



GASTEM International
Lecture Tour



Measurements, modelling and applications of the electro-kinetic properties of rocks

Paul Glover

Université Laval, Québec, Canada

Plan

- Introduction
- Origin
- Theory
- Laboratory determinations
- Applications
- Conclusions
- Future directions
- Acknowledgments



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An aerial photograph of a rugged coastline with numerous small, rocky islands and peninsulas. The water is a deep blue, and the rocks are a mix of brown and grey. A white rectangular box is superimposed over the center of the image, containing the word "Introduction" in a bold, red, sans-serif font.

Introduction

Introduction I

What are electro-kinetic properties?

Electro-kinetic phenomena

The generation of an electrical potential difference across a porous medium by the flow of fluid through it, or vice versa

Flow causes potential  Electro-kinetics
Potential causes flow  Electro-osmosis

Electro-seismic phenomena

The generation of an electro-magnetic wave in a porous medium by the passage of an elastic wave through it, or vice versa

Elastic wave causes EM wave  Seismo-electric conversion
EM wave causes elastic wave  Electro-seismic conversion



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Introduction II

Principal applications

➤ **Electro-kinetic phenomena**

- ✓ Hydrocarbon production
- ✓ Water reservoir management
- ✓ Remediation of polluted soils
- ✓ Volcano prediction
- ✓ Earthquake prediction
- ✓ Synthetic earthquakes

Polymer sciences, membrane sciences, catalysis, microfluidics,
food science, medical science

➤ **Electro-seismic phenomena**

- ✓ Hydrocarbon exploration & production
- ✓ Water reservoir management
- ✓ Volcano prediction
- ✓ Earthquake prediction



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Origins

Origin

- **The electrical “double” layer**
- **Debye thickness**
- **Surface conduction**
- **Electro-seismic conversion**

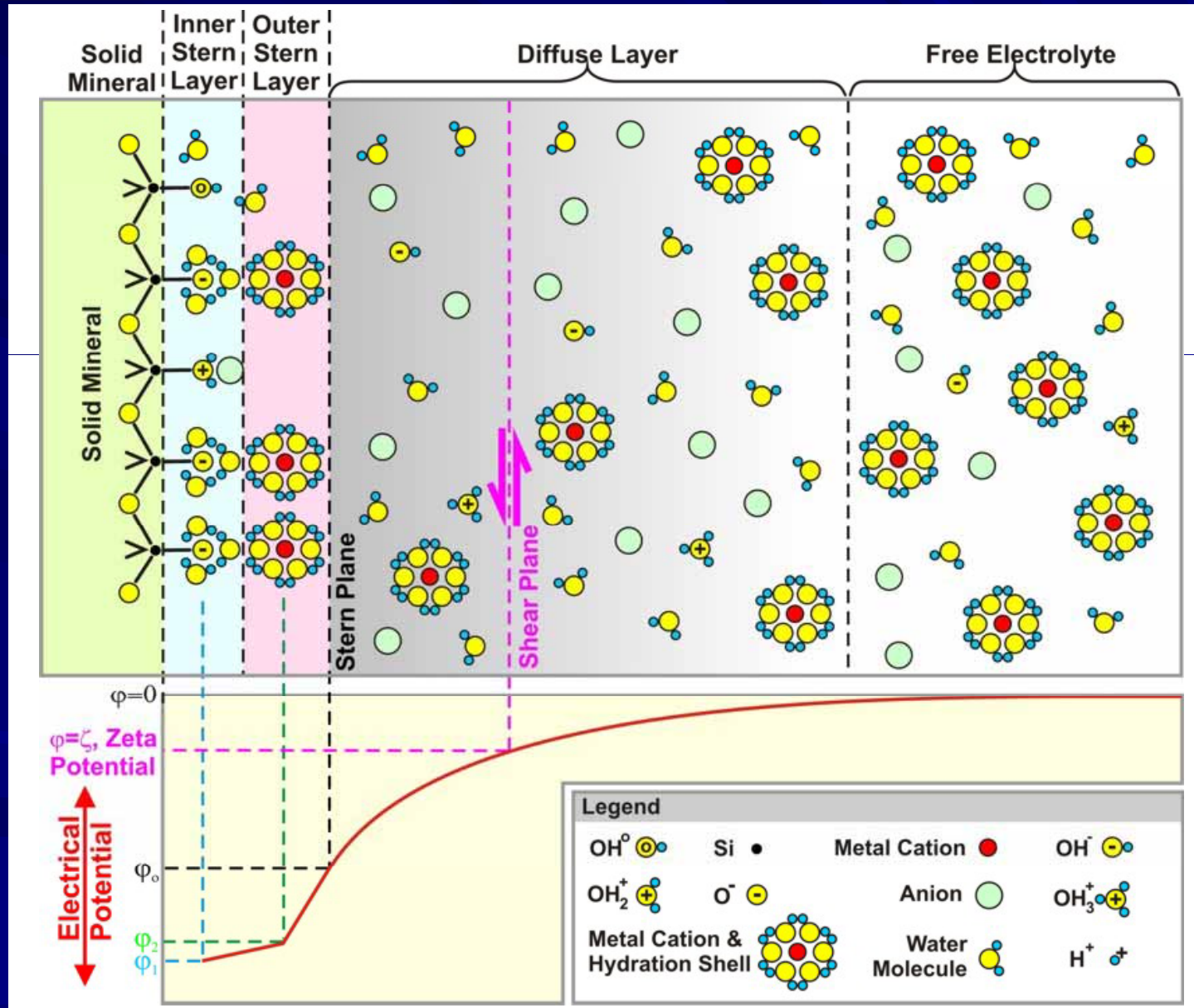


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Origin - The electrical double layer



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Origin - The electrical double layer

There exists:

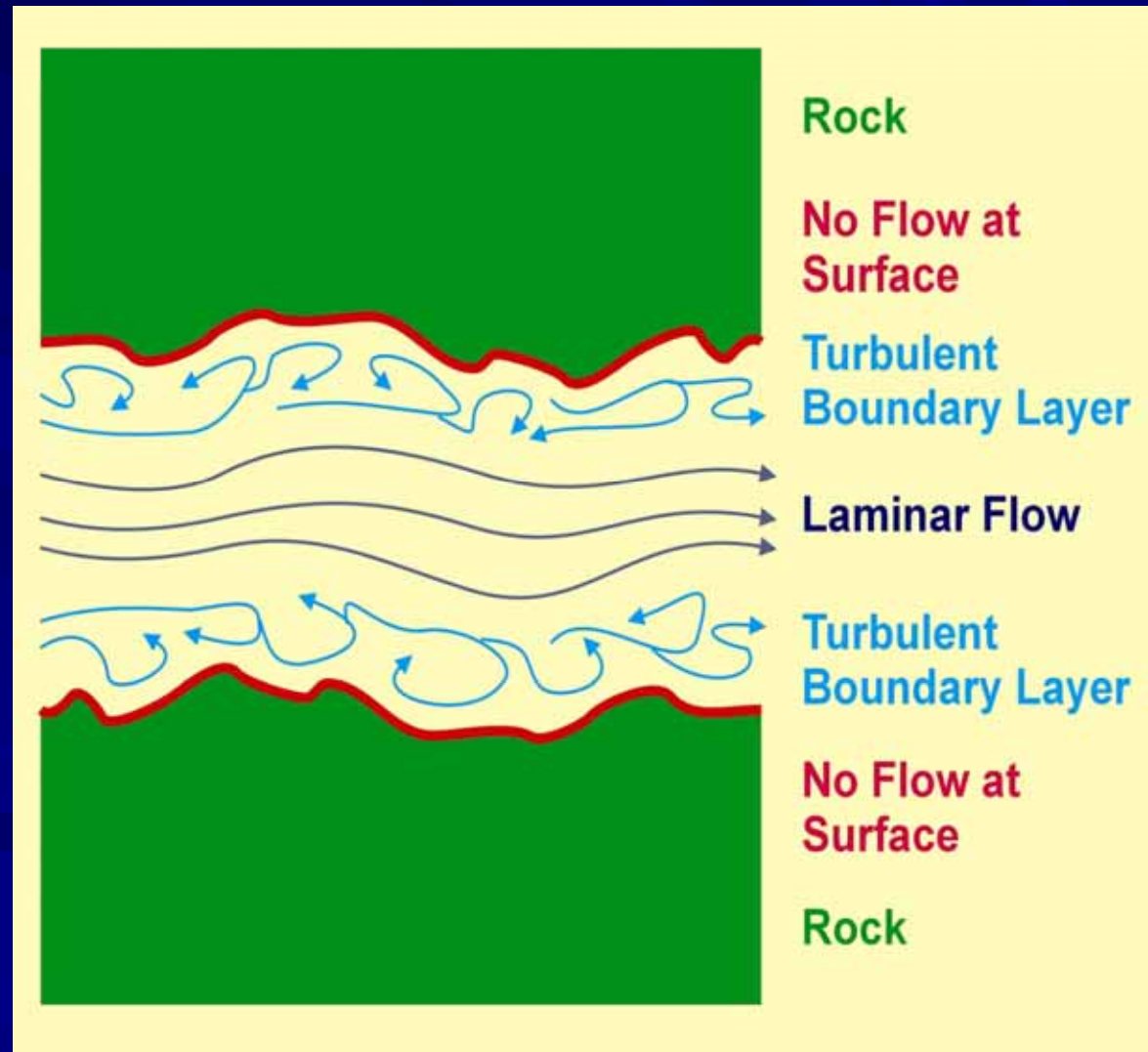
An undisturbed central zone of laminar flow,

and

A surface boundary layer of turbulent flow,

and

Zero flow at the rock surface



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Origin - The electrical double layer

There exists:

