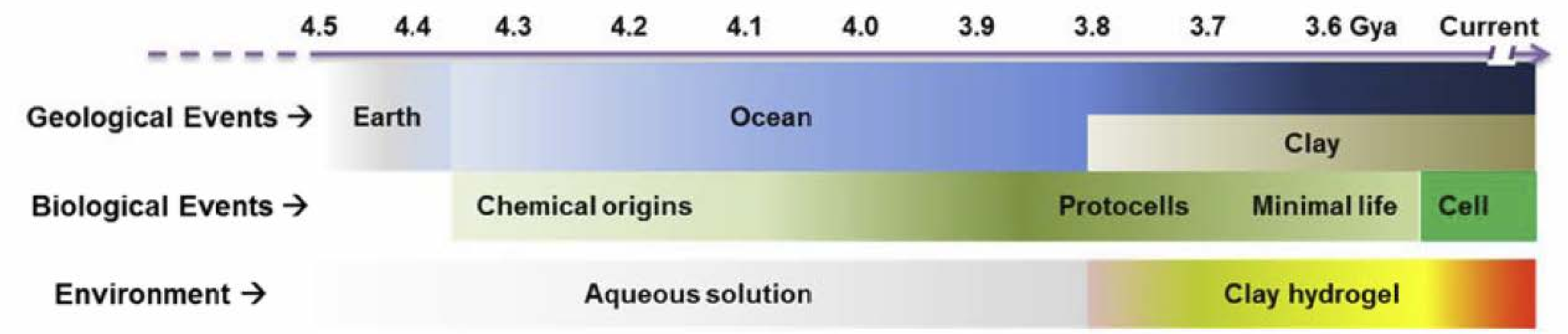
The Szostak Lab

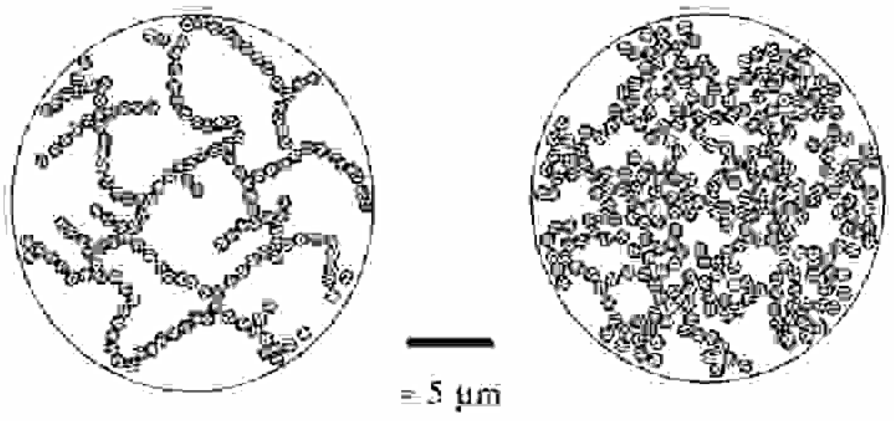
http://molbio.mgh.harvard.edu/szostakweb/

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

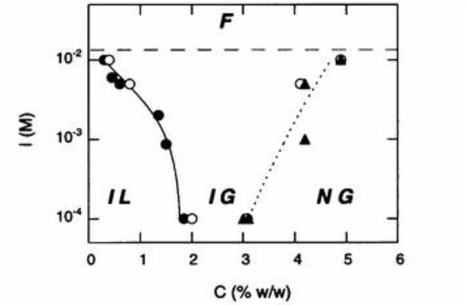
Enhanced transcription and translation in clay hydrogel and implications for early life evolution, Dayong Yang, Songming Peng, Mark R. Hartman, Tiffany Gupton-Campolongo, Edward J. Rice,Anna Kathryn Chang, Zi Gu, G. Q. (Max) Lu & Dan Luo, **SCIENTIFIC REPORTS , 3 : 3165, DOI: 10.1038/srep03165 (2013)**

~ RNA world

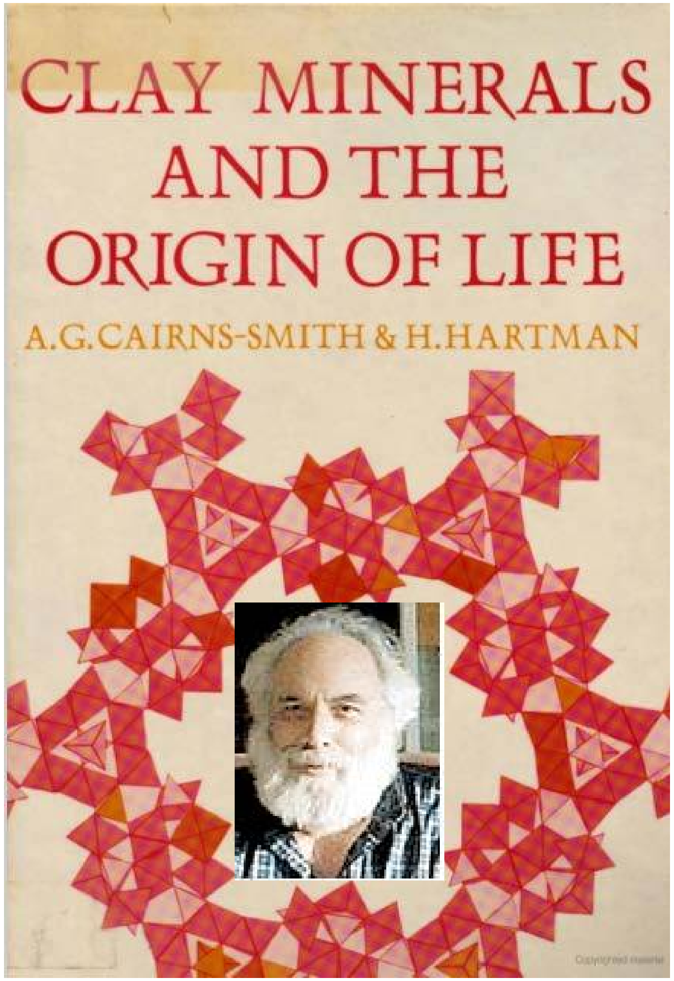




Confinement by clay hydrogel provide an effective environment for localized concentration and protection of nucleic acids.

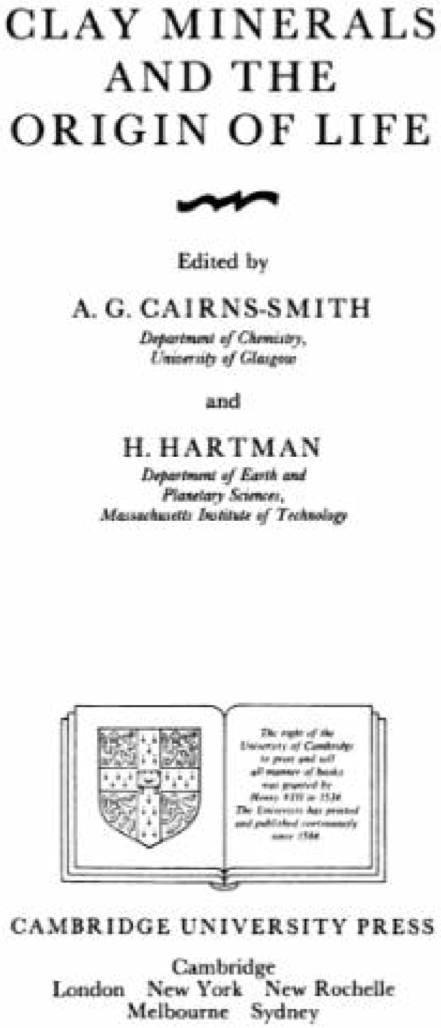


Bulk-scale clay hydrogel is easily broken down by shear forces into micro-particles, which act as the confinement for biomolecules and biochemical reactions



CLAY MINERALS AND THE ORIGIN OF LIFE

A.G.CAIRNS-SMITH & H.HARTMAN



CLAY MINERALS
AND THE
ORIGIN OF LIFE

Edited by

A. G. CAIRNS-SMITH
Department of Chemistry,
University of Glasgow

and

H. HARTMAN
Department of Earth and
Planetary Sciences,
Massachusetts Institute of Technology

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Melbourne Sydney

-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)

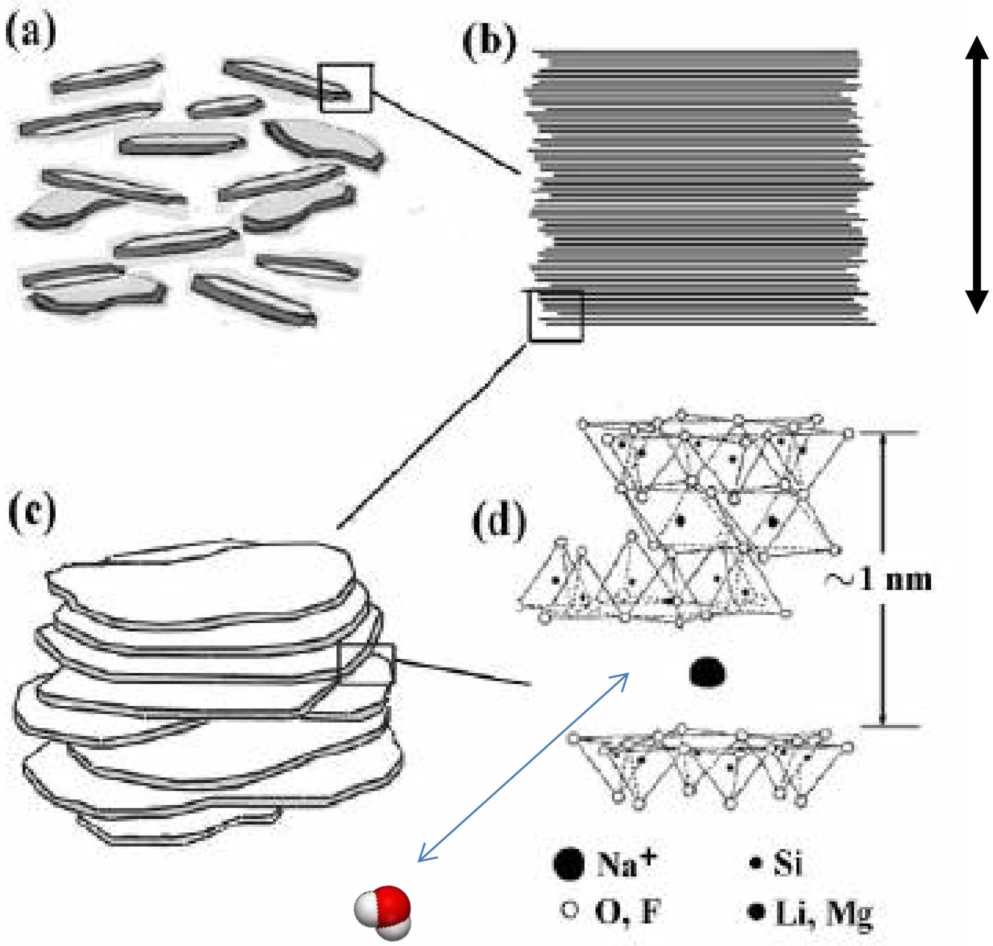
-Role of Clay Minerals in Chemical Evolution and the Origins of Life, Hideo Hashizume in Earth and Planetary Sciences » Geology and Geophysics » "Clay Minerals in Nature - Their Characterization, Modification and Application", book edited by Marta Valaškova and Gražyna Simha Martynkova, ISBN 978-953-51-0738-5,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

There is lots of work to do, and this is our goal? Liquid or Solid at will? Emerging life?

Molecular interactions with clay particles

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)

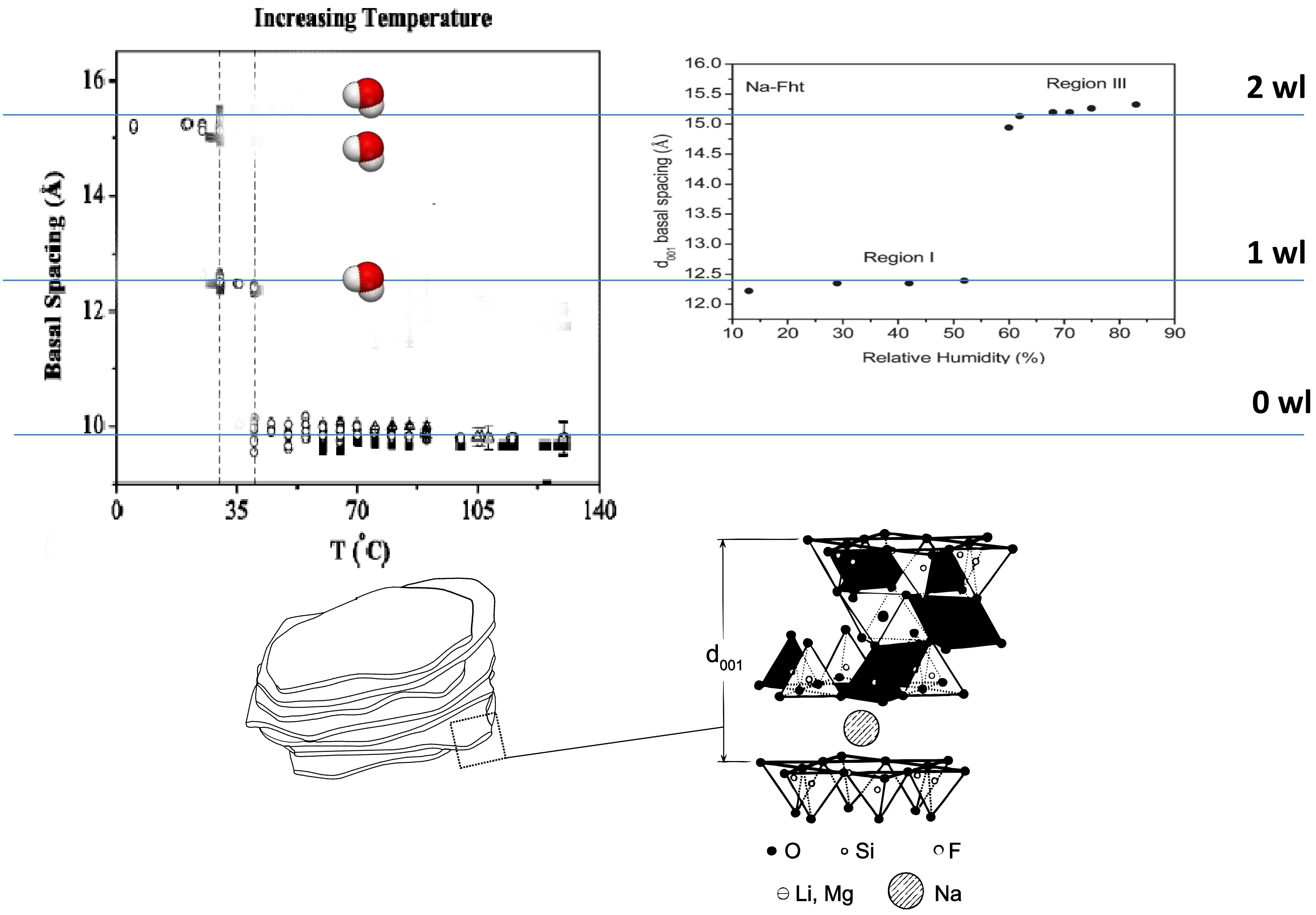


Water intercalation:

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

H_2O intercalation controlled by T/RH of sample environment:

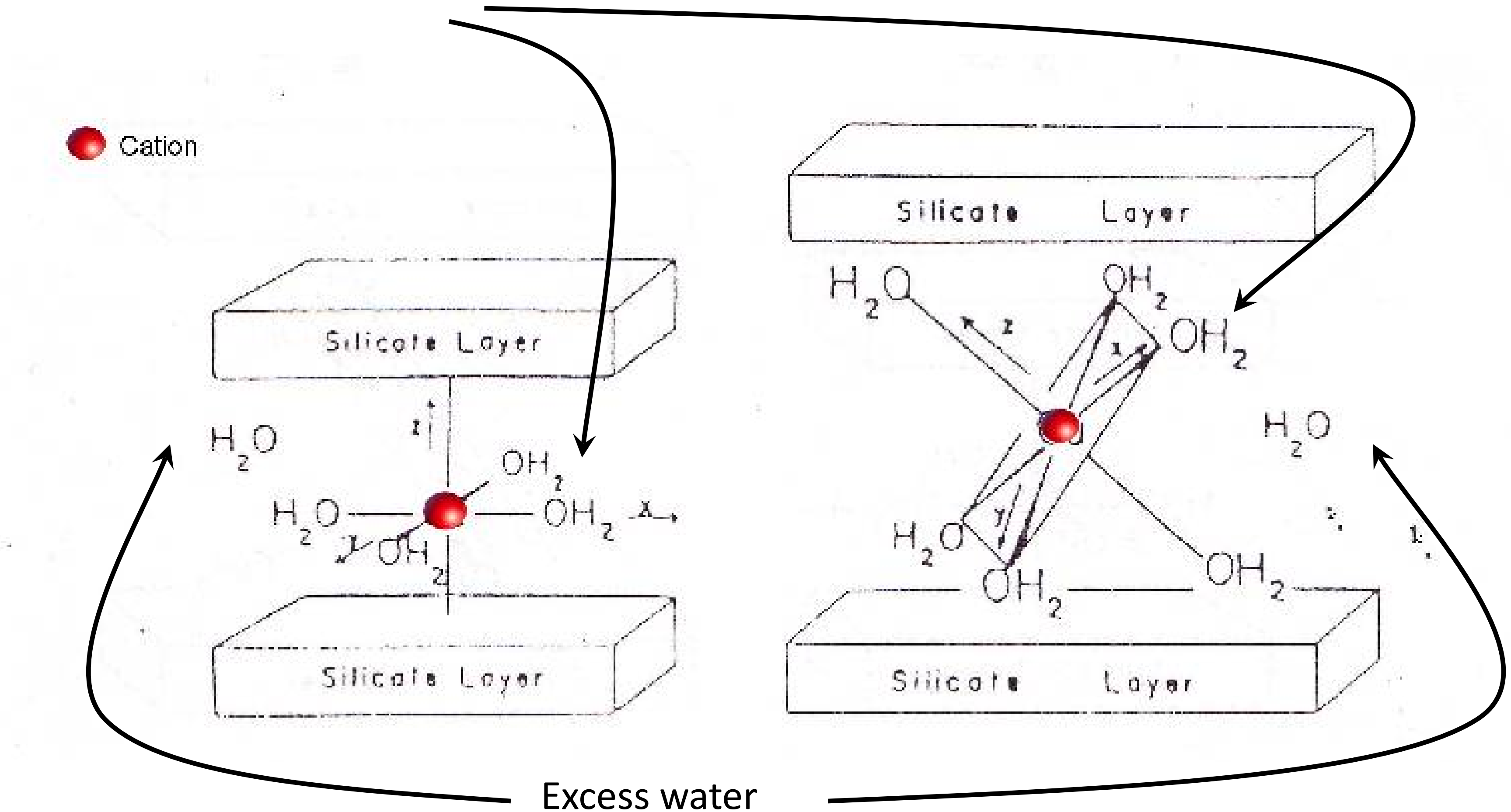
Na-fluorohectorite powder in humid air



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.**

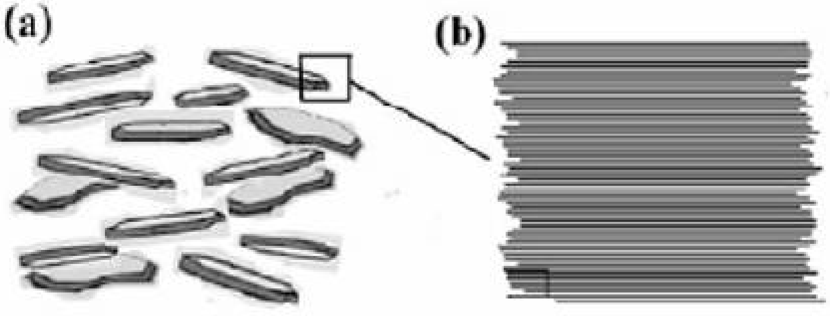
Two kinds of intercalated water:

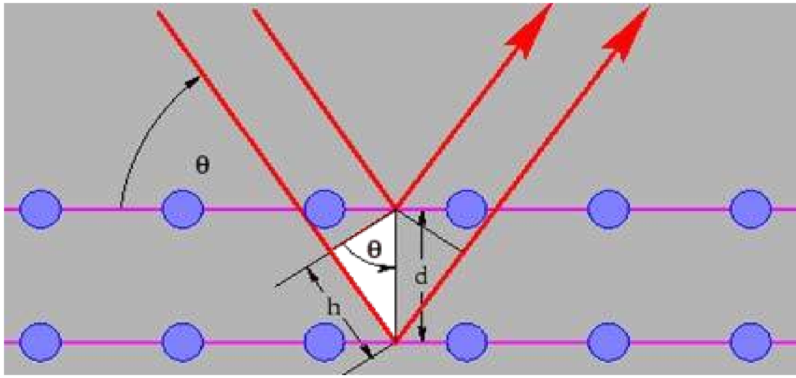


Water ”bound” in ion complexes

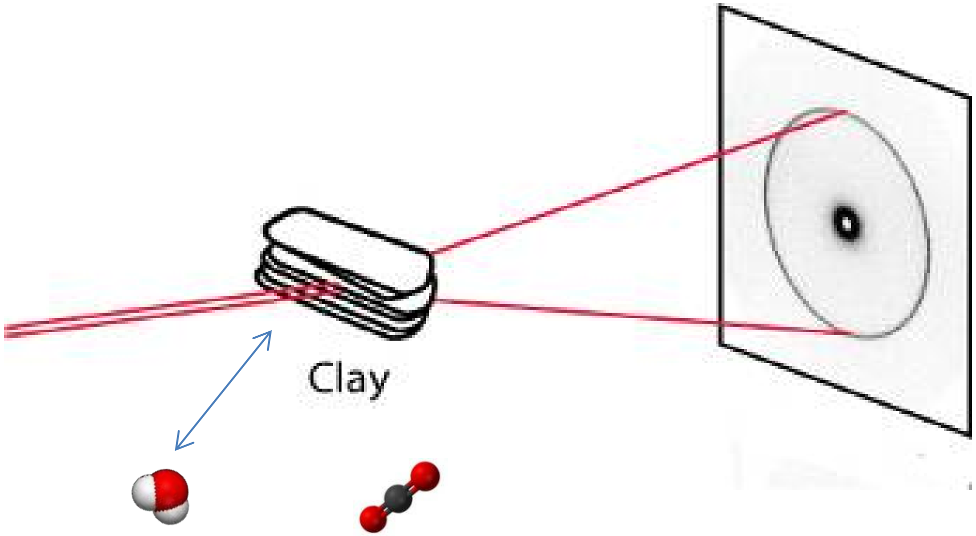
Excess water

Scattering of X-rays: Bragg’s law:

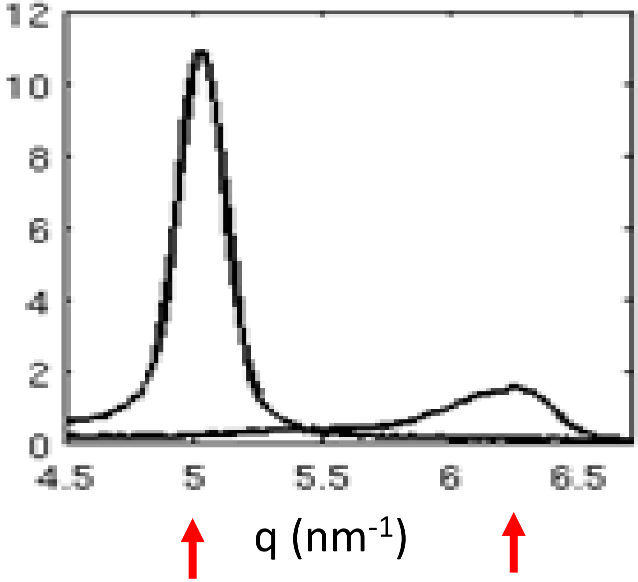




Constructive interference when $2h = \boxed{2d\sin\theta = n\lambda}$



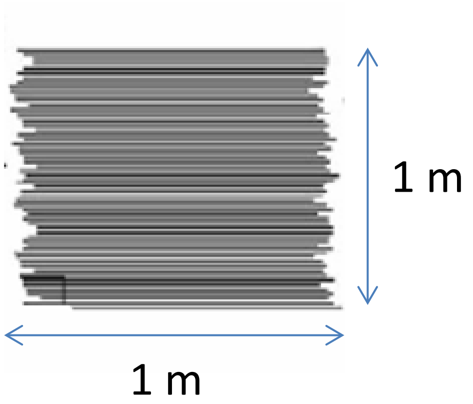
H_20 or CO_2



1.25 nm
1 layer H_2O intercalated

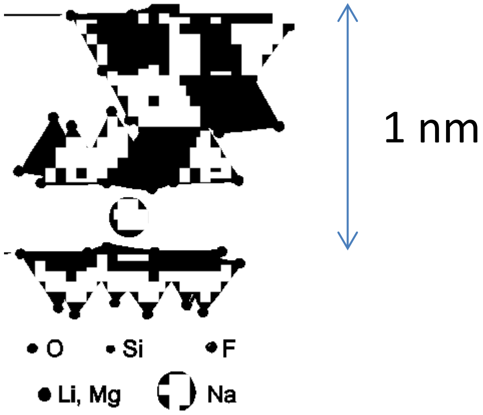
1 nm
Dry clay

How many "foreign" molecules are captured?

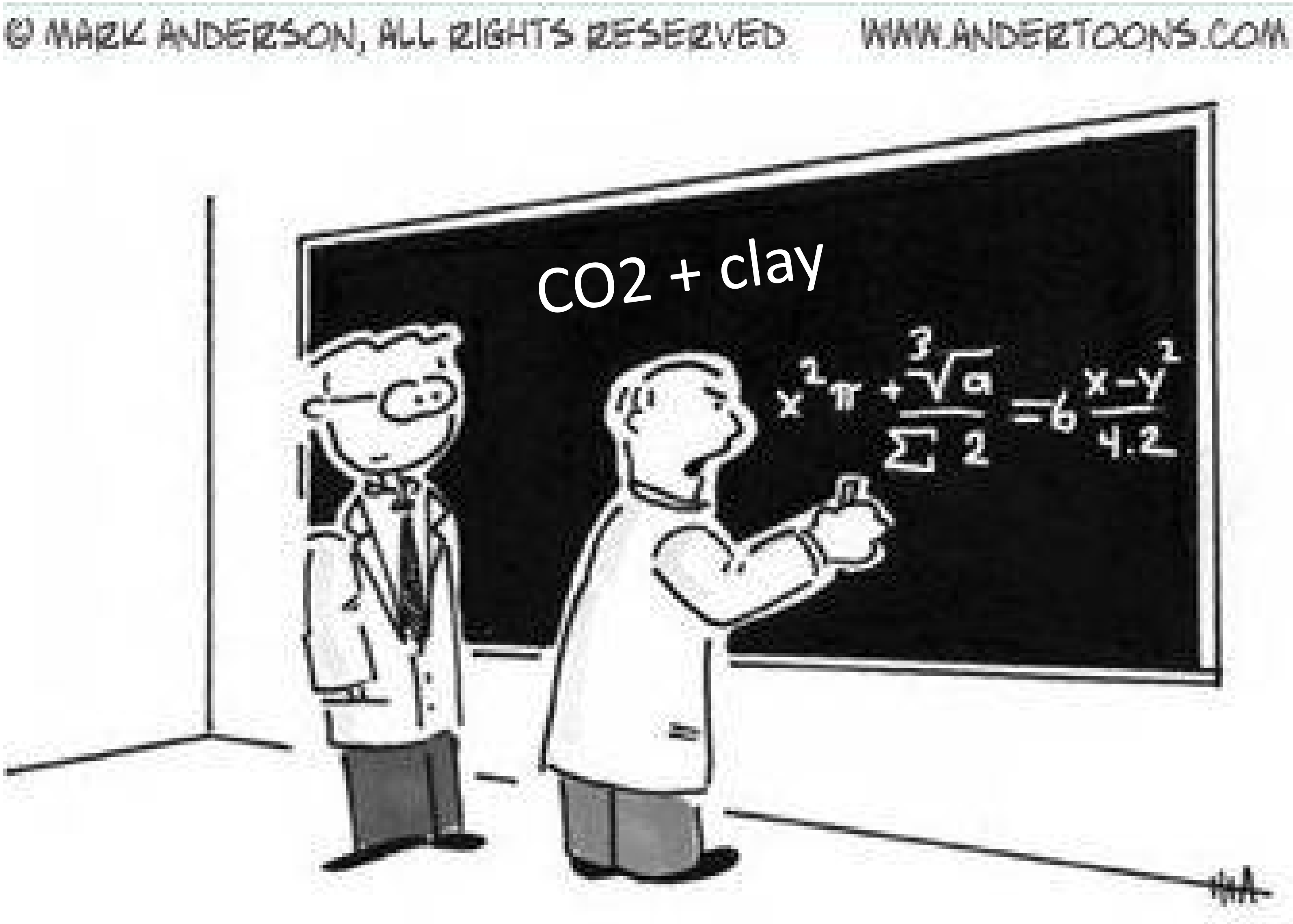


In 1 m^3 of compactly packed clay the total clay surface $2x10^9$ m^2 = 2000 $(km)^2$.
The typical packing density of our clay powder is 0.6, so
the total clay surface area available in 1 m^3 of clay powder is 0.6x2000 $(km)^2$ **~ 1200 $(km)^2$**.

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



Assumption:
~2 "foreign" molecules captured per $(nm)^2$, (NMR: ~ 2 water molecules complexed per cation at ambient conditions),

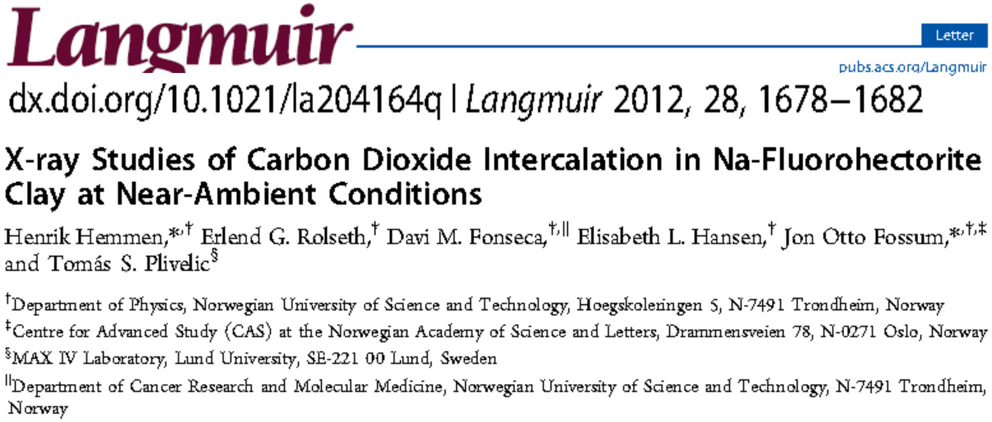


"It doesn't *have* to be politically correct!"

Before 2012:

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

The evidence presented in this study clearly shows that CO_2 at about -70 °C penetrates (intercalates) the smectite structure to a degree dependent upon the nature of the replaceable interlayer cation.