A **-ve** charged rock surface,

and

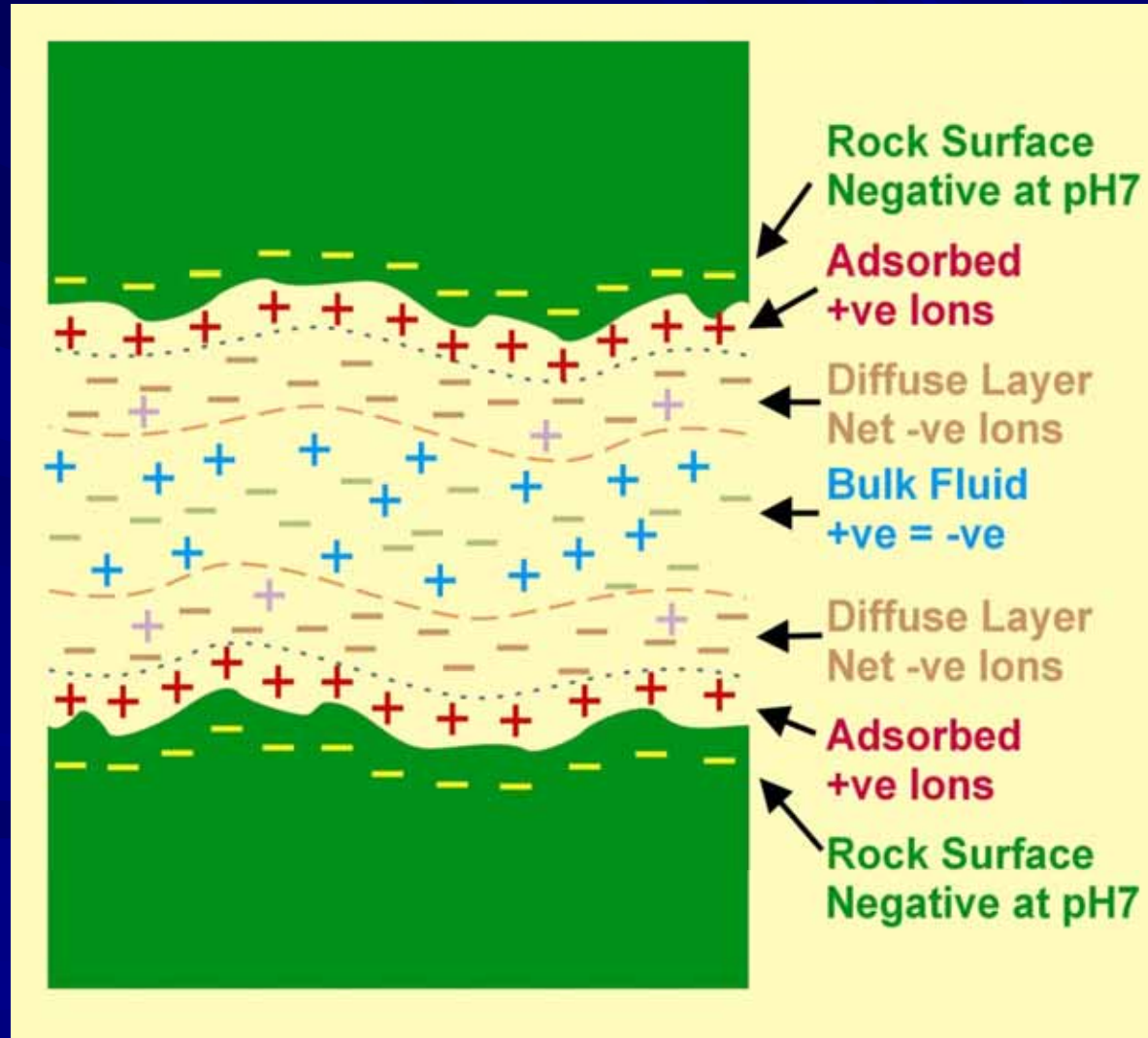
A layer of **+ve** adsorbed ions,

and

A net **-ve** diffuse layer
[thickness $f(\text{salinity})$]

and

Net **neutral** bulk fluid



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Origin - The electrical double layer

Boundary of moveable fluids is in diffuse layer

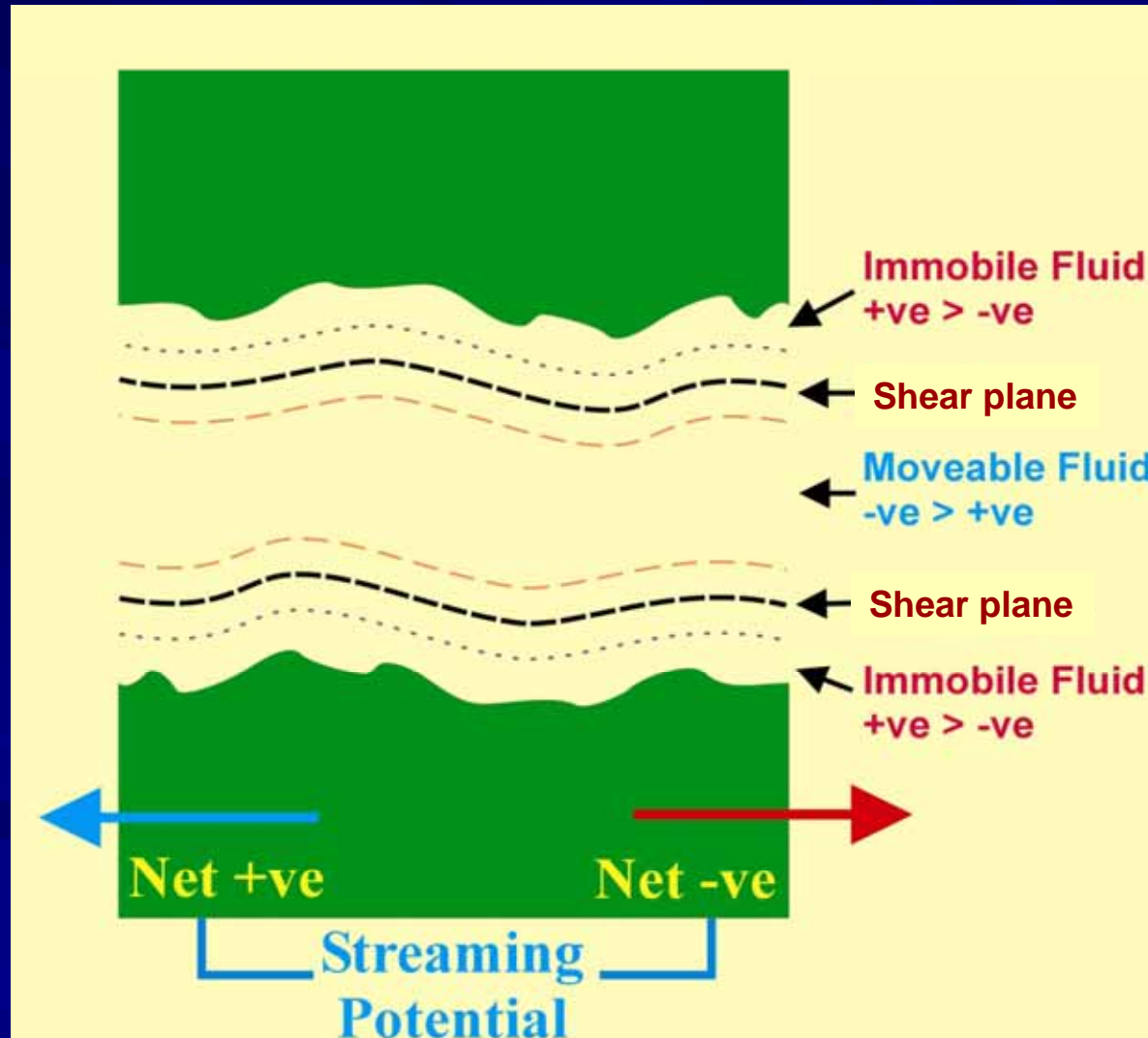
Flow separates -ve charges to the right

and

+ve charges are left behind

this

generates a potential difference called the **STREAMING POTENTIAL**



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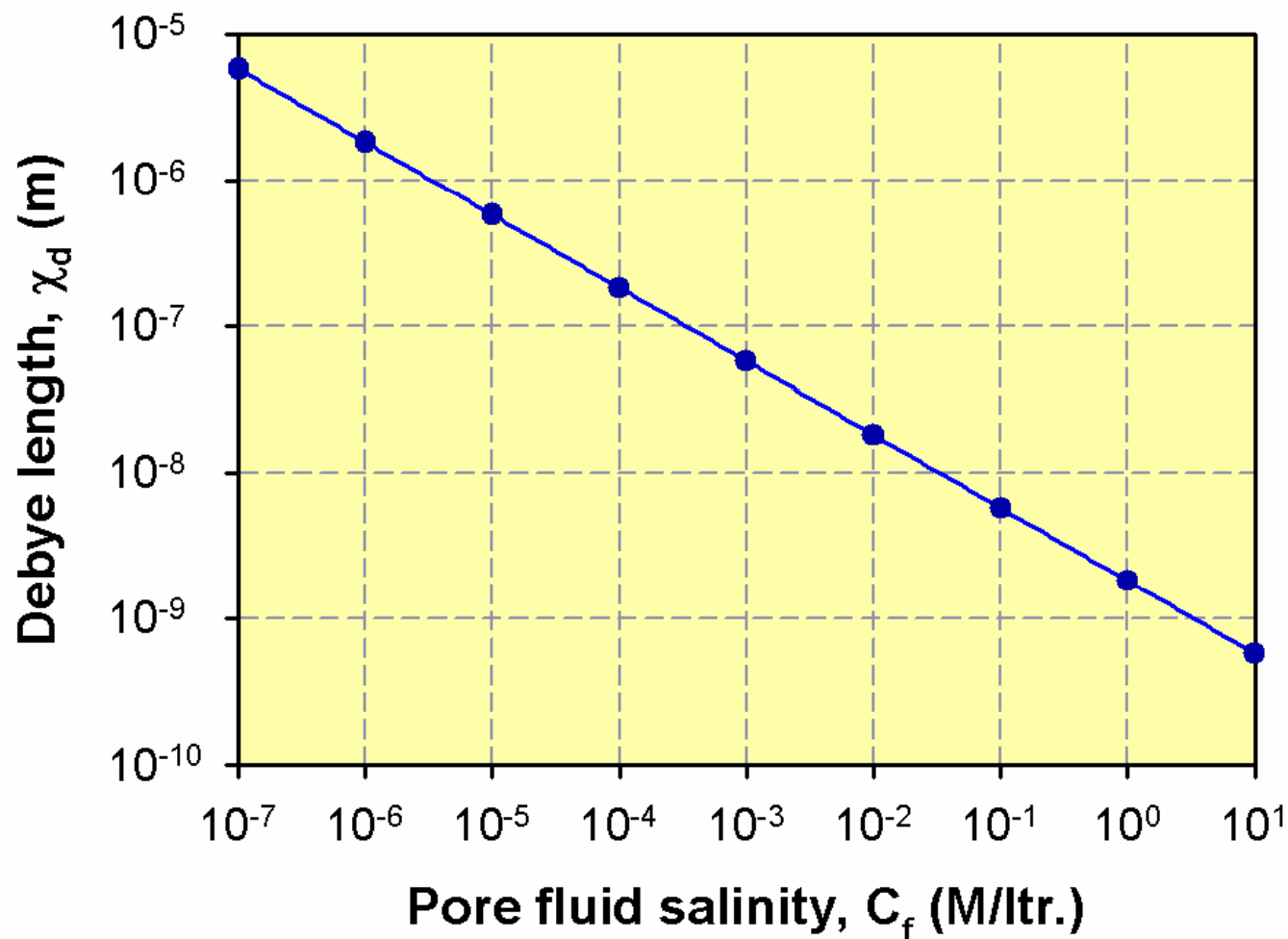
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Debye thickness λ

$$\lambda_d = \sqrt{\frac{\epsilon_f k_b T N_A}{2000 e^2 C_f}}$$



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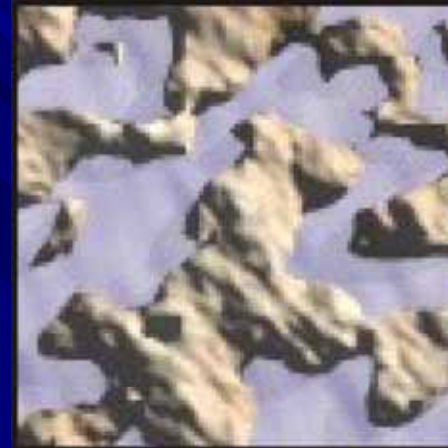
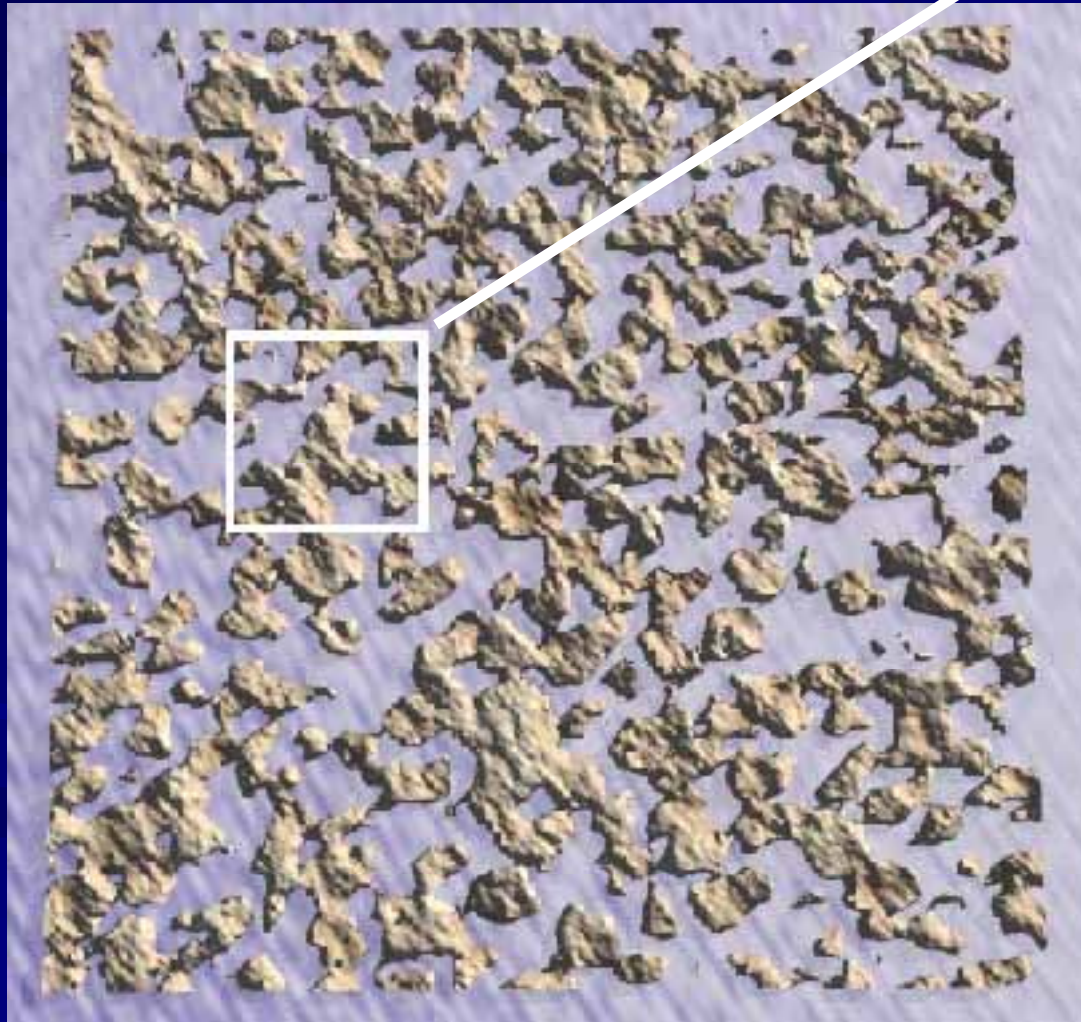
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Debye thickness ℓ



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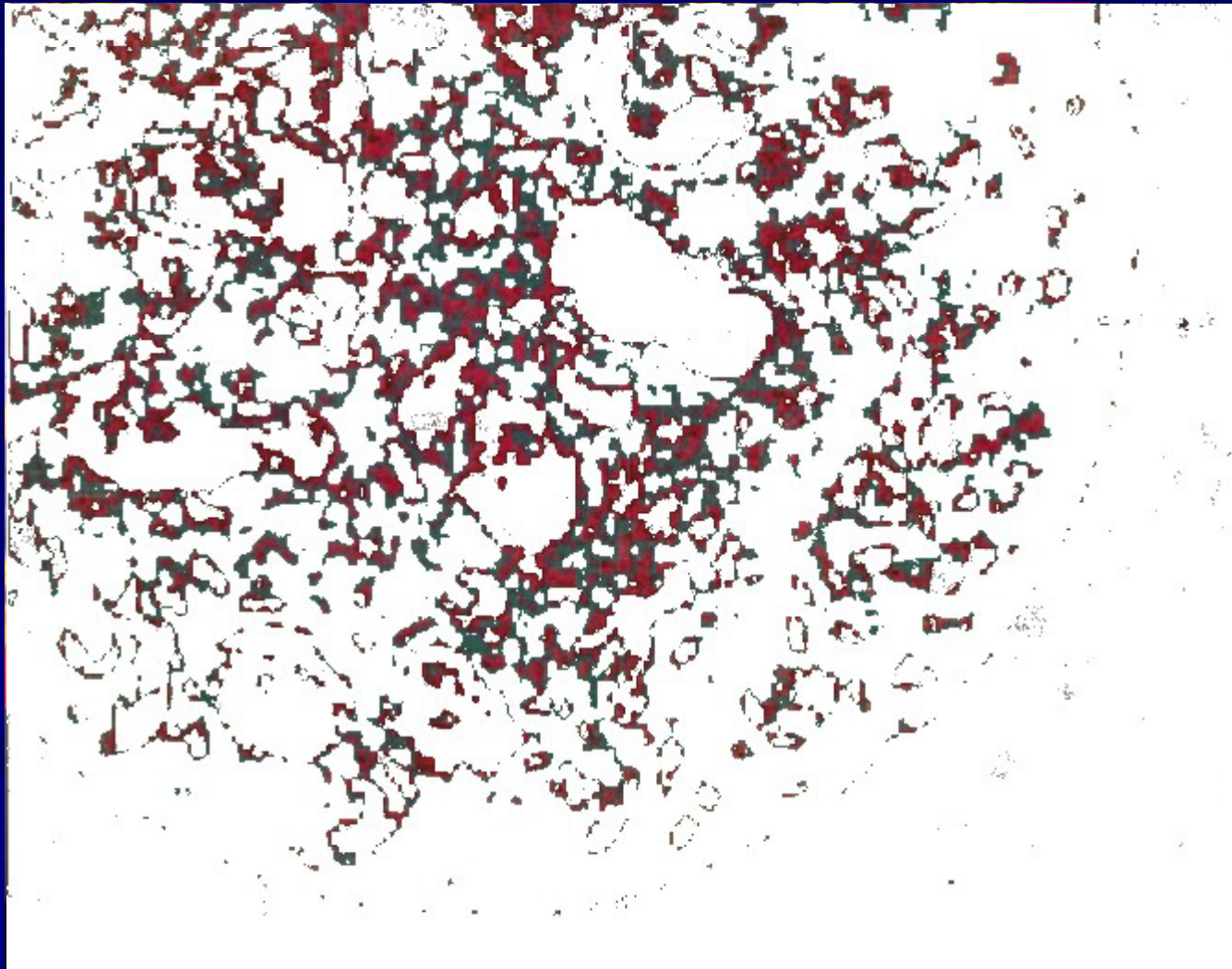
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Origin