Langmuir

Letter

pubs.acs.org/Langmuir

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. Plivelic[§]

[†] Department of Physics, Norwegian University of Science and Technology, Hoegskoleringen 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 + CO_2

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. Plivelic & G. J. da Silva

Affiliations | Contributions | Corresponding authors

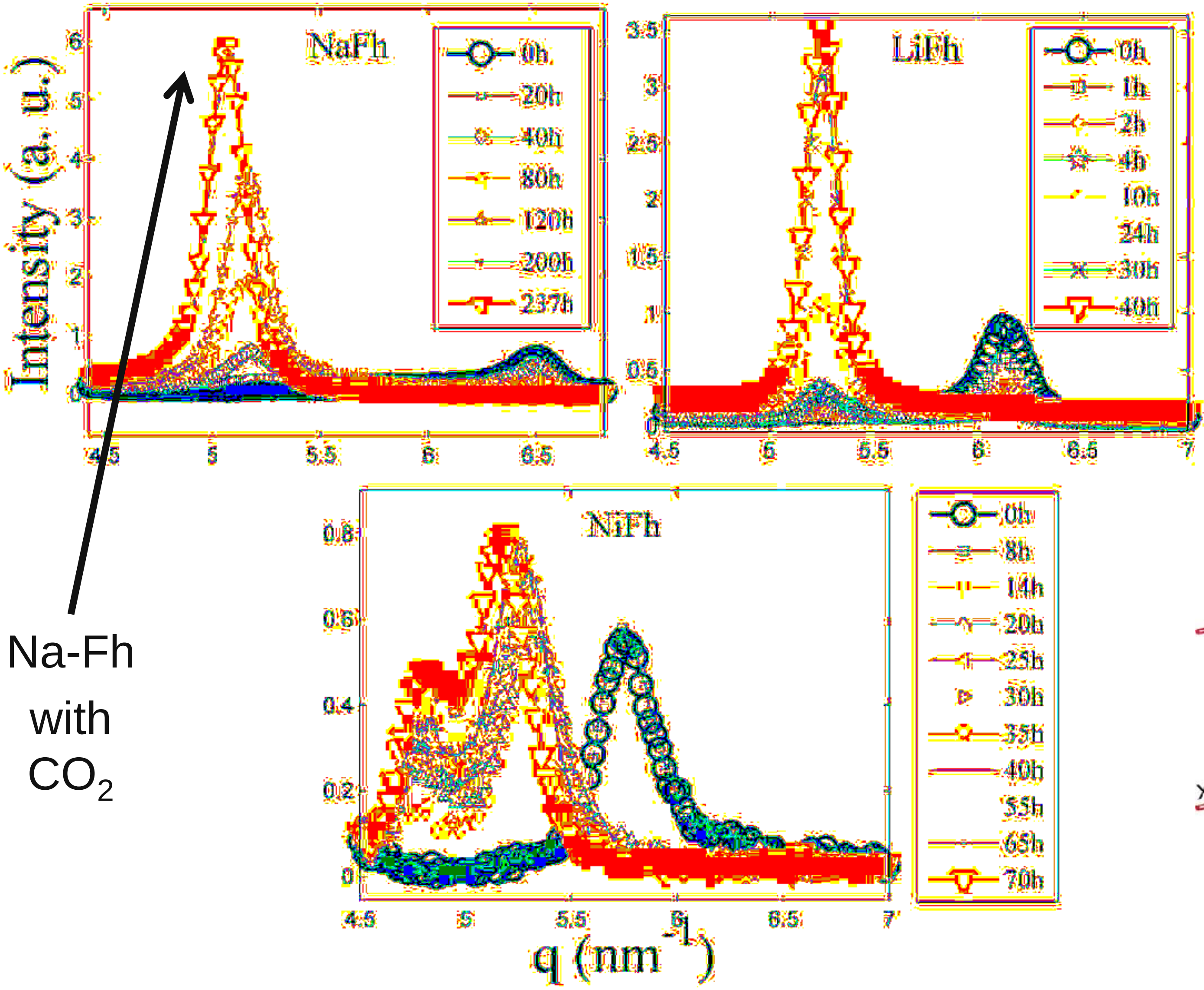
Scientific Reports **5**, Article number: 8775 | doi:10.1038/srep08775

Received 12 November 2014 | Accepted 29 January 2015 | Published 05 March 2015

CO_2 intercalation

$P = 20\ \text{bar}$

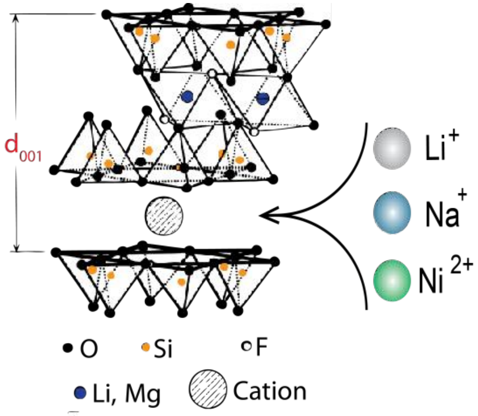
$T = -20^oC$

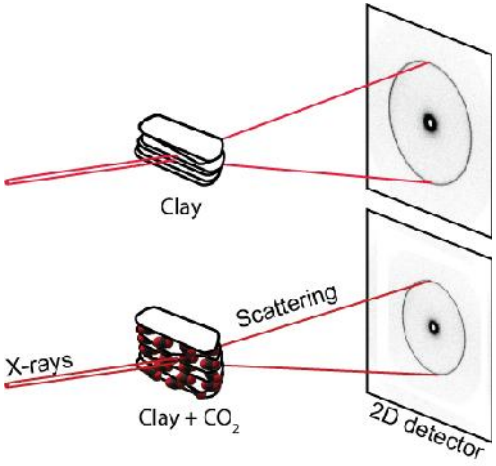


Na-Fh

with

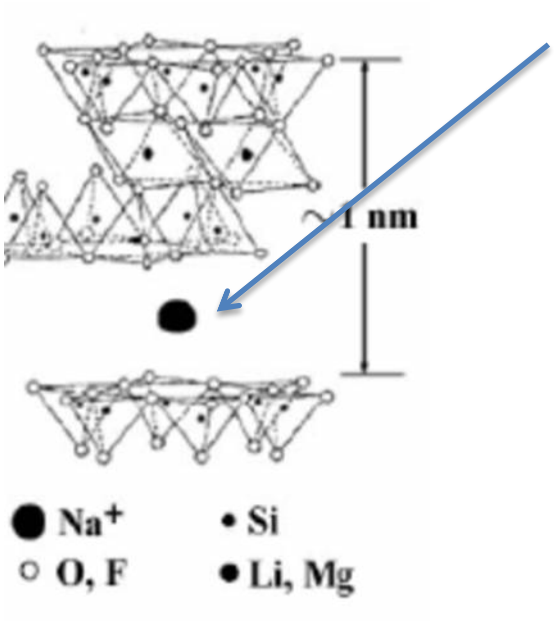
CO_2

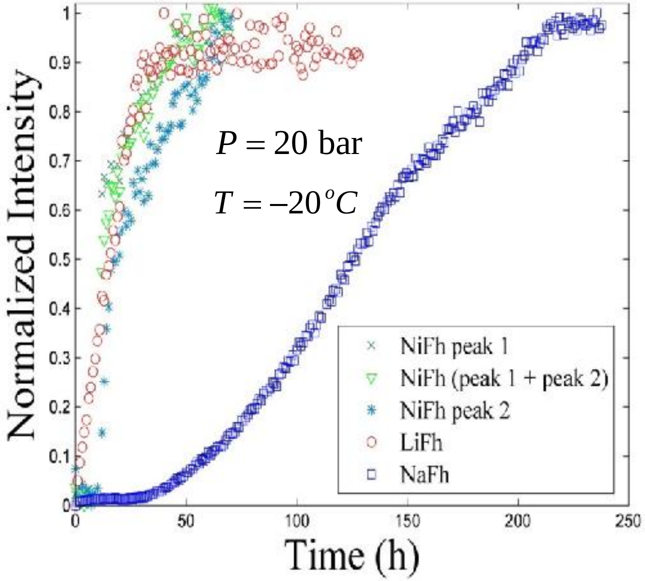




Powders are completelt dehydrated before exposed to CO_2: Blue data points above

Cation dependence



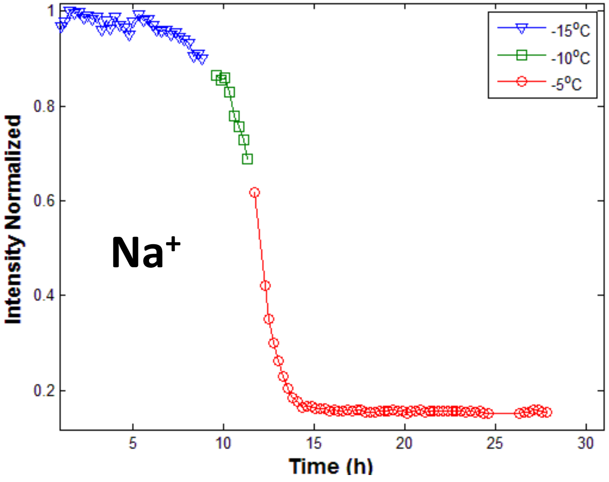


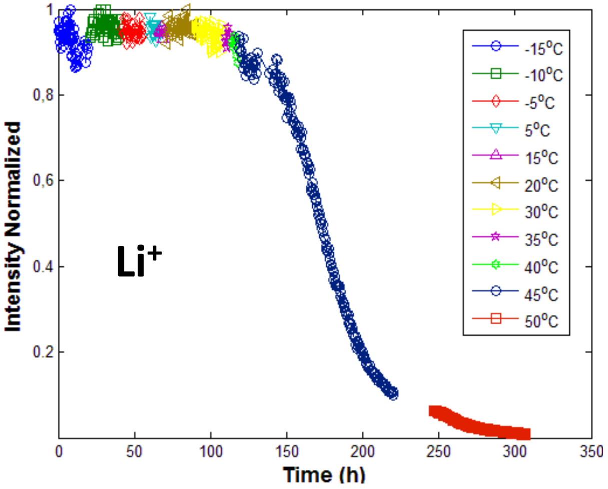
CO_2 Capture:

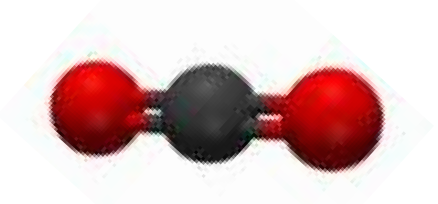
Faster uptake for:
Lower T or higher p

CO_2 Retention:

- N_2 flushing
- Increasing temperature





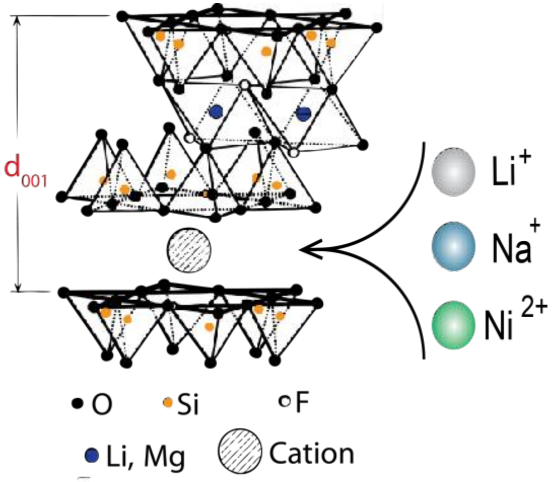


CO_2 polarisibility by Li^+ vs Na^+ ??

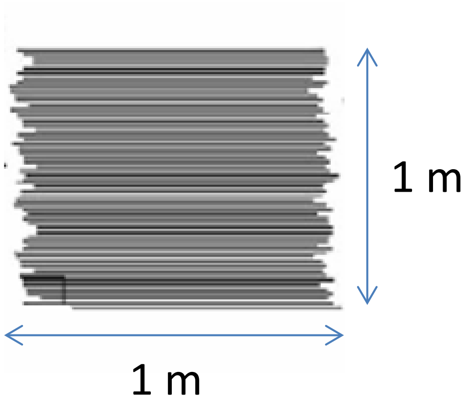
Simplest interpretation:

The clays provide a large surface area available for CO_2 capture.

The cations control capture and release of CO_2 (sometimes modified by clay swelling specifics).

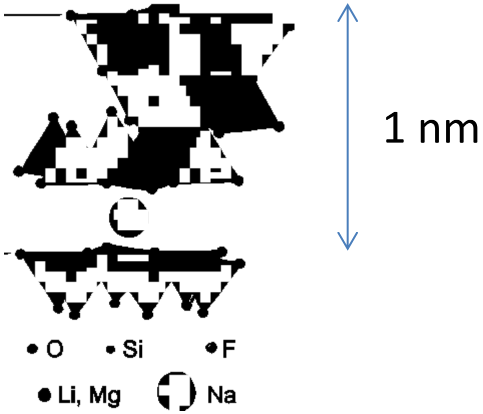


How much CO_2 is captured?



In 1 m^3 of compactly packed clay the total clay surface $2x10^9$ m^2 = 2000 $(km)^2$.
The typical packing density of our clay powder is 0.6, so **the total clay surface area available in 1 m^3 of clay powder** is 0.6x2000 $(km)^2$ **~ 1200 $(km)^2$**.

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



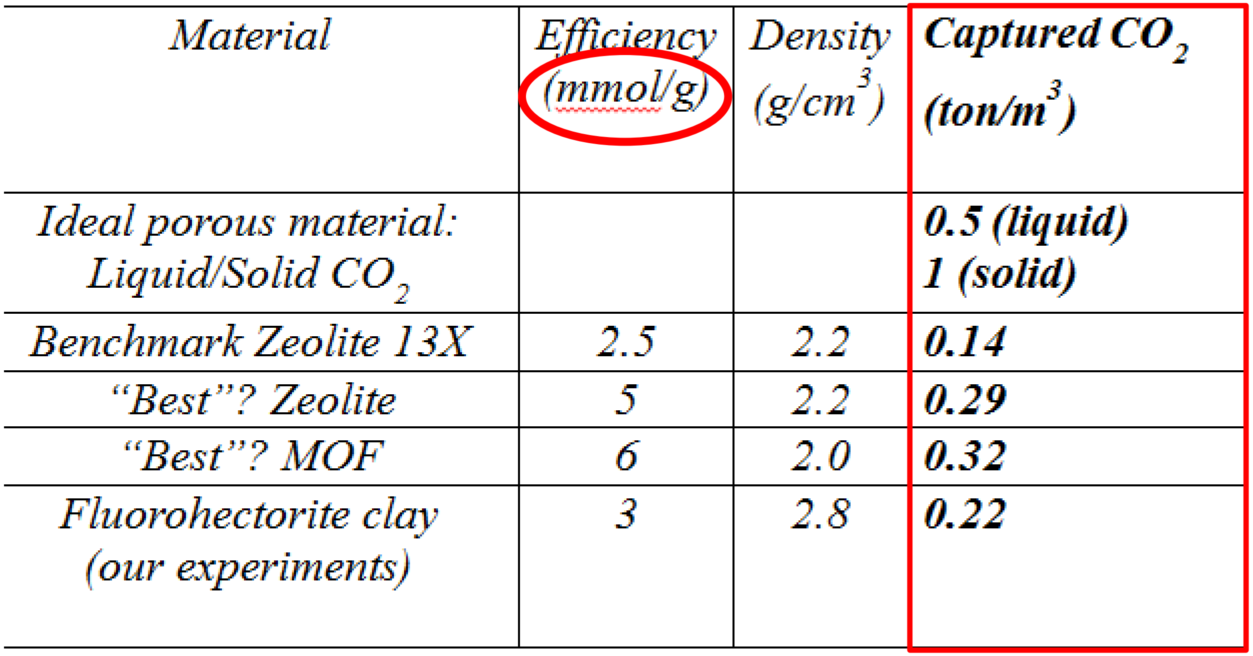
Assumption:
~2 CO_2 molecules captured per cation, (NMR: ~ 2 water molecules complexed per cation at ambient conditions), **which corresponds to ~ 2 CO_2 molecules captured per $(nm)^2$**.

~14% mass increase of the clay when saturated with CO_2, or ~0.22 tons CO_2/m^3 clay.

To check this we did:

pressure composition Temperature (pcT) experiments measure mass increase when sample is loaded with CO_2 => **15% mass increase, confirms assumption above**.

The amount of captured CO_2 for fluorohectorite clay compared with those of other materials.



Material	*Efficiency (mmol/g)*	*Density (g/cm^3)*	***Captured CO_2 (ton/m^3)***
Ideal porous material: Liquid/Solid CO_2			***0.5 (liquid) 1 (solid)***
Benchmark Zeolite 13X	*2.5*	*2.2*	***0.14***
"Best"? Zeolite	*5*	*2.2*	***0.29***
"Best"? MOF	*6*	*2.0*	***0.32***
Fluorohectorite clay (our experiments)	*3*	*2.8*	***0.22***

The density of liquid CO_2 is 0.77 ton/m^3 at 56 atm and 20 °C (the density of solid CO_2 is about twice of this) suggesting that ~1 ton CO_2 captured per m^3 is near the theoretical "perfect and unachievable" upper limit for CO_2 capture by any porous material, zeolite, MOF, carbon based, clay, or other.

Our synthetic fluorohectroite 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.

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Clays in BIONANOTECHNOLOGY

Parrots of the Amazones:

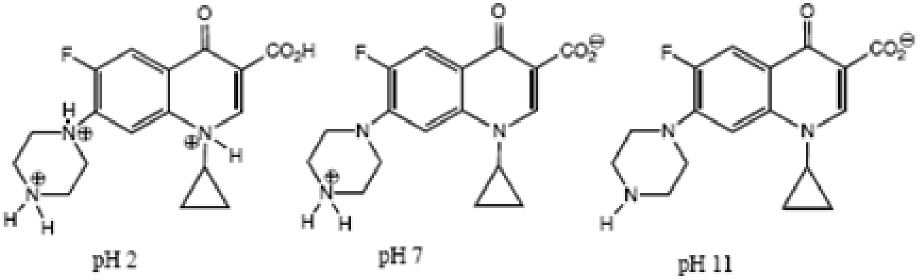
Parrots of the Amazon eat clay at riverbanks for breakfast in order to prevent stomach-ache from alkaloid poisons of the seeds in the fruits they eat for lunch.

Shows that clays may be interesting drug delivery systems

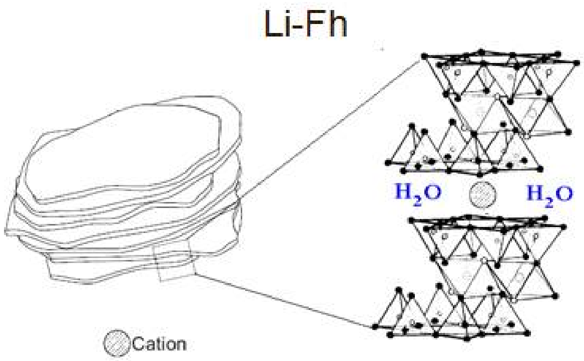
Cipro (ciprofloxacin) is an antibiotic in a group of drugs called fluoroquinolones (flor-o-KWIN-o-lones). It is used to fight bacteria in the body. Cipro is used to treat different types of bacterial infections. It may also be used to prevent or slow anthrax after exposure.

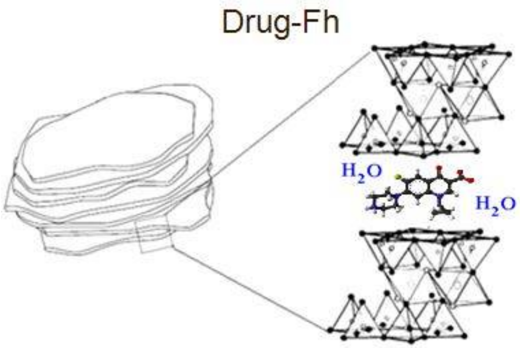
$C_{17}H_{18}FN_3O_3$

Zwitterionic



Positive **Dipole** **Negative**

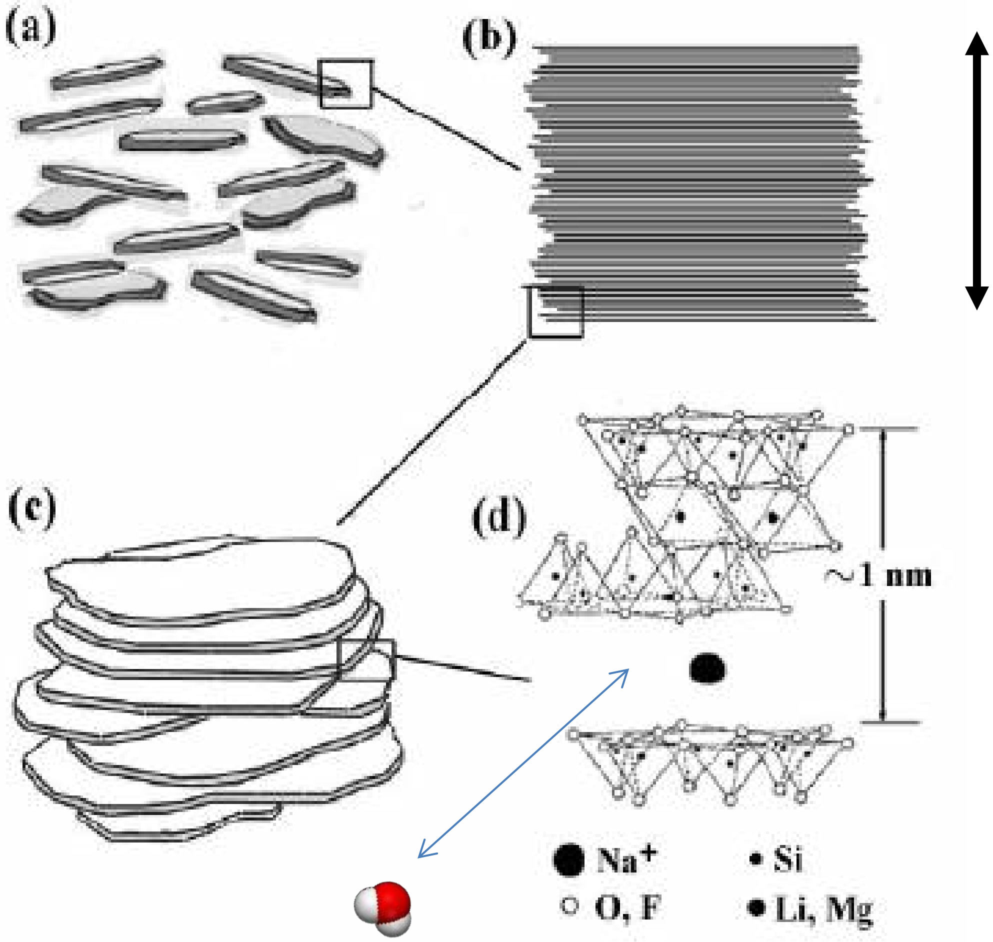




Intercalates by far best for acid pH
Different intercalation mechanism at pH 7?
Rapid release at basic pH
Techniques: XRD, UV-VIS Spectroscopy

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)

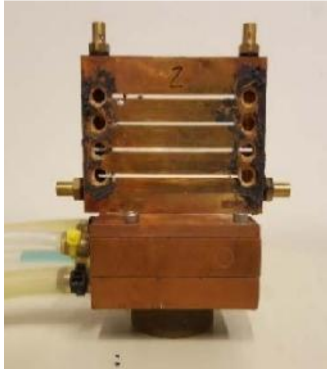


~ 100 nm

Water intercalation:

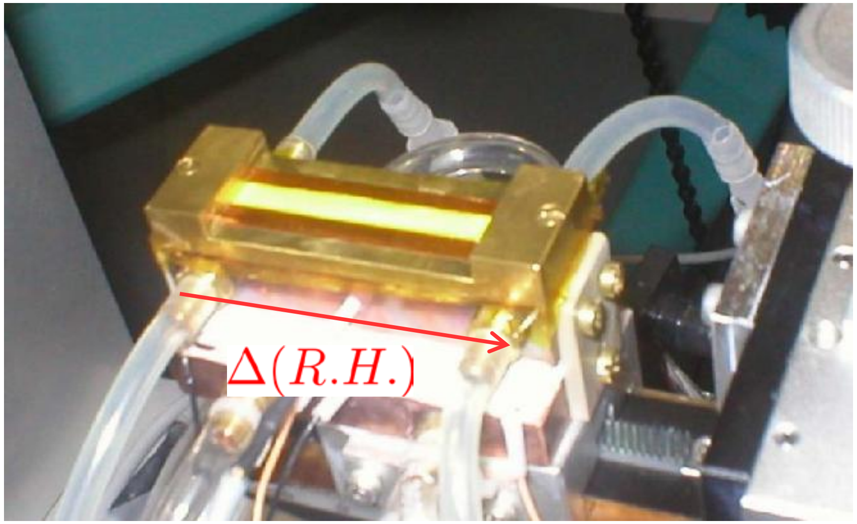
G. J. da Silva, J. O. Fossum, E. DiMasi, and K. J. Maloy,
Phys. Rev. B 67, 094114 2003.
G. J. da Silva, J. O. Fossum, E. DiMasi, K. J. Maloy, and S. B.Lutnaes,
Phys. Rev. E 66, 011303 2002.
R. P. Tenorio, L. R. Alme, M. Engelsberg, J. O. Fossum, and F. Hallwass,
J. Phys. Chem. C 112, 575 2008.
R. P. 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

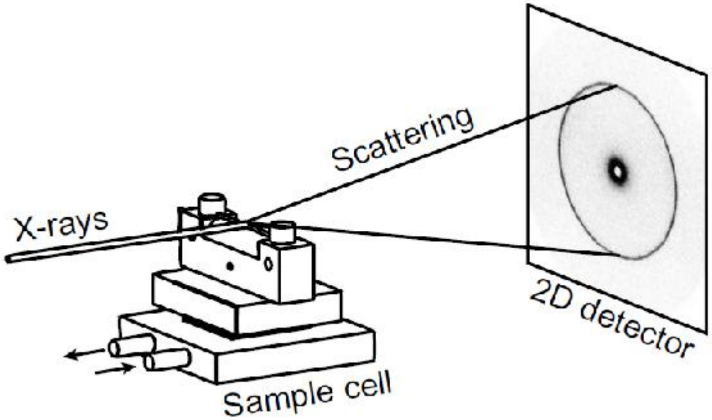
Water Transport Experiment

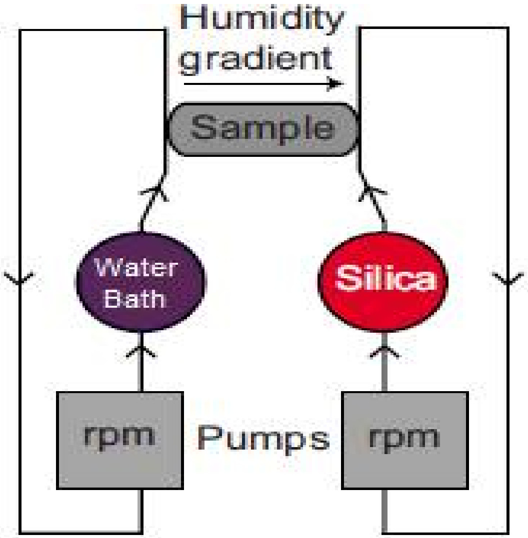


Only 2 cm of the capillary was observed using x-rays

→ Diffusive transport



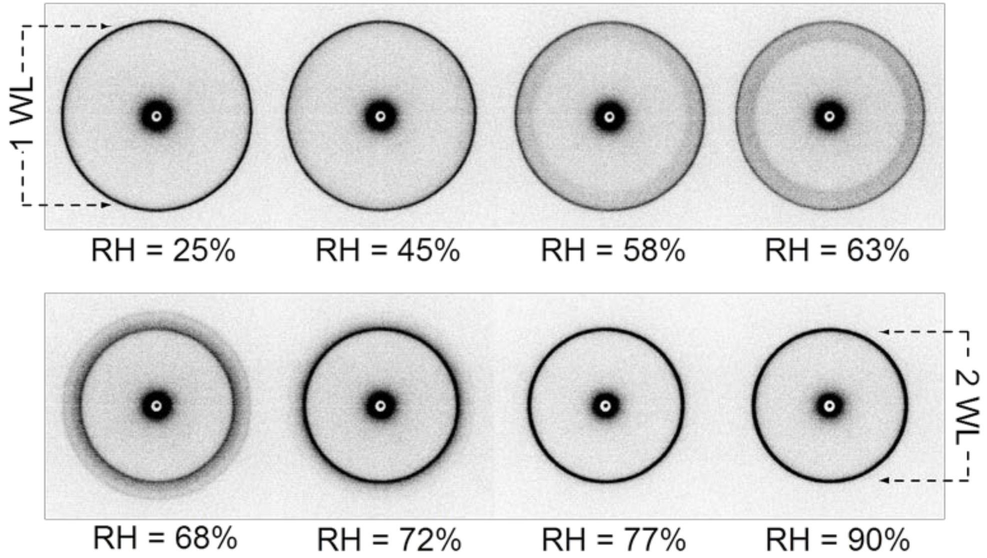


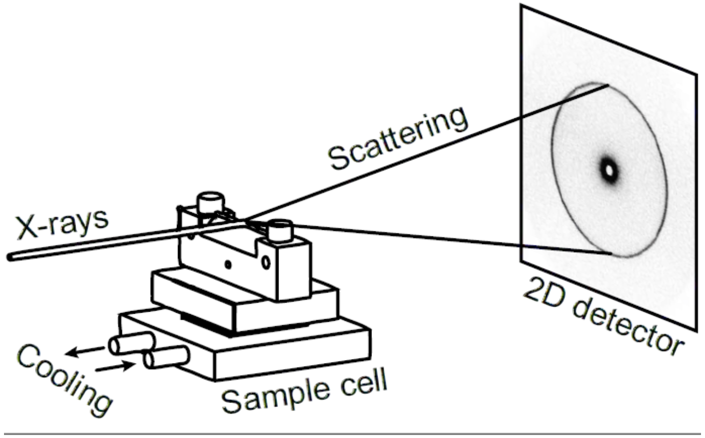


The Fluorohectorite was placed in 1 mm glass capillaries open in both ends, one end exposed to high relative water humidity (96%), the other end exposed to dry air (0.4%)

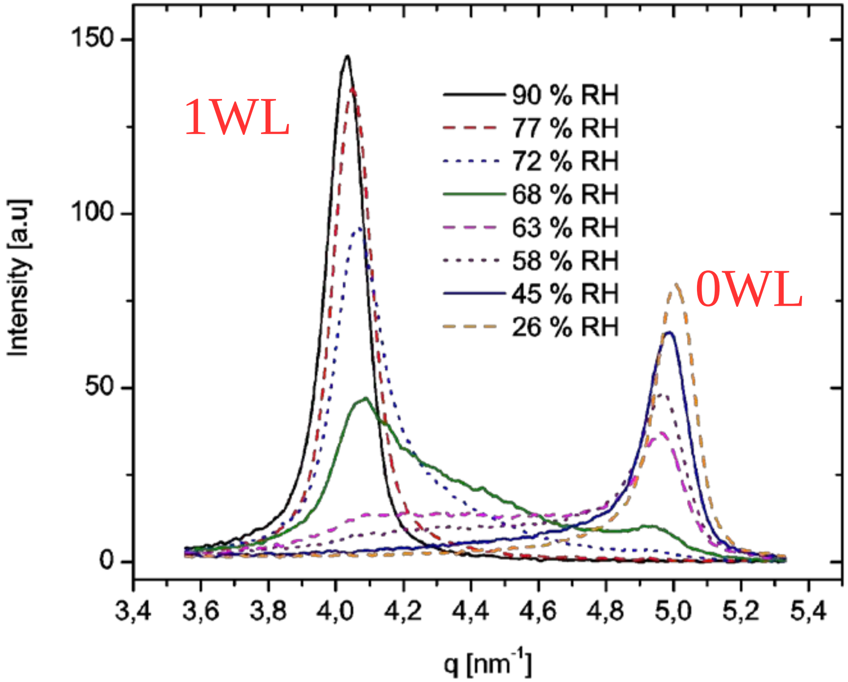
The sample is scanned forth and back in front of the X-ray beam:

- The 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
- diffaction spectra

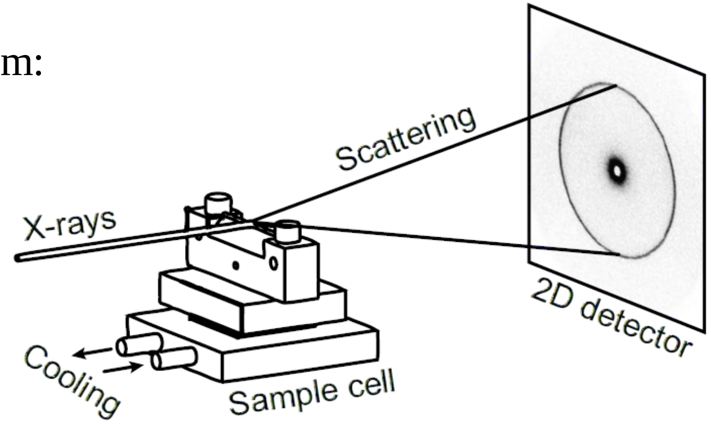


- The position of the peak is related to d_{001} :