PET Visualisation of the electrical double layer



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Surface conduction

Two conduction mechanisms

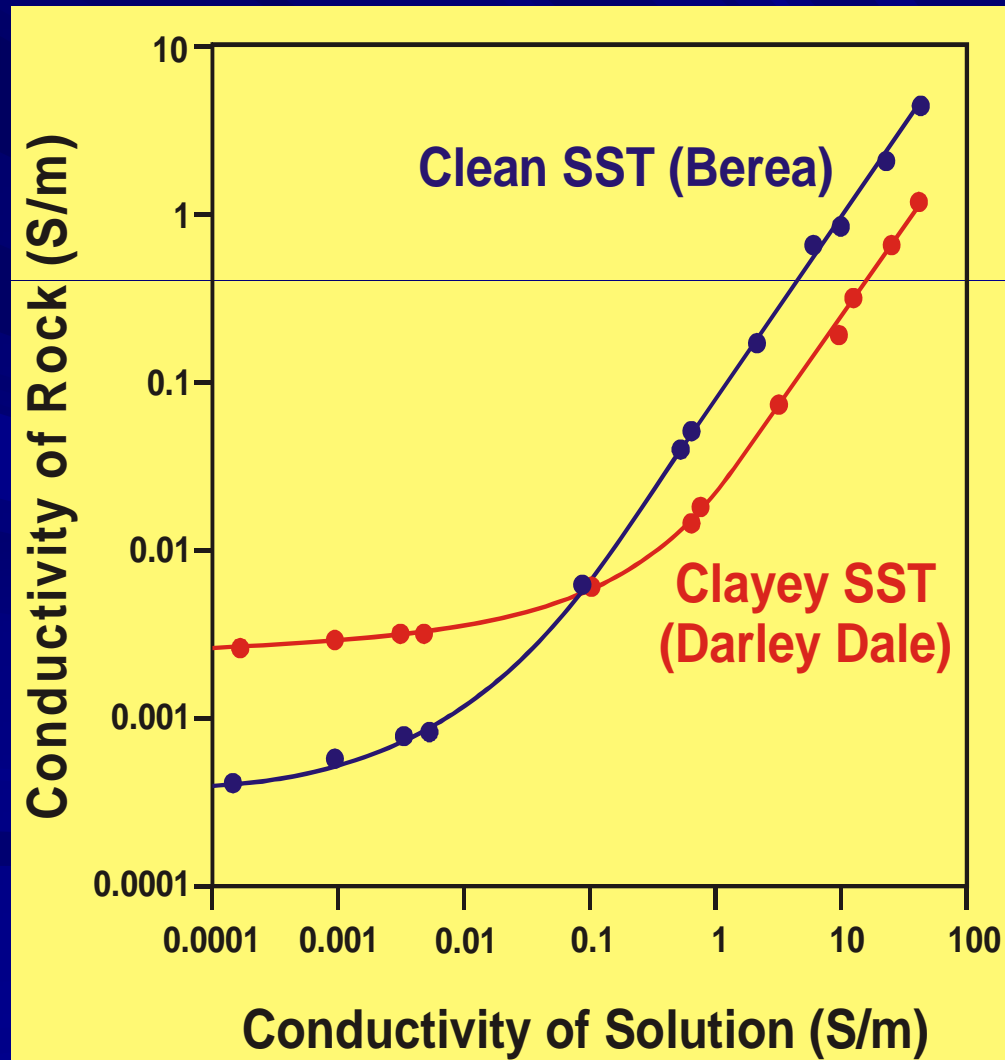
A. via the bulk fluid

B. via the diffuse and Stern layers

The latter is surface conduction

Surface conduction more effective than bulk fluid conduction

At low salinities – the EDL is thick – Surface conductivity dominates



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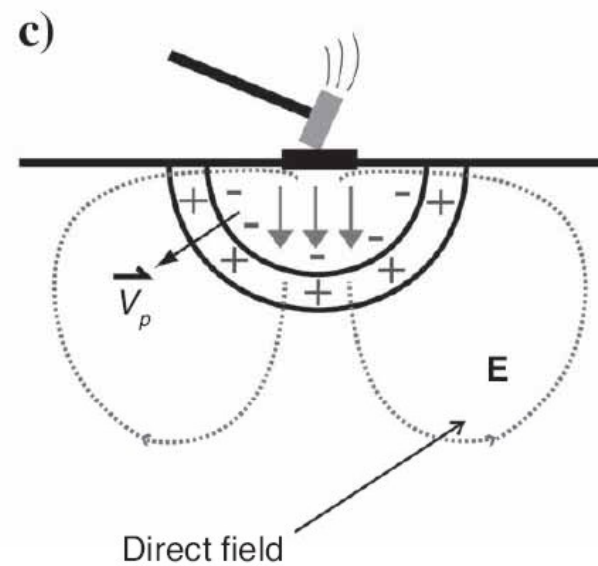
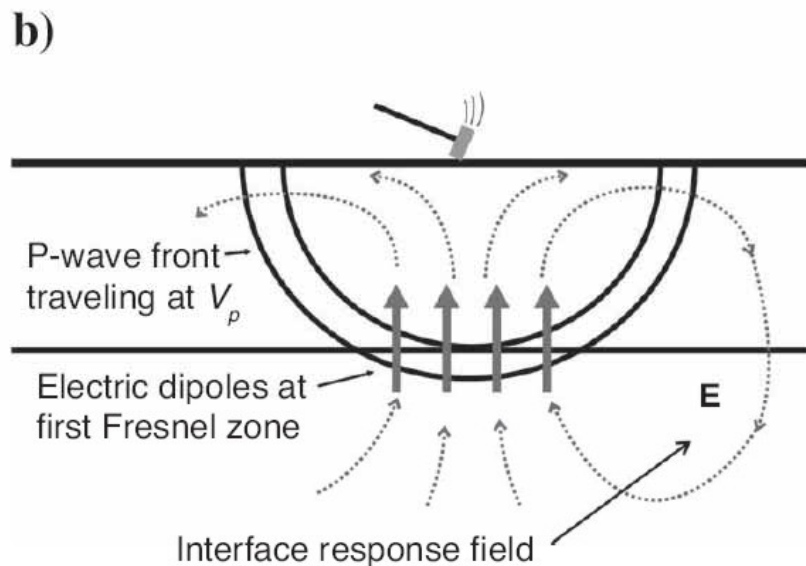
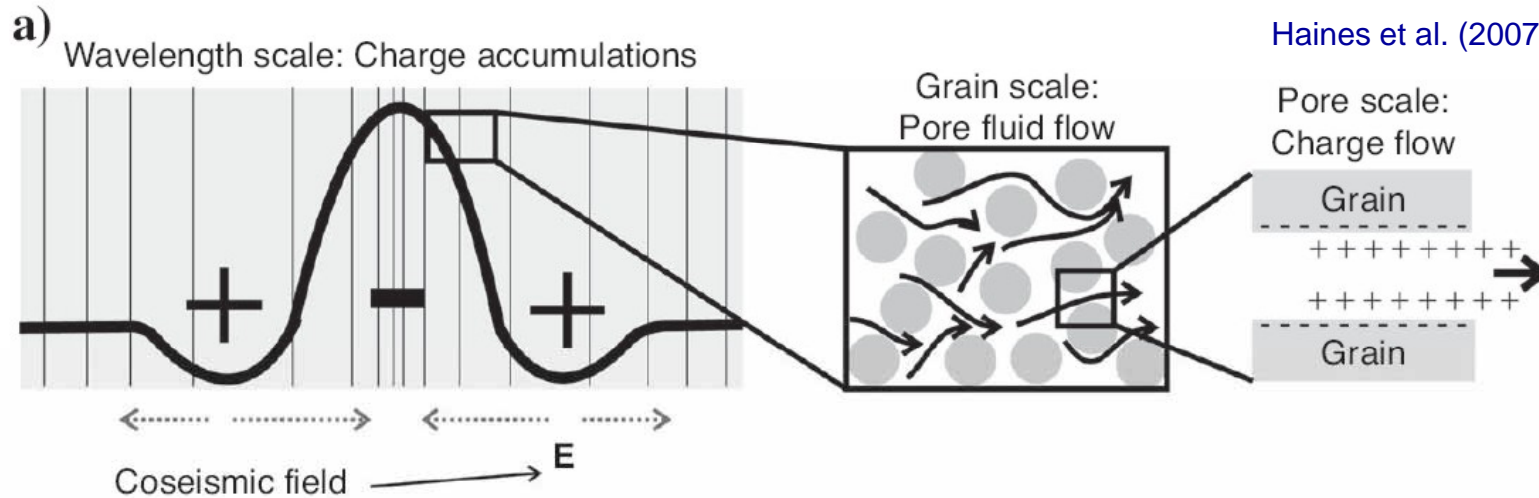
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Origin

Electro-seismic conversion

Haines et al. (2007)



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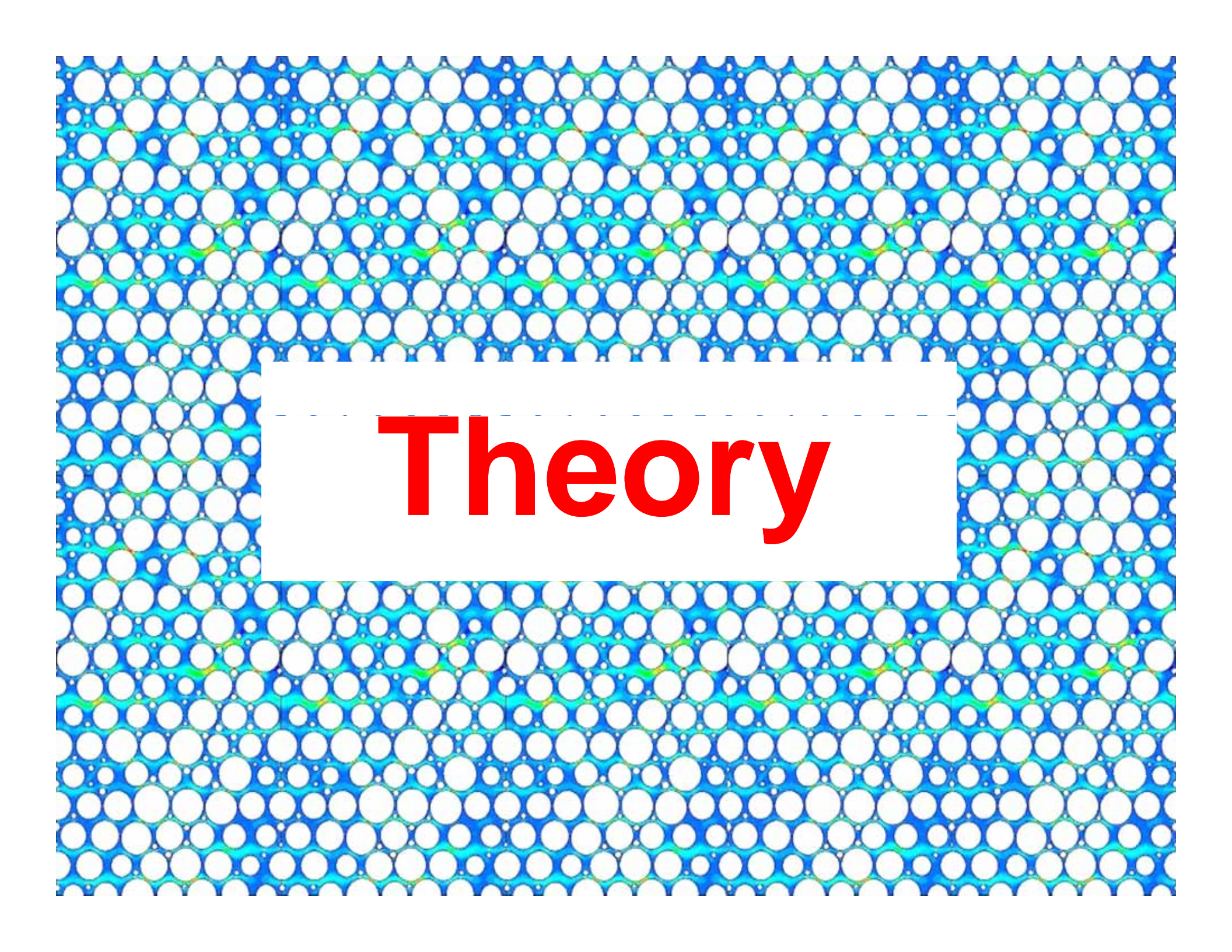
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Theory

Theory

- DC Theory
- The Helmholtz-Smoluchowski equation
- Formulation in continuous media
- What controls the zeta potential?
- AC Theory



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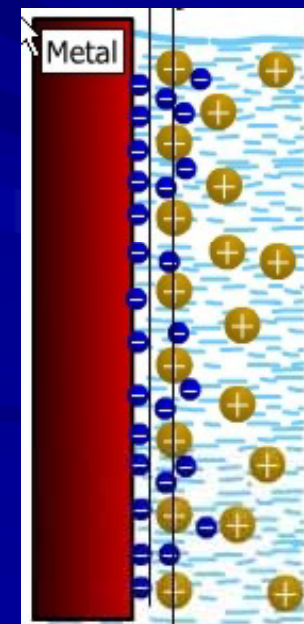
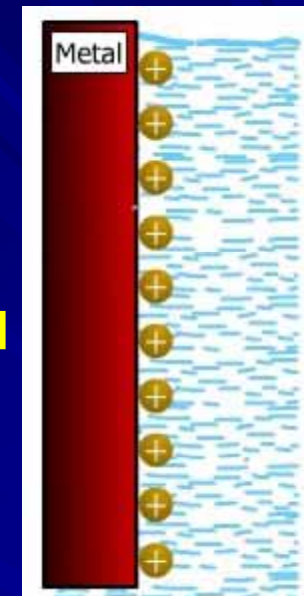
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Theory

DC theory - Historical

- **Helmholtz (1879)** Simple mineral surface neutralized by a monolayer of counterions from the fluid
- **Gouy (1910) & Chapman (1913)** Replaces monolayer with a diffuse layer composed of counterions and coions (monolayer affected by thermal agitation)
- **Stern (1924)** Proposes amalgamation of the two previous models



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Theory

The Helmholtz-Smoluchowski equation

By equating the convective and conductive currents (Overbeek, 1952)

$$\Delta V = - \frac{\varepsilon \zeta}{\eta \left(\sigma_f + \frac{2 \Sigma_s}{\Lambda} \right)} \Delta P$$

C_s is the electro-kinetic coupling coefficient is defined as the ratio of the streaming potential to the fluid pressure difference that created it (V/Pa)

$$C_s = \frac{\Delta V}{\Delta P} = \frac{\varepsilon \zeta}{\eta \sigma^*} \quad \text{where} \quad \sigma^* = \sigma_f + \frac{2 \Sigma_s}{\Lambda}$$

Sources of error

1. Not including surface conduction
2. Using $\varepsilon = 80$ at low fluid salinities
3. Using bulk fluid pH (zeta potential is a strong function of pH)



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Formulation in continuous media

Darcy's law, $L_{11} = k/\eta$

$$\begin{bmatrix} Q \\ J \end{bmatrix} = - \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \nabla P \\ \nabla \varphi \end{bmatrix}$$

Electro-kinetic phenomena

$$L_{21} = L_{12} = \varepsilon \zeta / \eta$$

Ohm's law,

$$L_{22} = \sigma_f$$

- k permeability (m^2)
- σ_f fluid conductivity (S/m)
- ε fluid dielectric constant
- ζ zeta potential (V)
- η fluid viscosity ($Pa.s$)
- P fluid pressure (Pa)
- φ electrical potential (V)
- Q fluid flow (L/m^2),
- J electric current density (A/m^2)

$$\text{or } J = \frac{\varepsilon \zeta}{\eta} \nabla P - \sigma_f \nabla \varphi \quad \text{and} \quad Q = -\frac{k}{\eta} \nabla P + \frac{\varepsilon \zeta}{\eta} \nabla \varphi$$

✓ OK for capillaries

✗ To be verified for rocks



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Theory

What controls the zeta potential?

The streaming potential depends upon 4 parameters

- Fluid* dielectric constant
- Fluid* viscosity
- Fluid* conductivity
- Zeta potential

Therefore any control of the streaming potential exercised by the rock rests in the zeta potential

What controls the zeta potential?



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Controls on the zeta potential

- **Salinity**
- **pH**
- **Porosity**
- **Pore microstructure – connectedness G**
- **Flow rate**
- **Fluid viscosity**
- **Pore/fracture surface roughness**
- **Saturation**
- **Temperature, applied, pore and effective pressure**
- **Chemical composition of mineral and fluid**



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Theory - AC Theory I

We propose

$$\frac{\Delta V}{\Delta P} = f^*(\omega) \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*}$$

Glover (2007)

For the hydraulic coupling coefficient

$$\frac{v(\omega)}{\Delta P(\omega)} = \frac{1}{\eta l k^2} \left[\frac{2 J_1(ka)}{ka J_0(ka)} - 1 \right]$$

Packard (1953)

The streaming potential coupling coefficient becomes

$$C(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*} \left[-\frac{2 J_1(ka)}{ka J_0(ka)} \right]$$

Packard (1953)

Reppert & Morgan (2001)

$$C(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*} \left[1 - \frac{2}{a} \sqrt{\frac{\eta_f}{\omega \rho_f}} \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} i \right) \right]$$



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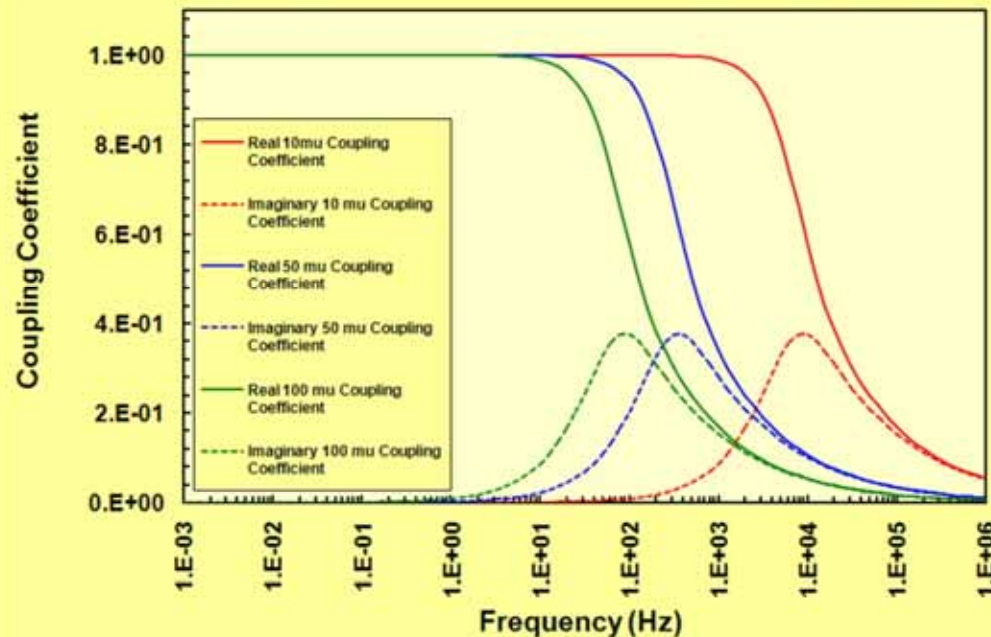
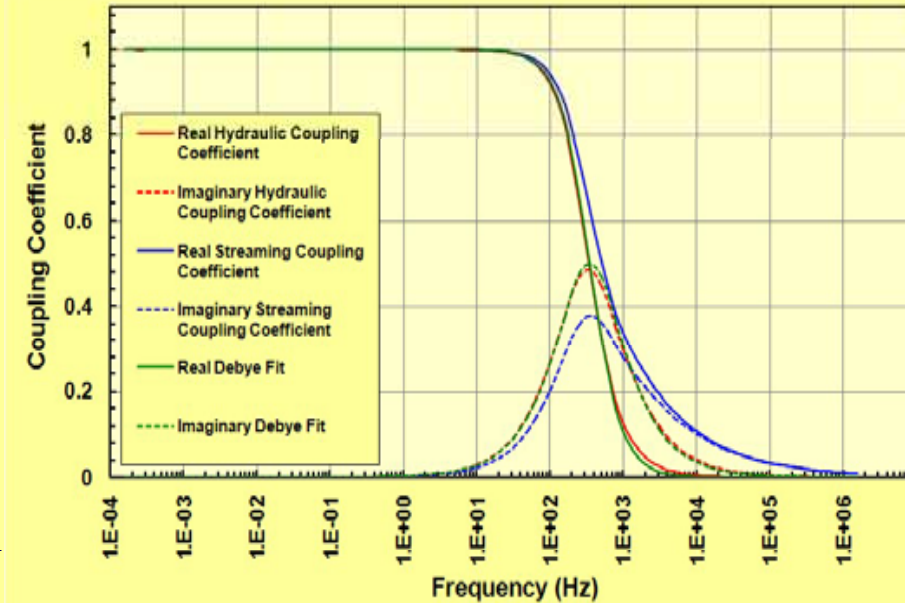
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AC Theory II

Hydraulic coupling coefficient is almost Debye-like

Streaming coupling coefficient is not Debye-like

The smaller the grain size the higher the frequency of the dispersion



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Apparatus

Apparatus

- **Early DC measurement cells**
- **DC measurement cells at ULaval**
- **Early AC measurement cells**
- **AC measurement cells at ULaval**



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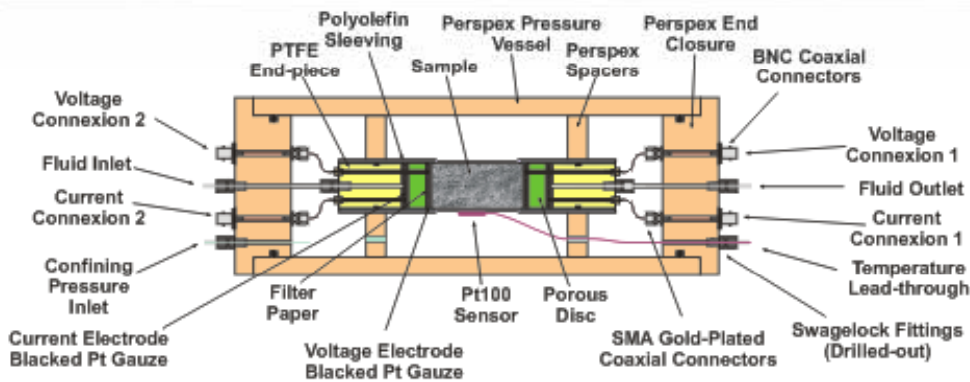
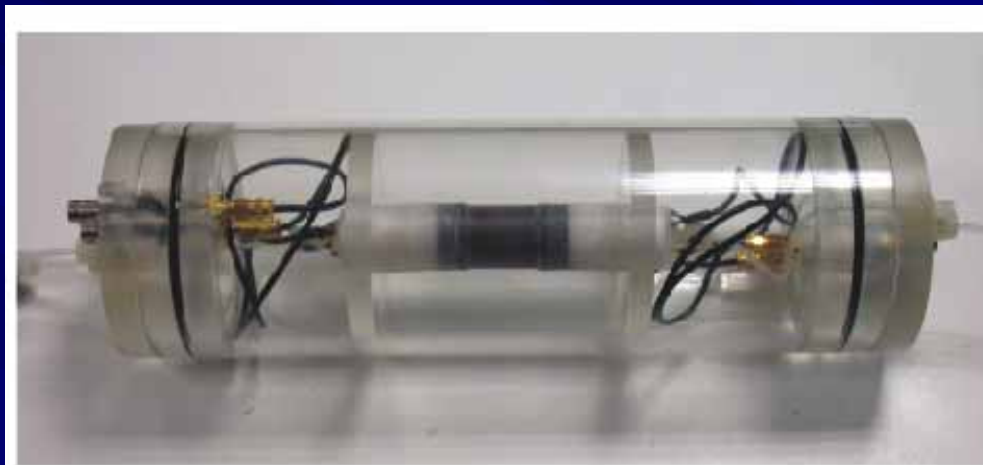
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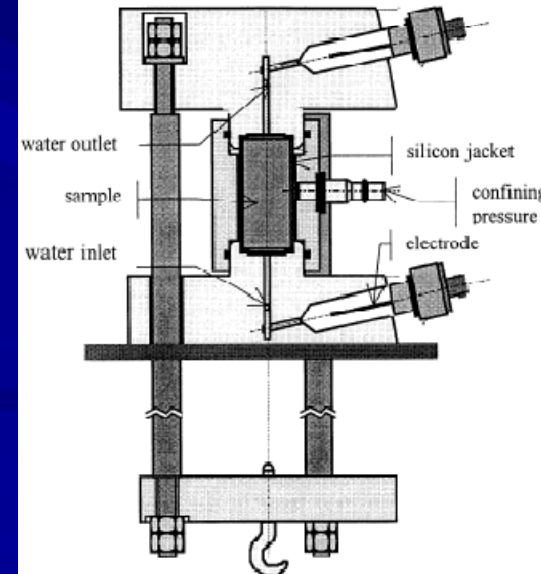
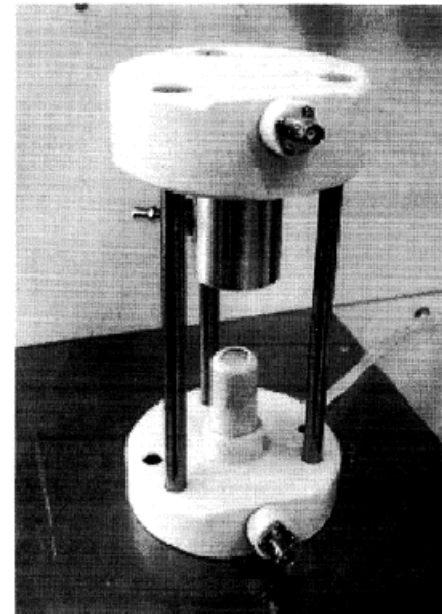
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Early DC cells