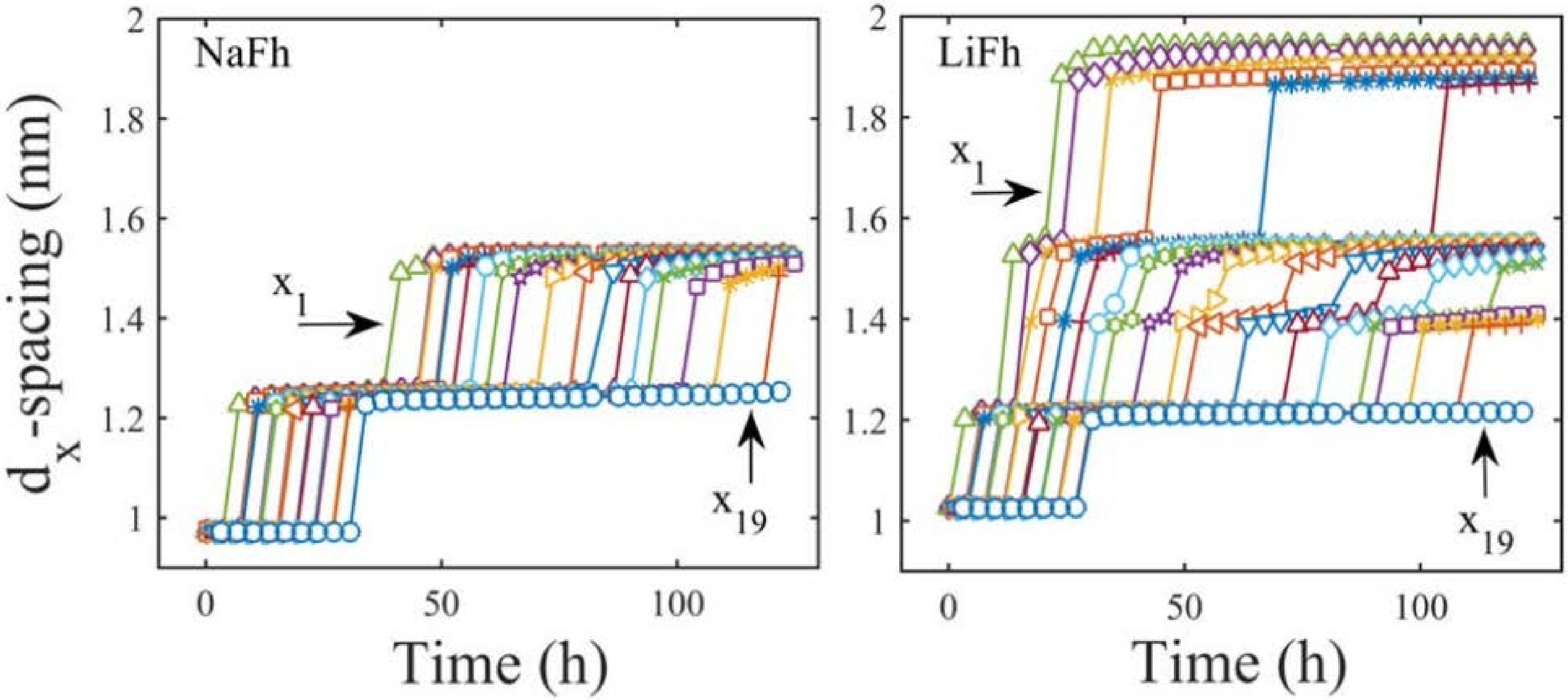
$$q = \frac{2\pi}{d}$$ (Bragg's law)

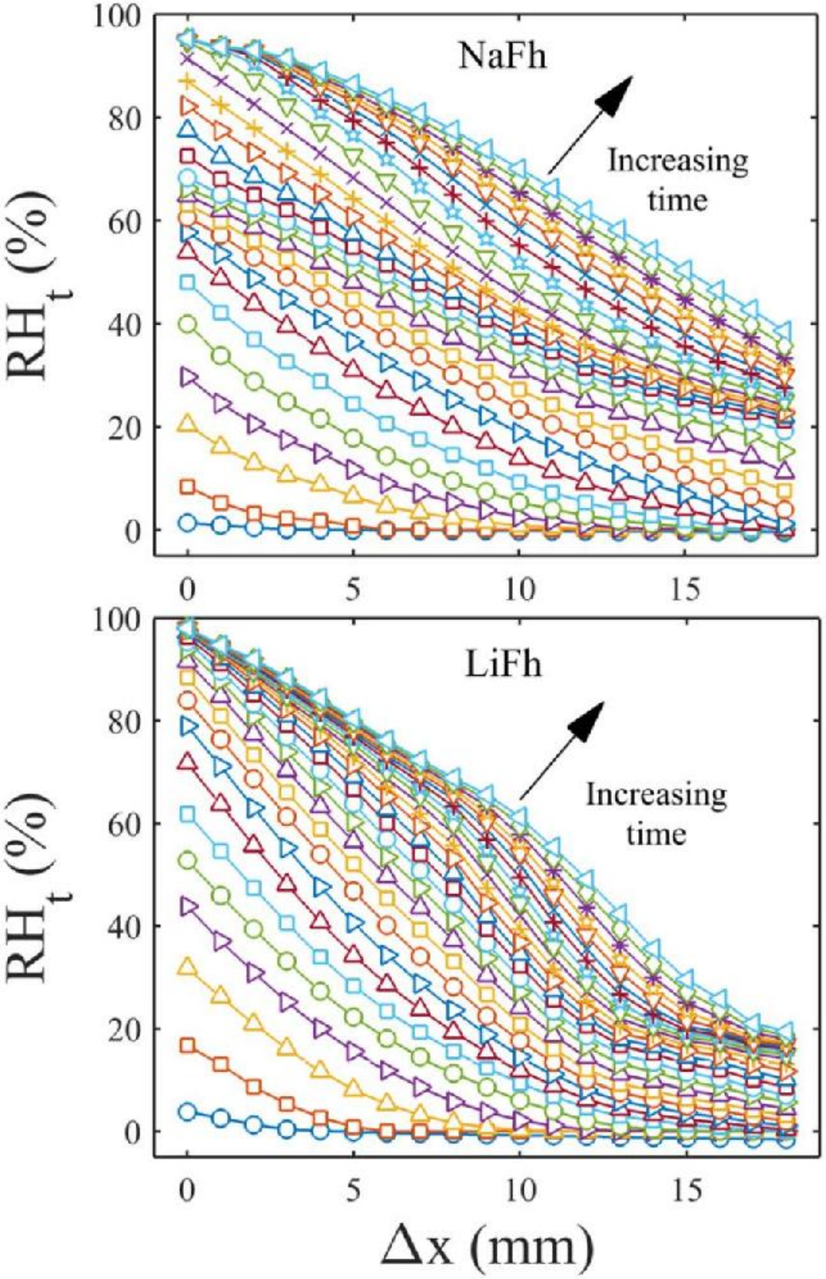
$q = (4\pi/\lambda) \sin\theta$

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:




NaFh
Increasing time
LiFh
Increasing time
RH_t (%)
RH_t (%)
0
20
40
60
80
100
0
5
10
15
Δx (mm)

Normal diffusion

- Diffusion equation (Fick's law): RH = W

$$\left\langle (\Delta x)^2 \right\rangle = 2Dt$$

$$\frac{\partial W(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(W) \frac{\partial}{\partial x} W(x,t) \right]$$

- Semi-infinite media:

$$W(x=0,t) = W_0 \quad \forall t > 0$$

$$W(x \to \infty, t) = 0$$

$$W(x, t=0) = 0$$

- Boltzmann transformation $\eta = x / t^{1/2}$

$$-\frac{1}{2}\eta \frac{dW}{d\eta} = \frac{d}{d\eta}\left(D(W) \frac{dW}{d\eta} \right)$$

$$D(W) = -(1/2)\left(\frac{d\eta}{dW} \right) \int_0^W \eta(W) dW'$$

Anomalous diffusion

- Fractal diffusion equation: (Riemann-Louiville fractional derivative)

$$\left\langle (\Delta x)^2 \right\rangle = \frac{2D_\gamma t^\gamma}{\Gamma(1+\gamma)} \qquad \frac{\partial^\gamma W(x,t)}{\partial t^\gamma} - \frac{t^{-\gamma}}{\Gamma(1-\gamma)} W(x,0) = \frac{\partial}{\partial x}\left(D_\gamma(W) \frac{\partial W(x,t)}{\partial x} \right)$$

$$\frac{\partial^\gamma W(x,t)}{\partial t^\gamma} = \frac{1}{\Gamma(1-\gamma)} \frac{\partial}{\partial t} \int_0^t W(x,t')\,dt' \Big/ (t-t')^\gamma$$

- Boltzmann transformation: $\eta = x/t^\gamma$

$$\frac{1}{\Gamma(1-\gamma)} \int_0^1 \left((1-\gamma) W\left(\eta/u^{\gamma/2}\right) - (\gamma/2)\eta \frac{\partial W\left(\eta/u^{\gamma/2}\right)}{\partial \eta} \right) \frac{du}{(1-u)^\gamma} = \frac{\partial}{\partial \eta}\left(D_\gamma(W) \frac{\partial W}{\partial \eta} \right)$$

$$D_\gamma(W) = \frac{d\eta}{dW} \frac{1}{\Gamma(1-\gamma)} \int_\infty^\eta d\eta' \int_{\eta'}^\infty \left((2/\gamma)(1-\gamma) \frac{W(\xi)}{\xi} - \frac{dW(\xi)}{d\xi} \right) \frac{(\eta'/\xi)^{2/\gamma}\, d\xi}{\left[1-(\eta'/\xi)^{2/\gamma} \right]^\gamma}$$

→ If valid, the profiles W(η) are independent of the time at which they are recorded !

Anomalous diffusion

- Fractal diffusion equation: (Riemann-Louiville fractional derivative)

$$\left\langle \left(\Delta x\right)^2 \right\rangle = \frac{2D_\gamma t^\gamma}{\Gamma\left(1+\gamma\right)}$$

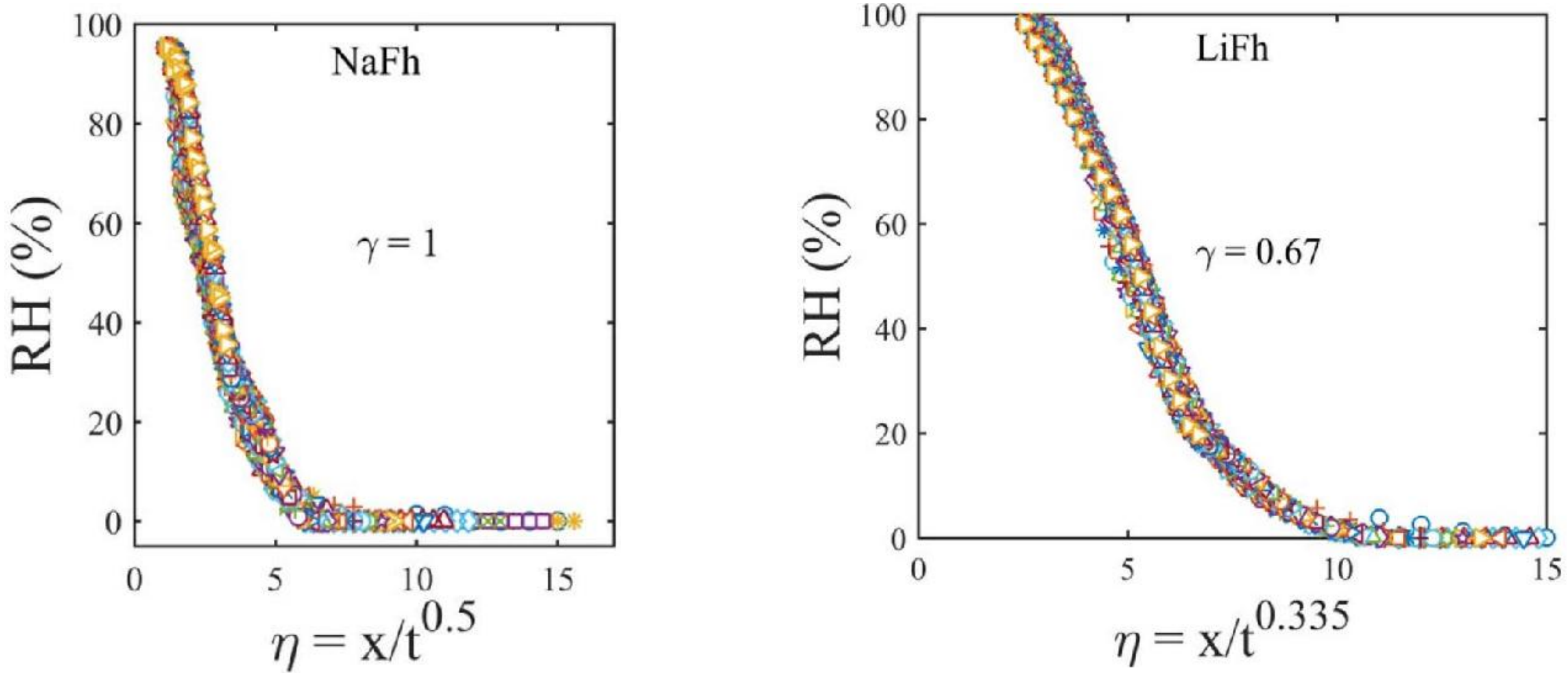
$$\frac{\partial^\gamma W\left(x,t\right)}{\partial t^\gamma} - \frac{t^{-\gamma}}{\Gamma\left(1-\gamma\right)} W\left(x,0\right) = \frac{\partial}{\partial x}\left(D_\gamma\left(W\right)\frac{\partial W\left(x,t\right)}{\partial x}\right)$$

$$\frac{\partial^\gamma W\left(x,t\right)}{\partial t^\gamma} = \frac{1}{\Gamma\left(1-\gamma\right)}\frac{\partial}{\partial t}\int_0^t W\left(x,t'\right)dt' \Big/ \left(t-t'\right)^\gamma$$

Signification of γ:

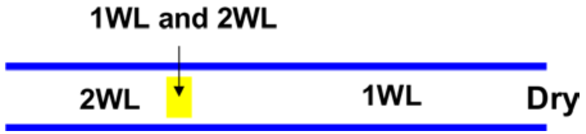
→Reduces to the standard diffusion equation for $\gamma=1$
→$\gamma>1$ indicates a superdiffusive behavior
→$\gamma<1$ indicates a subdiffusive behavior

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

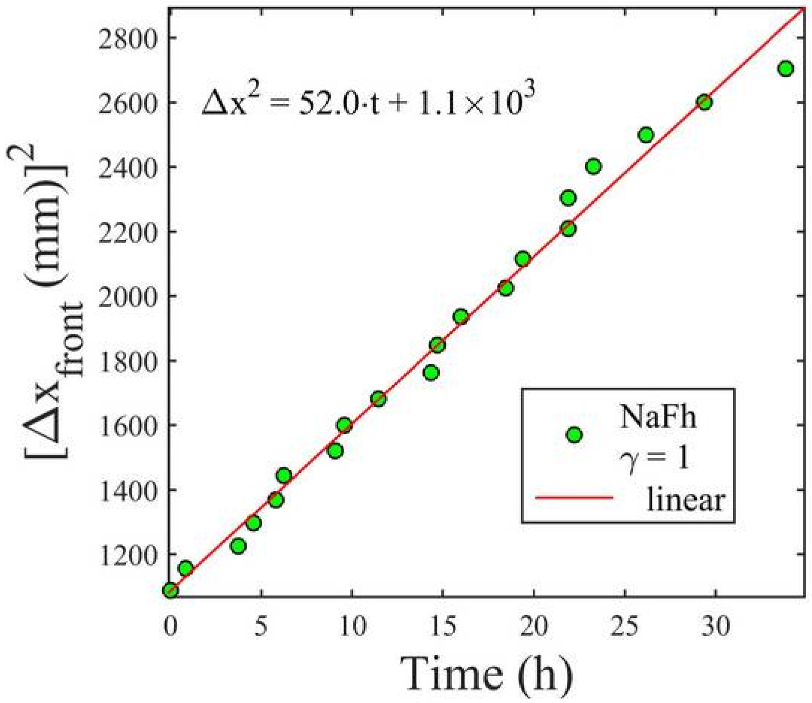


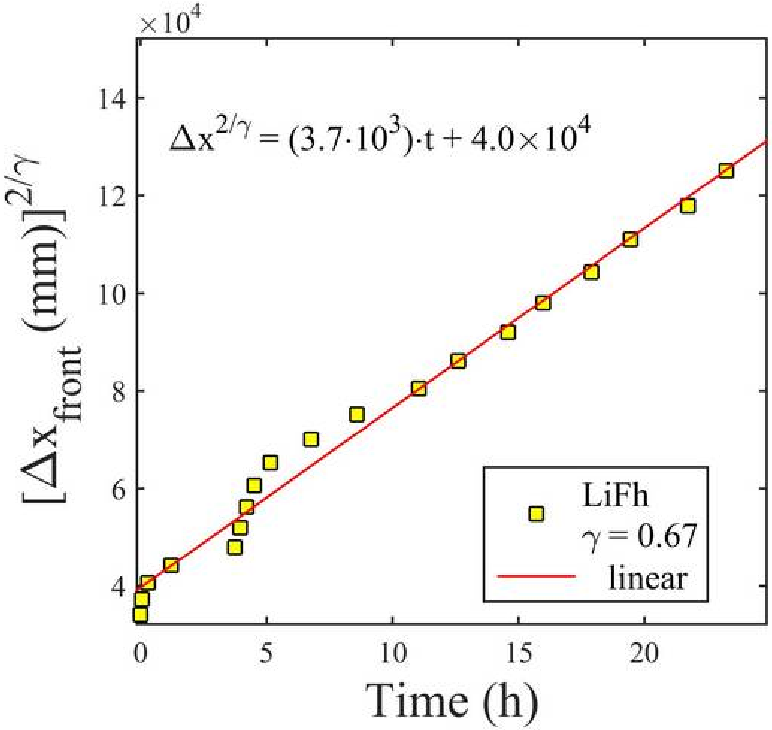
→Suggests anomalous transport for LiFh, normal transport for NaFh
→We now need to consider the concentration field in the mesoporous space

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: $\mathbf{t_{1meter}} \approx$ 26 hours/(2600*10^{-6}) $\approx 10^4$ hours $\approx$ **1 year**
LiFh: $\mathbf{t_{1meter}} \approx$ 24 hours/(12*10^4*10^{-9}) $\approx 2*10^5$ hours $\approx$ **20 years**

Permanent and safe storage of nuclear waste

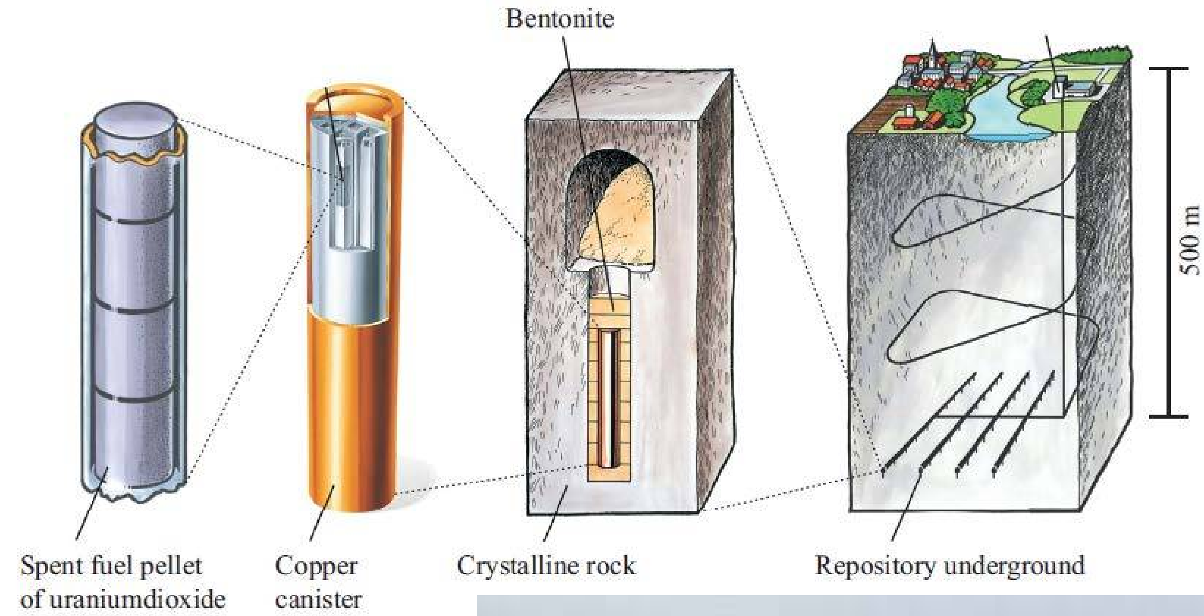
Swedish Nuclear Fuel and Waste Management Company (Svensk Kärnbränslehantering Aktiebolag, abbreviated **SKB**):
Swedish demand for clays as nuclear waste barriers amounts to about one shipload per year.

The Bentonite Barrier

Swelling properties, redox chemistry and mineral evolution

P. Daniel Svensson

LUND
UNIVERSITY



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 CO_2 capture and improved living conditions

Trees or agriculture in Sahara or similar dry environments? For large scale CO_2 capture?

www.desertcontrol.com

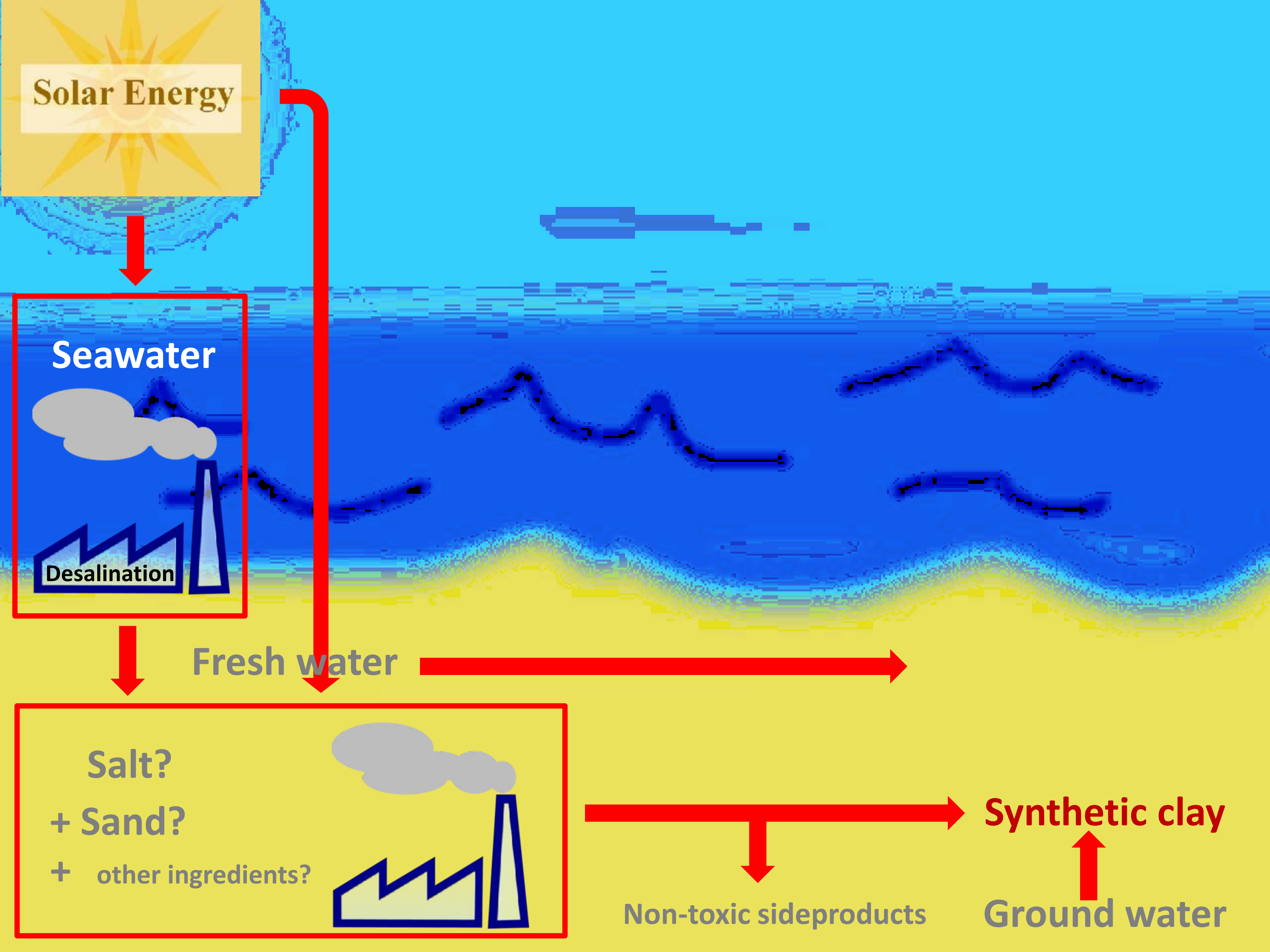
Kristian P. Olesen

CEO

Patent Holder

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

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



Solar Energy

Seawater

Desalination

Fresh water

Salt?

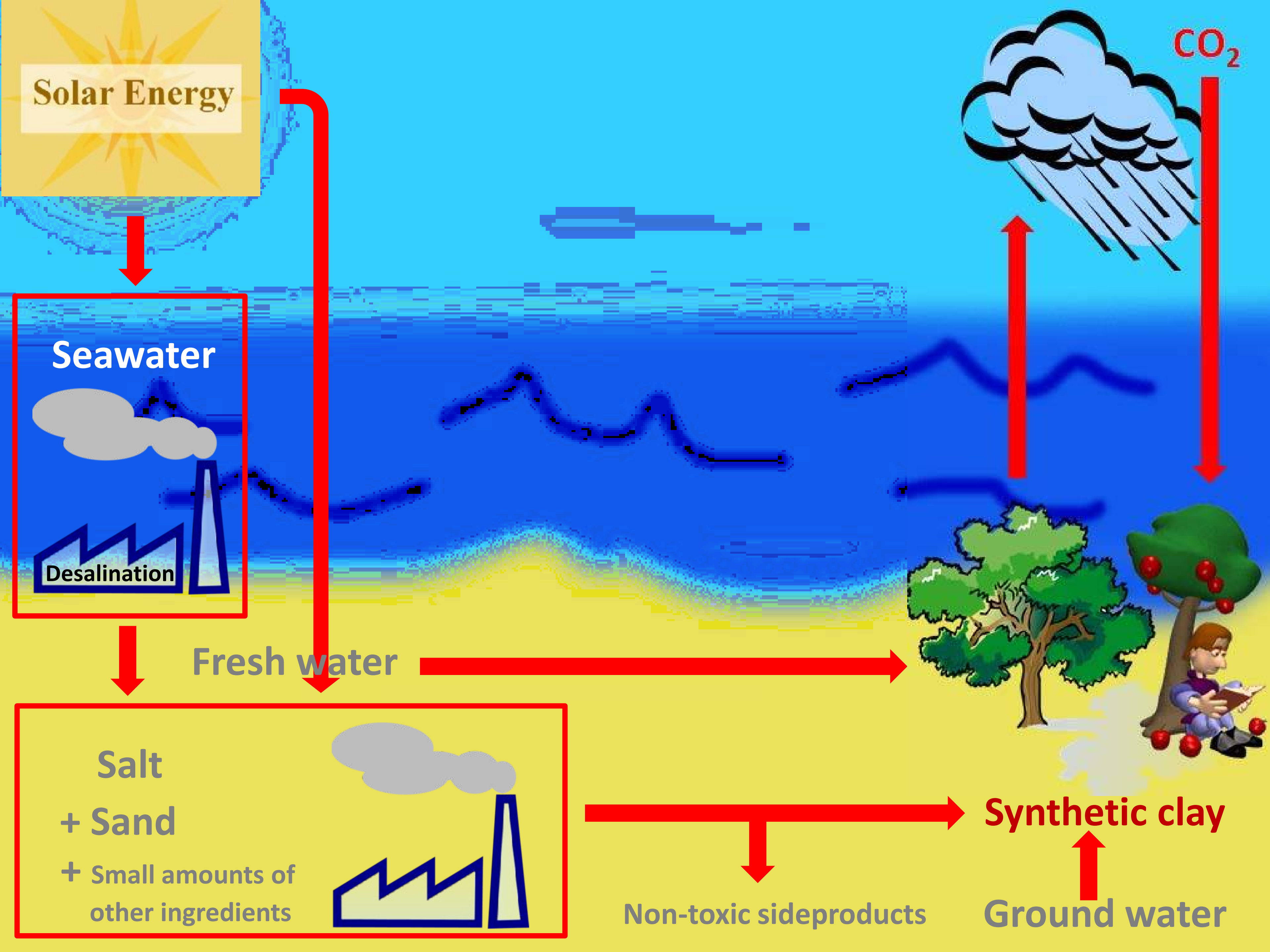
+ Sand?

+ other ingredients?

Synthetic clay

Non-toxic sideproducts

Ground water



Solar Energy

CO_2

Seawater

Desalination

Fresh water

Salt

+ Sand

+ Small amounts of other ingredients

Synthetic clay

Non-toxic sideproducts

Ground water

Clay based electronics:

Take part in Nature Publishing Group's annual reader survey here for the chance to win a Macbook Air.

NATURE | LETTER

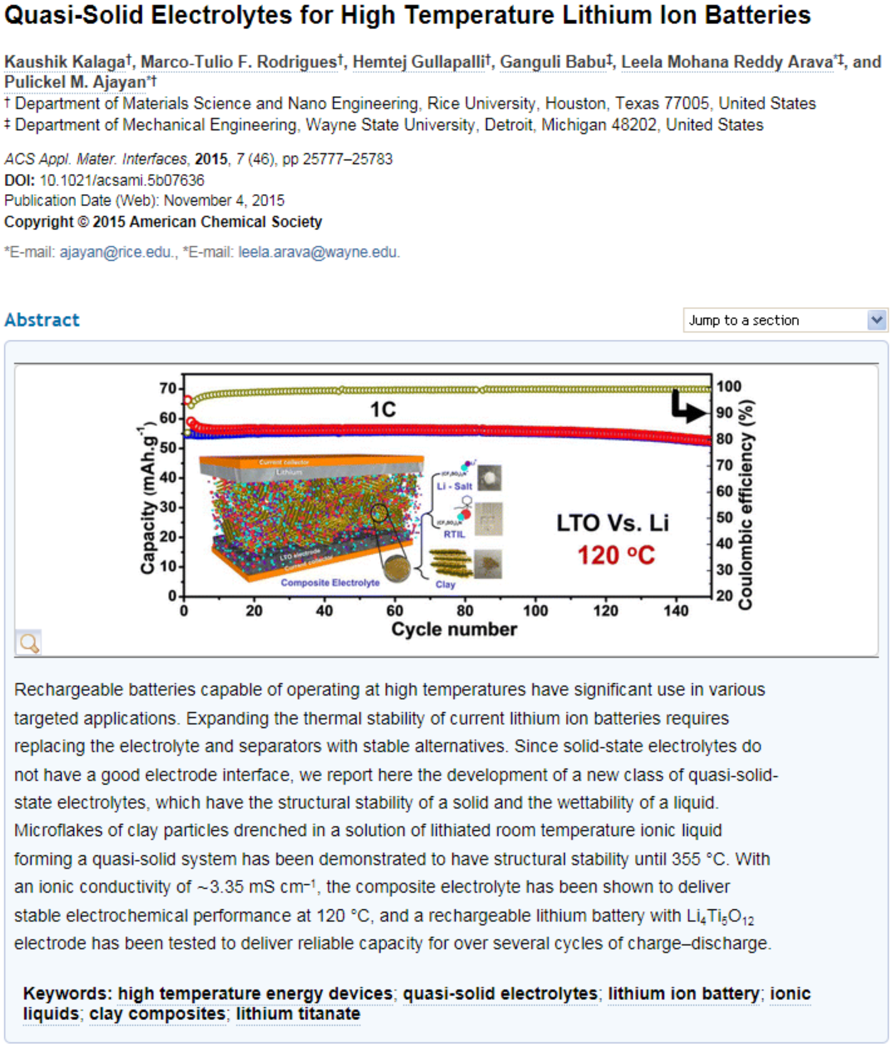
日本語要約

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

Michael Ghidiu, 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**, 78–81 (04 December 2014) | doi:10.1038/nature13970
Received 08 August 2014 | Accepted 13 October 2014 | Published online 26 November 2014



Quasi-Solid Electrolytes for High Temperature Lithium Ion Batteries

Kaushik Kalaga†, Marco-Tulio F. Rodrigues†, Hemtej Gullapalli†, Ganguli Babu‡, Leela Mohana Reddy Arava*‡, and Pulickel M. Ajayan*†
† Department of Materials Science and Nano Engineering, Rice University, Houston, Texas 77005, United States
‡ Department of Mechanical Engineering, Wayne State University, Detroit, Michigan 48202, United States

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@wayne.edu.