- From two existing cells:
 - Jouniaux et al. (2000)
 - Glover (2001)



Glover (2001)



Jouniaux et al. (2000)

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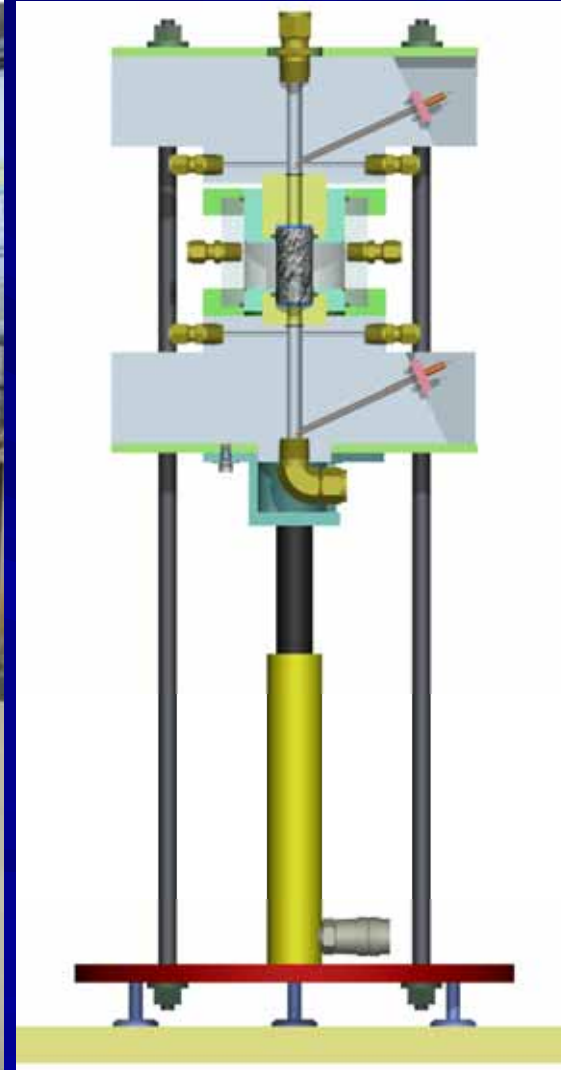
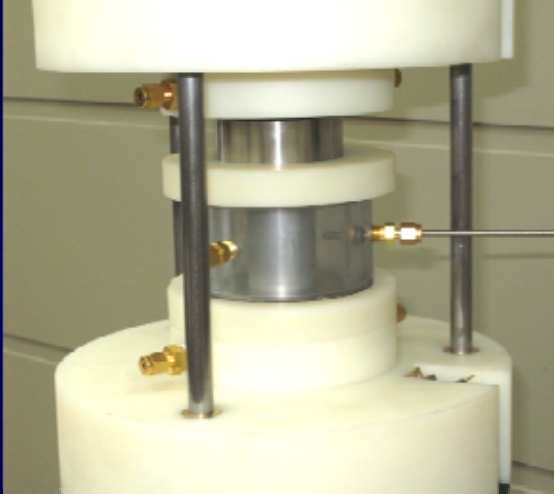
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DC measurement cells



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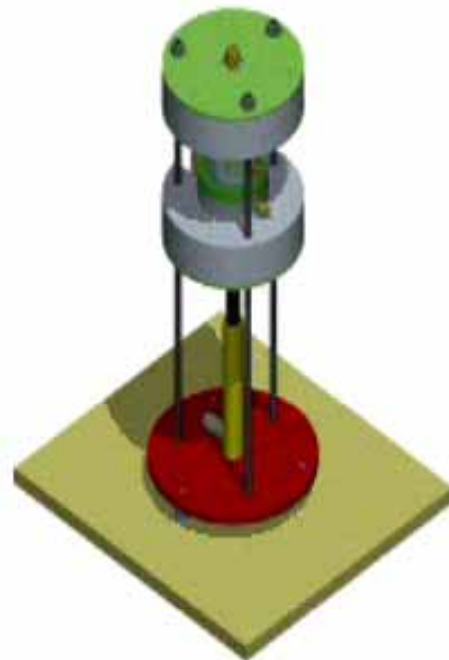
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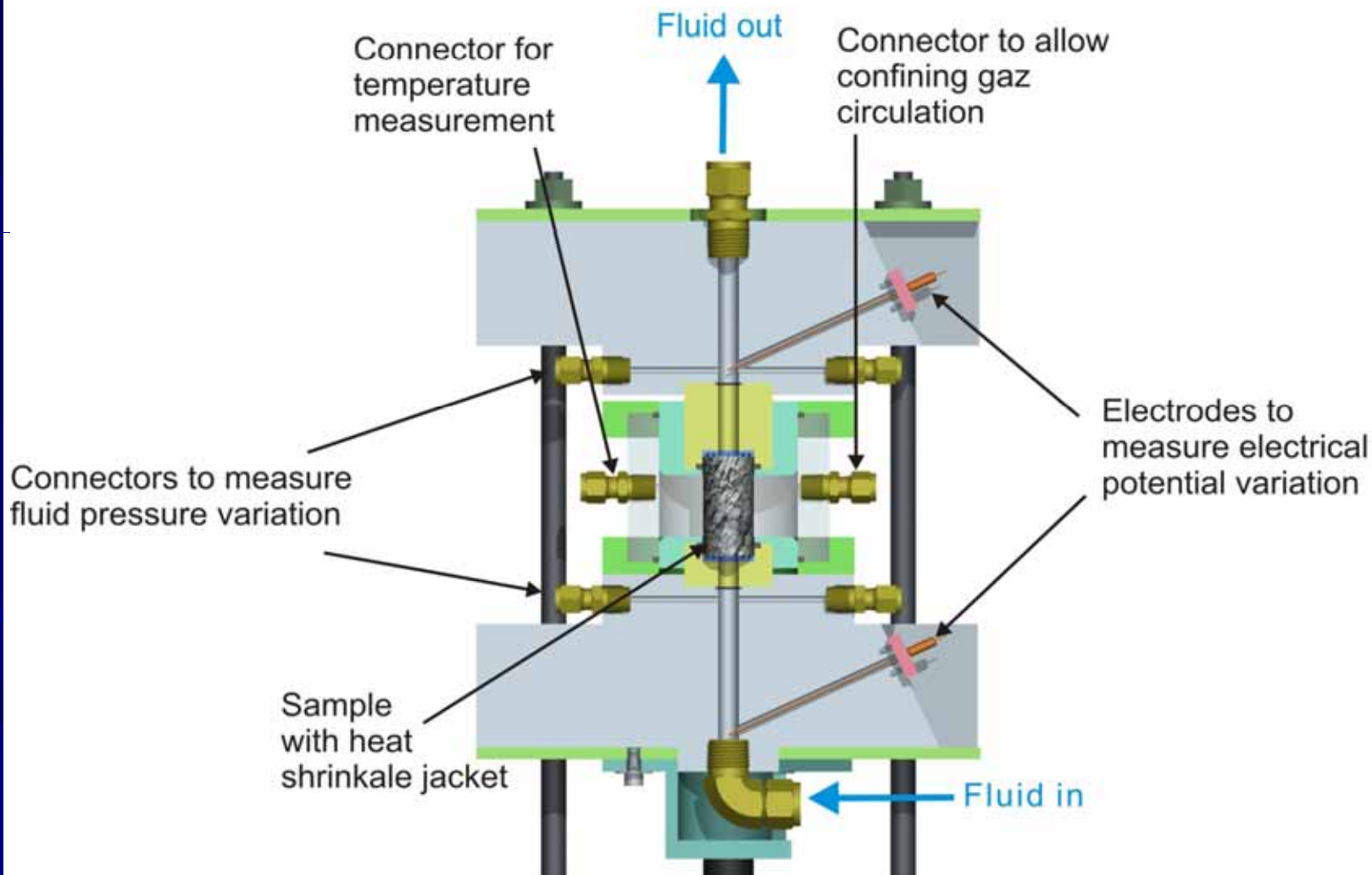
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DC measurement cells



Mark 3 cell can be used at higher
Confining pressures within the
same hydraulic press



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Early AC measurement cells

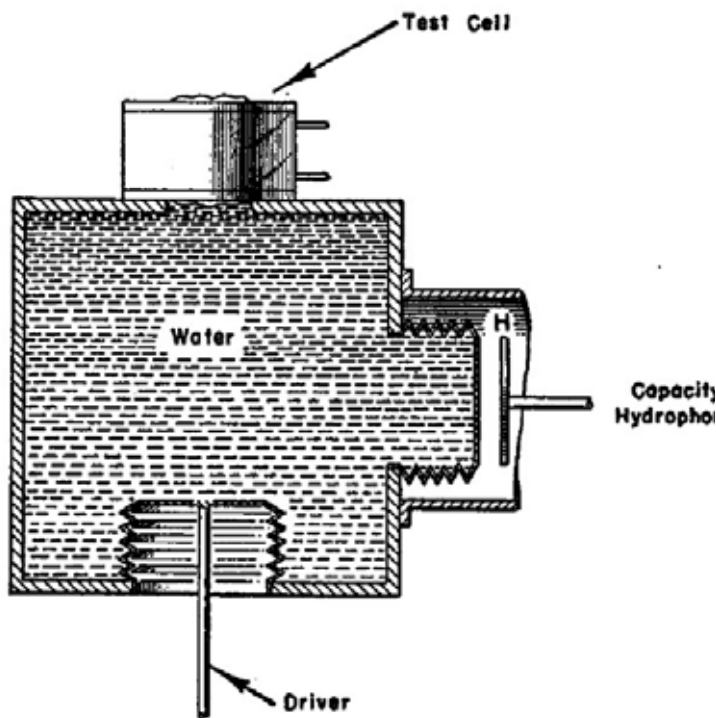


FIG. 2. Cross-sectional view of main test chamber with test cell attached.