Abstract

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 ~3.35 mS cm^{-1}, the composite electrolyte has been shown to deliver stable electrochemical performance at 120 °C, and a rechargeable lithium battery with $Li_4Ti_5O_{12}$ 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

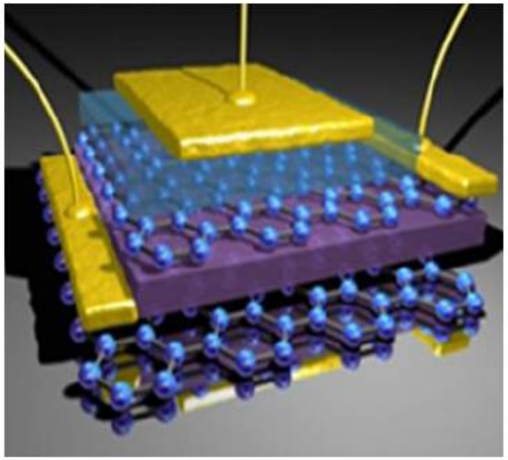


Figure 1:
Principal sketch of our graphene-clay electronic device, manually assembled at Univ. Manchester in Prof. Novoselov's group, using manual exfoliation techniques developed in that laboratory.

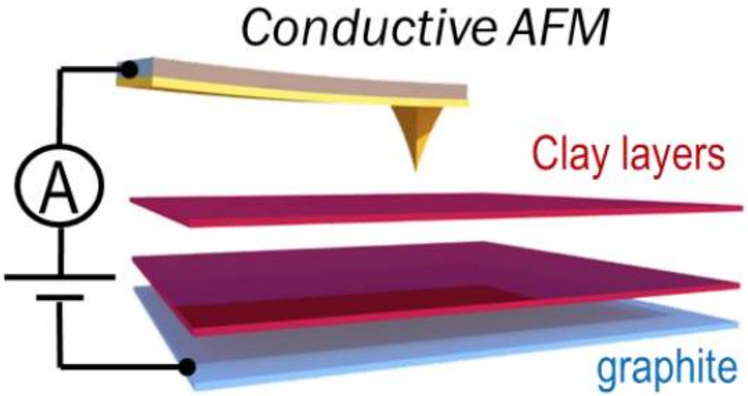


Figure 2:
Principle sketch of experimental set-up for measurements of IV-characteristic of our prototype graphene-clay device. The experiments were performed at Univ. Manchester in Prof. Novoselov's group.

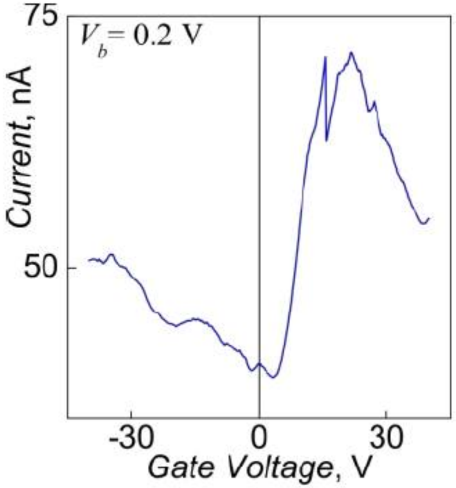
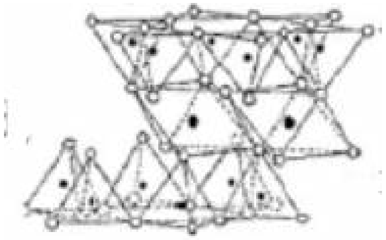


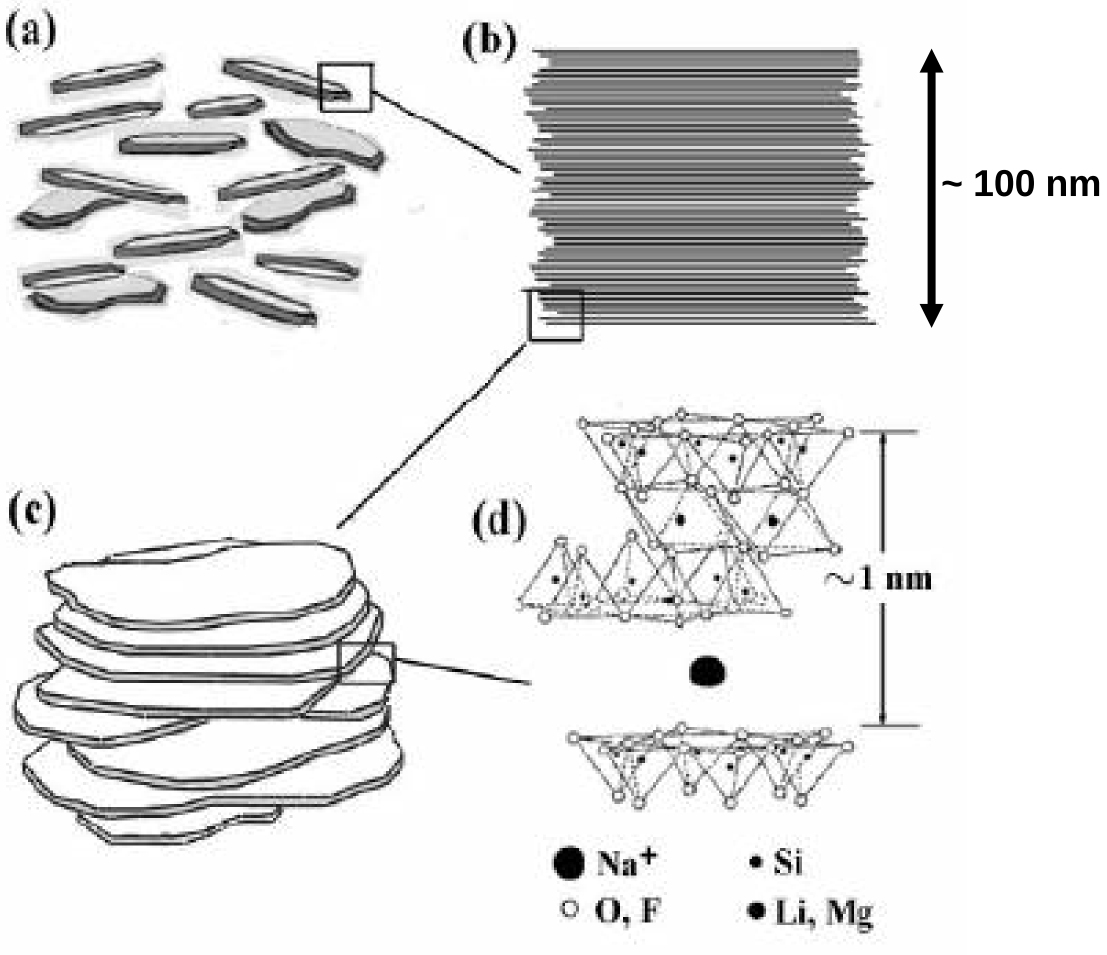
Figure 3:
Preliminary tunneling I-V characteristics for our prototype graphene-clay device. The experiments performed at Univ. Manchester.

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)



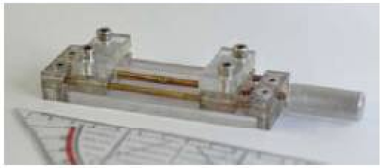
Sources of fluorohectorite:

Corning Inc.
x ≈ 0.6 ± 0.05
Lateral ~ 0.5-10 μm
(incl. 20% known impurities)

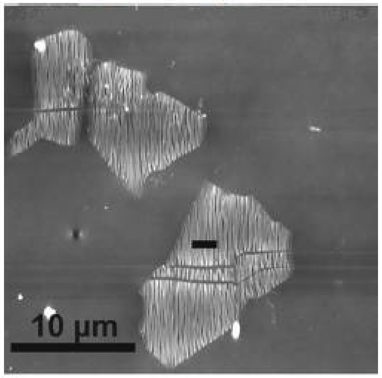
Inorg. Chem.
Univ. Bayreuth, Germany
Prof. Josef Breu
x = (0.2 <->0.6) ± 0.005
Lateral > 100 μm
(pure)

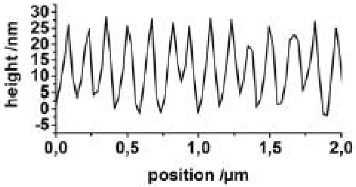
Nanomechanics – Wrinkling

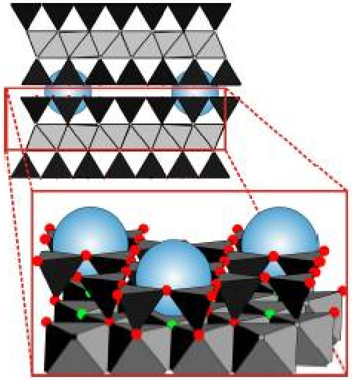
$$E_p = \frac{3E_s\left(1-\nu_p^2\right)}{\left(1-\nu_s^2\right)}\left(\frac{\lambda}{2\pi h}\right)^3$$



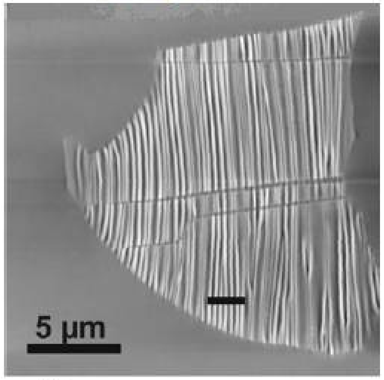
Monolayer

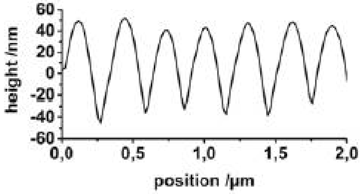






Bilayer

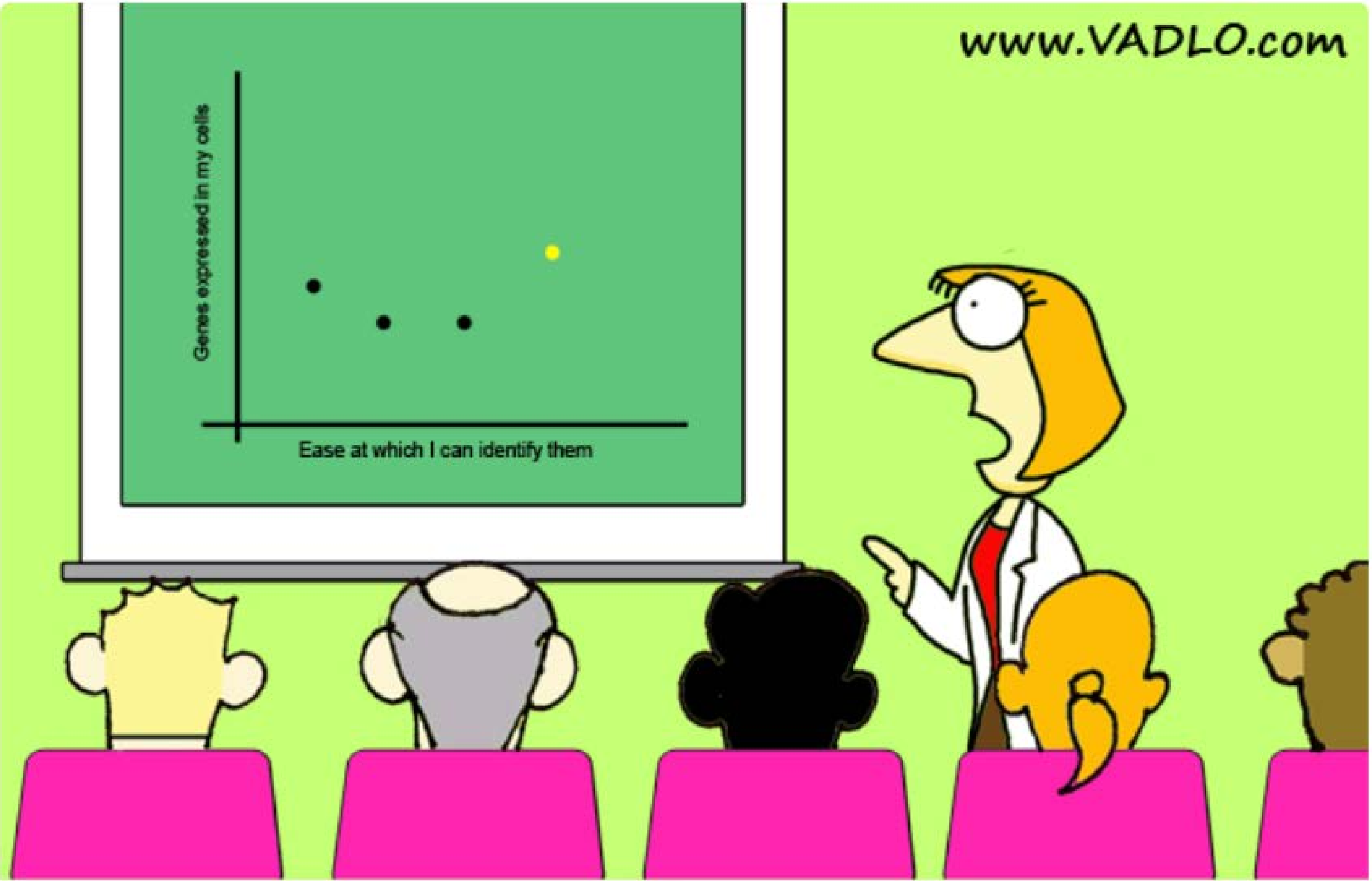




wavelength: 145 ± 7 nm
In-plane modulus: 0.15 ± 0.02 TPa

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

D.A. Kunz et al., *Adv. Mater.* **2013** *25* 1337.
D.A. Kunz et al. *ACS Appl.Mat.Interf.* **2013**. 5, 5851.

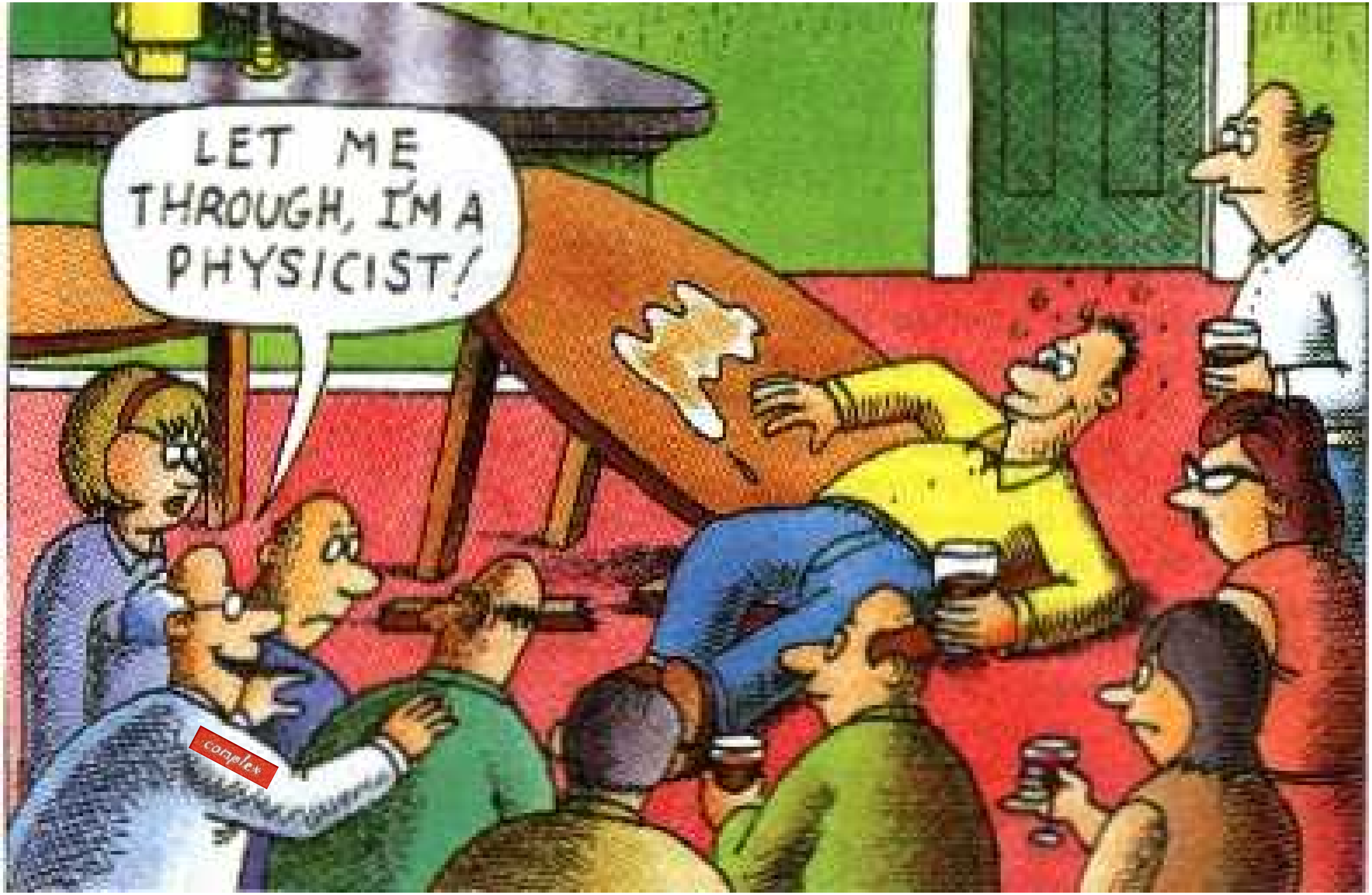


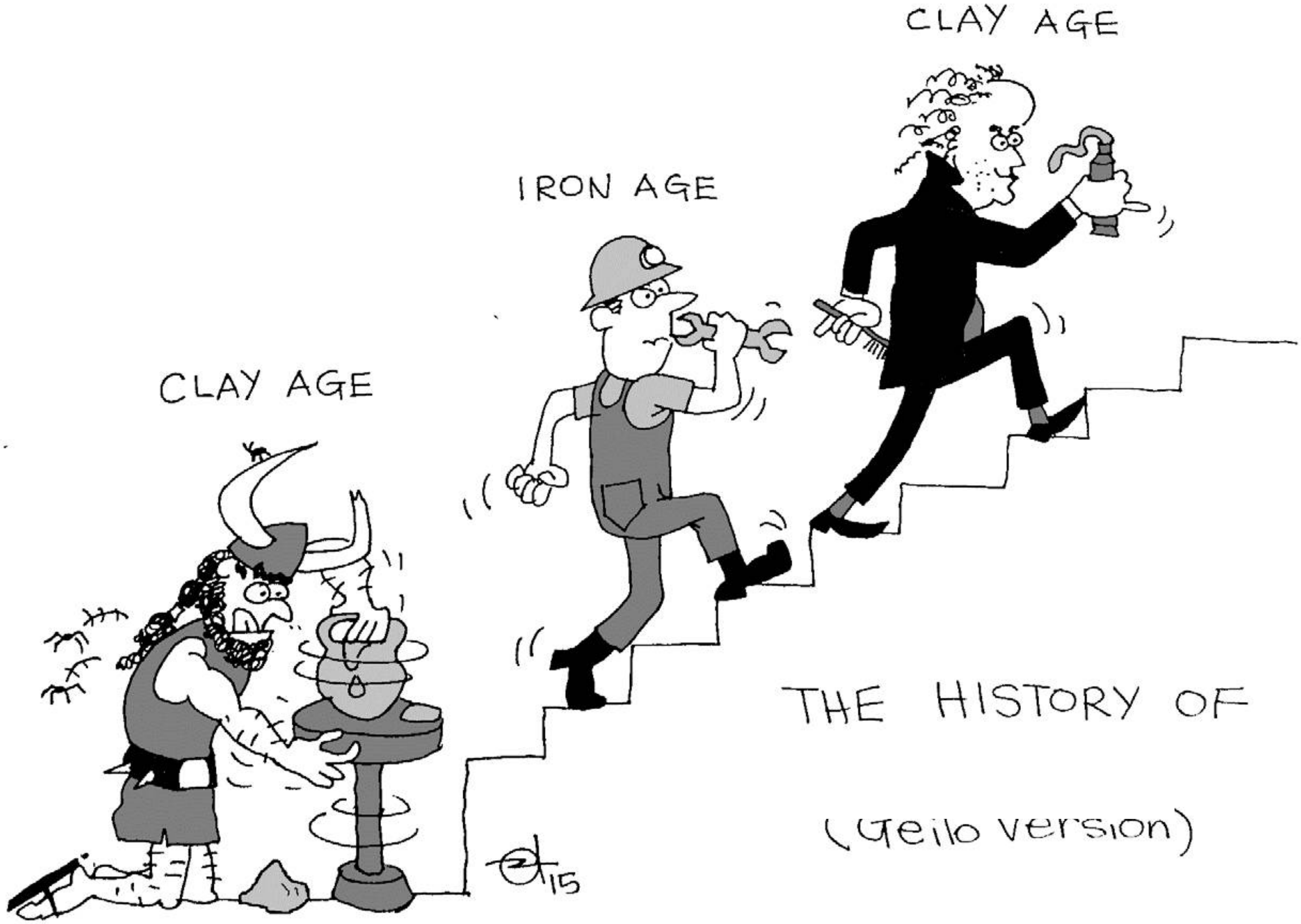
"Same graph as last year,
but now I have an additional dot."

true for Geilo talks

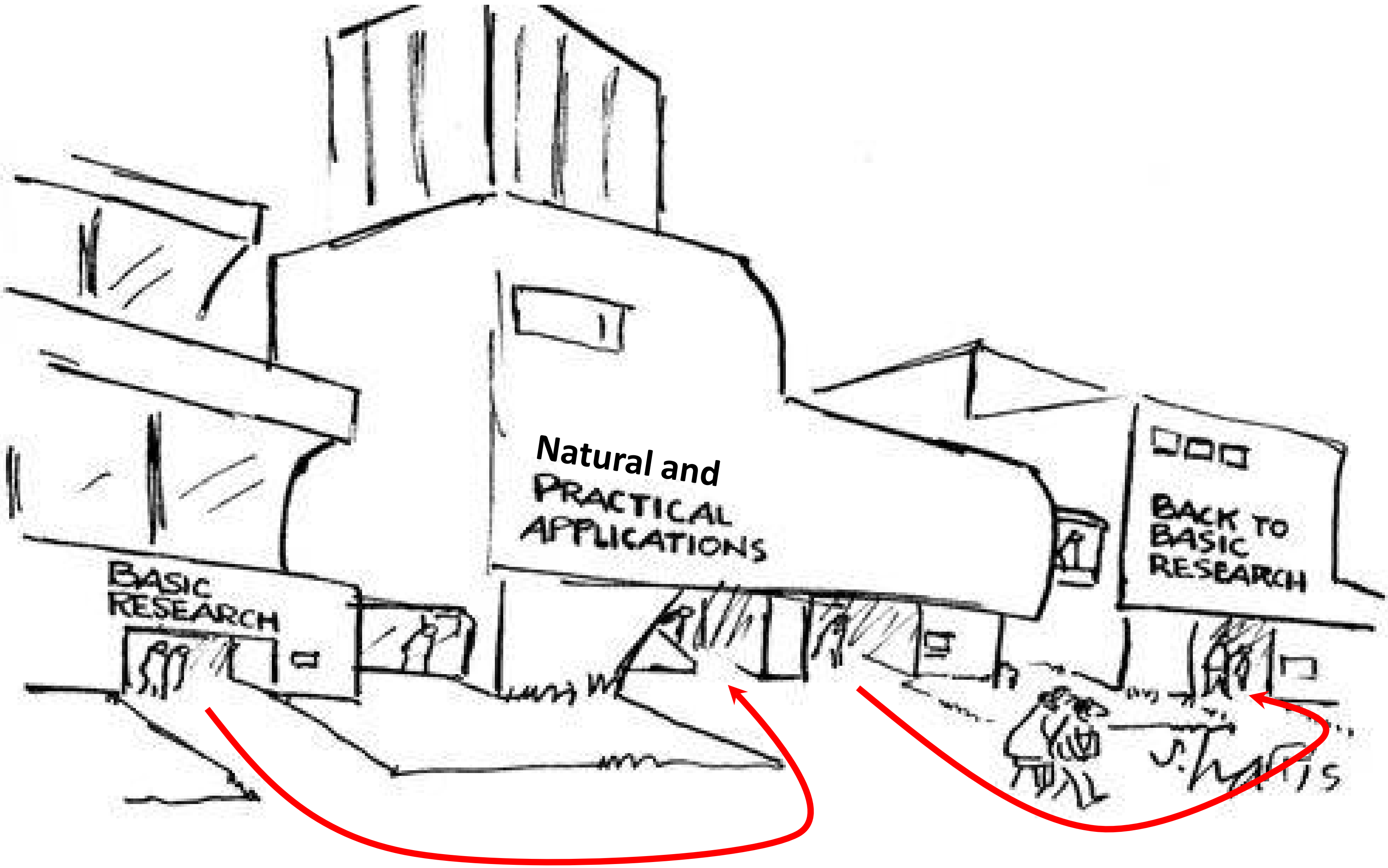
Curiosity driven research

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


LET ME THROUGH, I'M A PHYSICIST!
complex



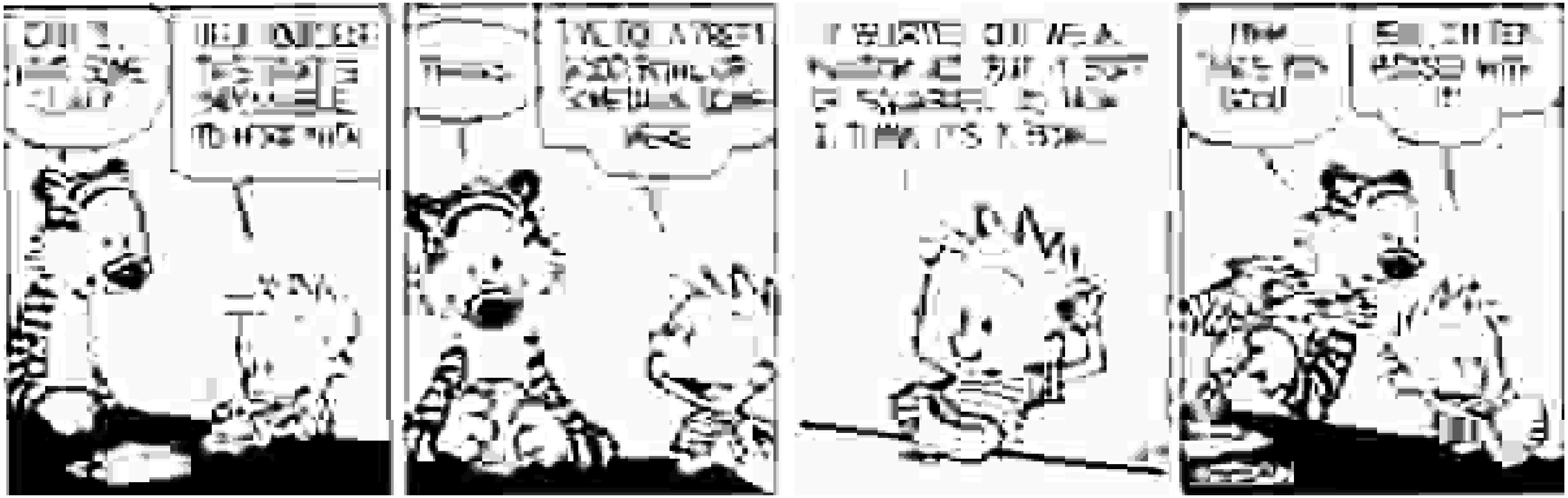
Drawing by Ernesto Altshuler


Natural and
PRACTICAL APPLICATIONS
BASIC RESEARCH
BACK TO BASIC RESEARCH

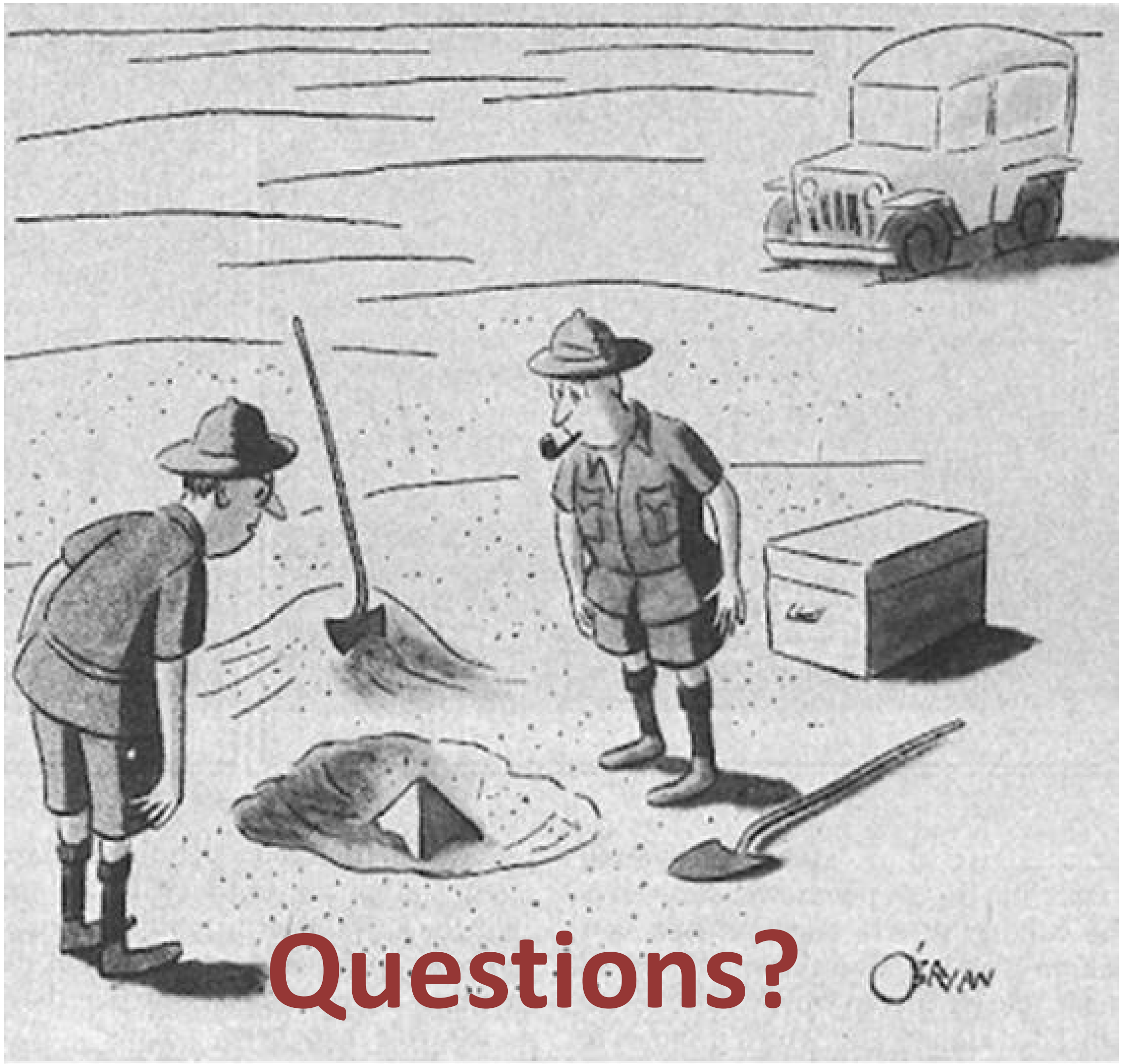
Acknowledgements to

MSc + PhD students, postdocs,
Collaborators in several countries

Clay baths will prolong your life:



Thank you for your attention!



Questions?

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