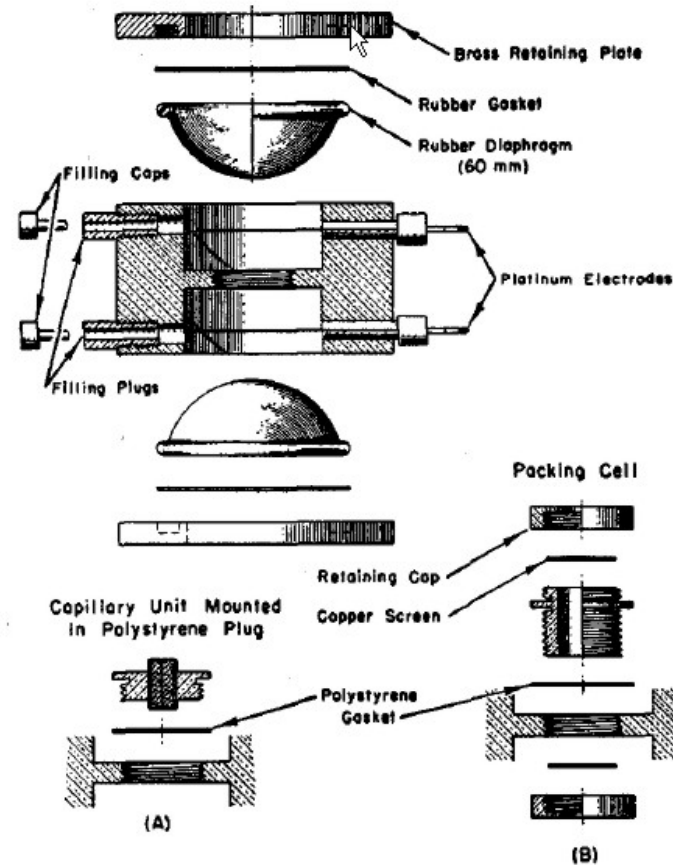


FIG. 3. Diagrammatic view of test cell, showing capillary unit. Dimensions of test cell: internal diameter: 1.75 in.; outer diameter: 3.00 in.; height polystyrene body: $1\frac{1}{4}$ in.; distance between electrodes: $1\frac{1}{2}$ in.; length platinum electrodes: $1\frac{1}{2}$ in.; diameter platinum electrodes: 0.016 in.; thickness threaded section: $\frac{3}{8}$ in.; diameter threaded section: $\frac{7}{8}$ in.



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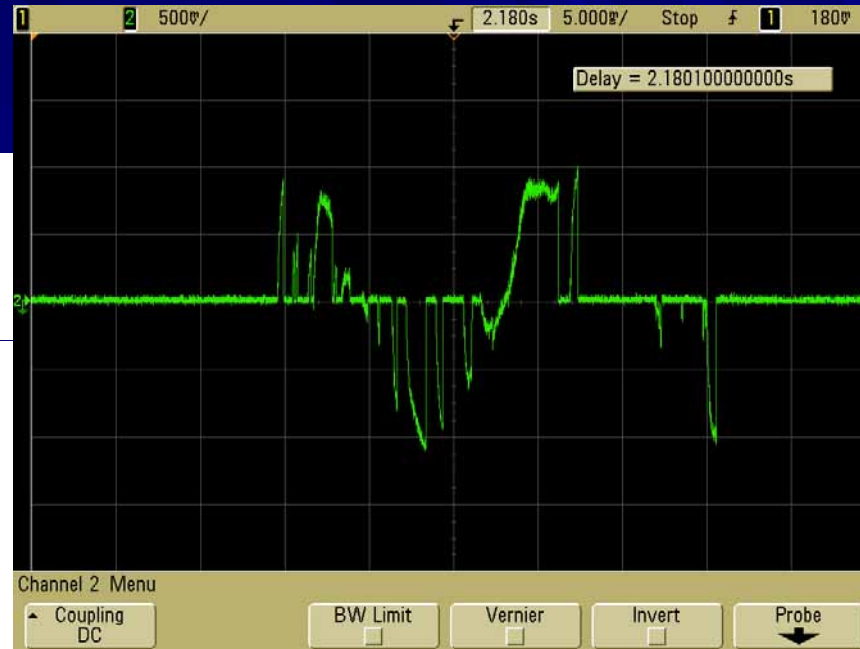
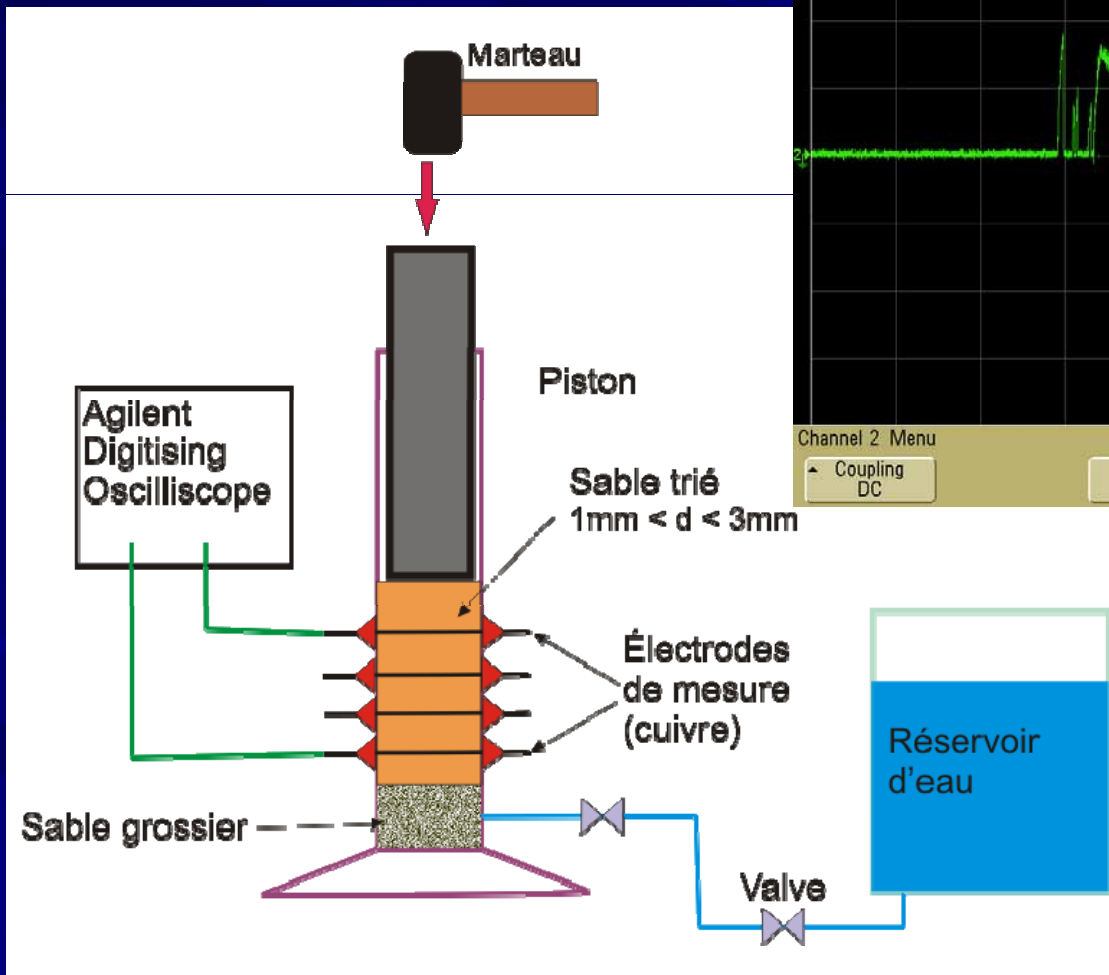
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Apparatus

Early AC measurement cells

Vertical scale: 1 square = 1 V
 Horizontal scale: 1 square = 5 ms

Electrical potential from a fluid pulse : The « Hammer test »



Ottawa sand
 Grain diameter between 0.1 mm and mm
 Saturated with 0.1M de NaCl
 Glover (2007)



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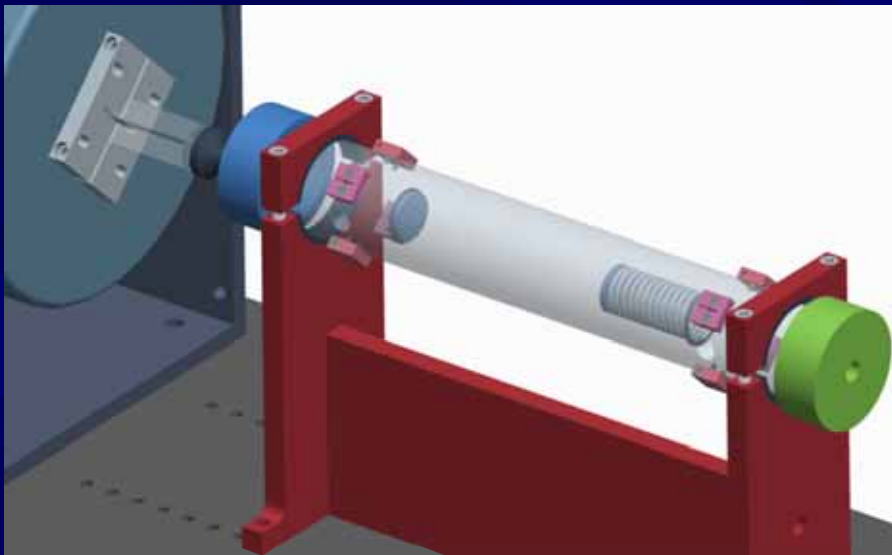
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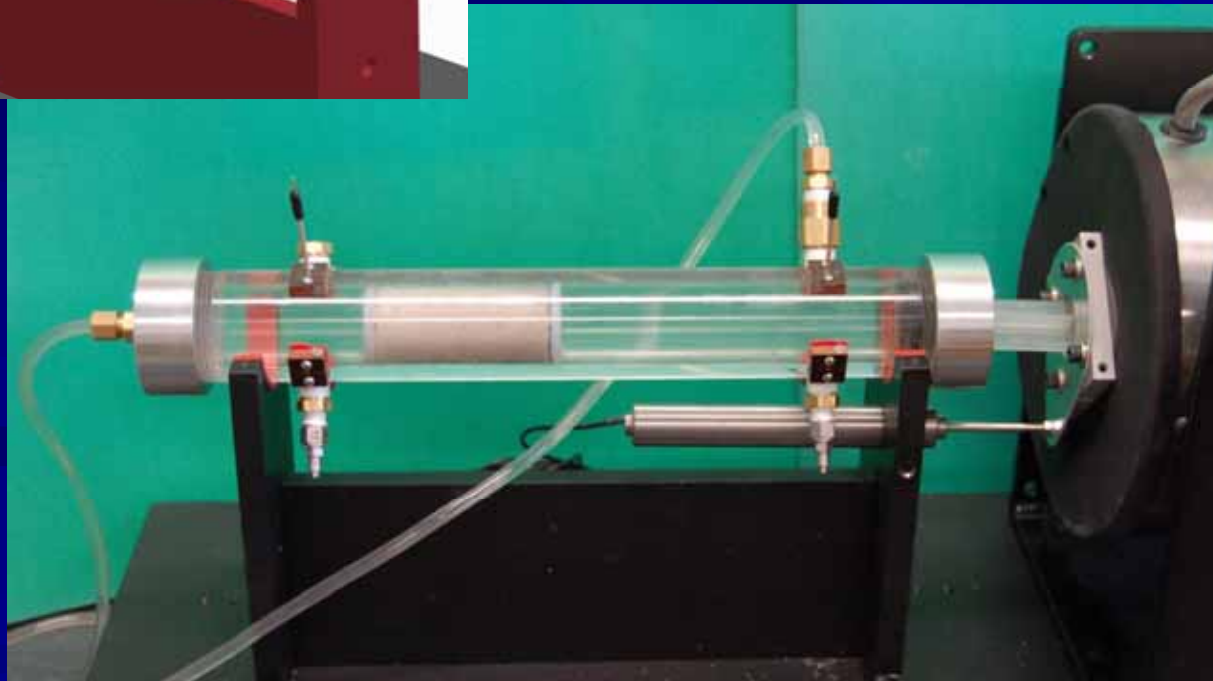
AC measurement cells



The design takes a piston or a rubber membrane

An LVDT allows a servo-locked amplifier to control the shaker with precision

Measurements can be made with or without an imposed DC fluid flow



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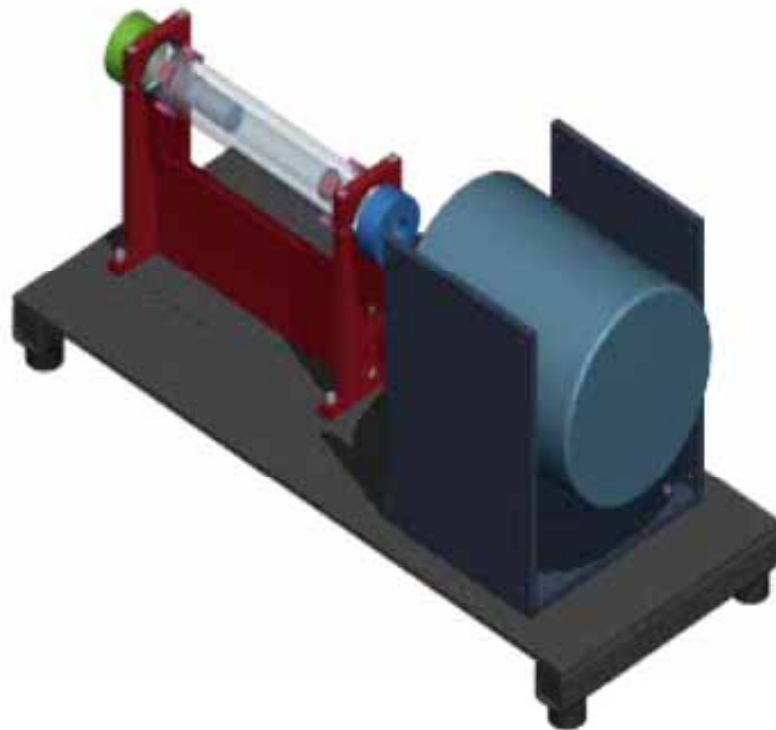
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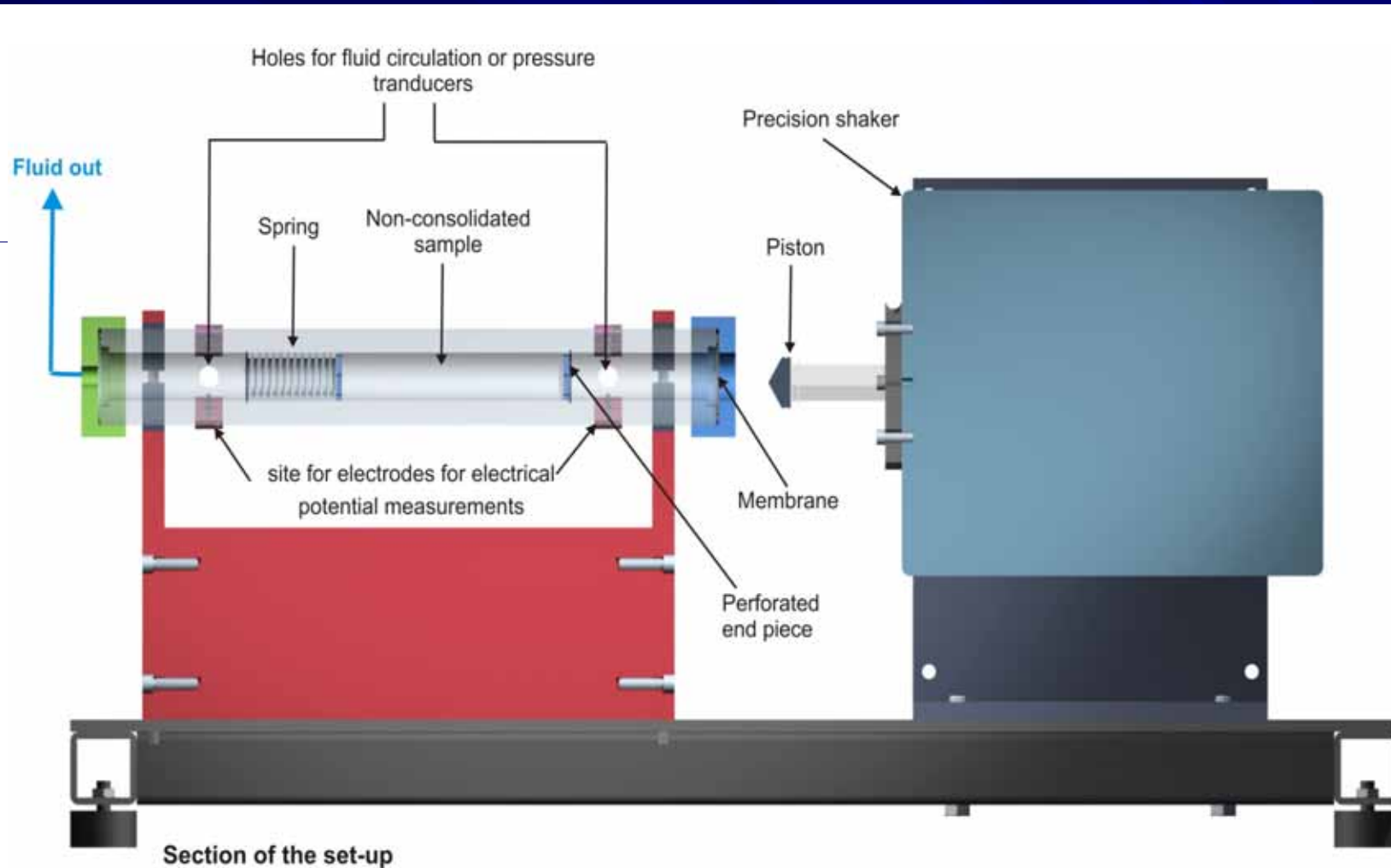
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Laboratory determinations

- Pore fluid chemistry
- Pore fluid salinity
- Pore fluid pH
- Mineralogy
- Grain size
- Temperature
- Saturation
- Frequency



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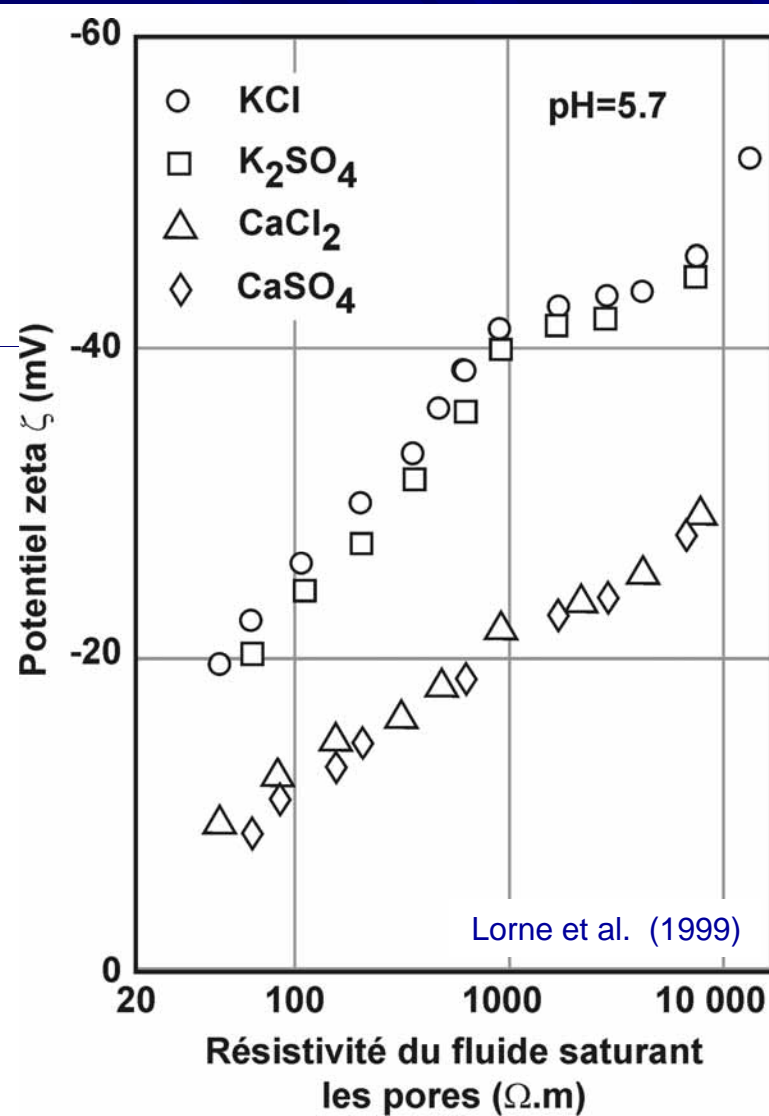
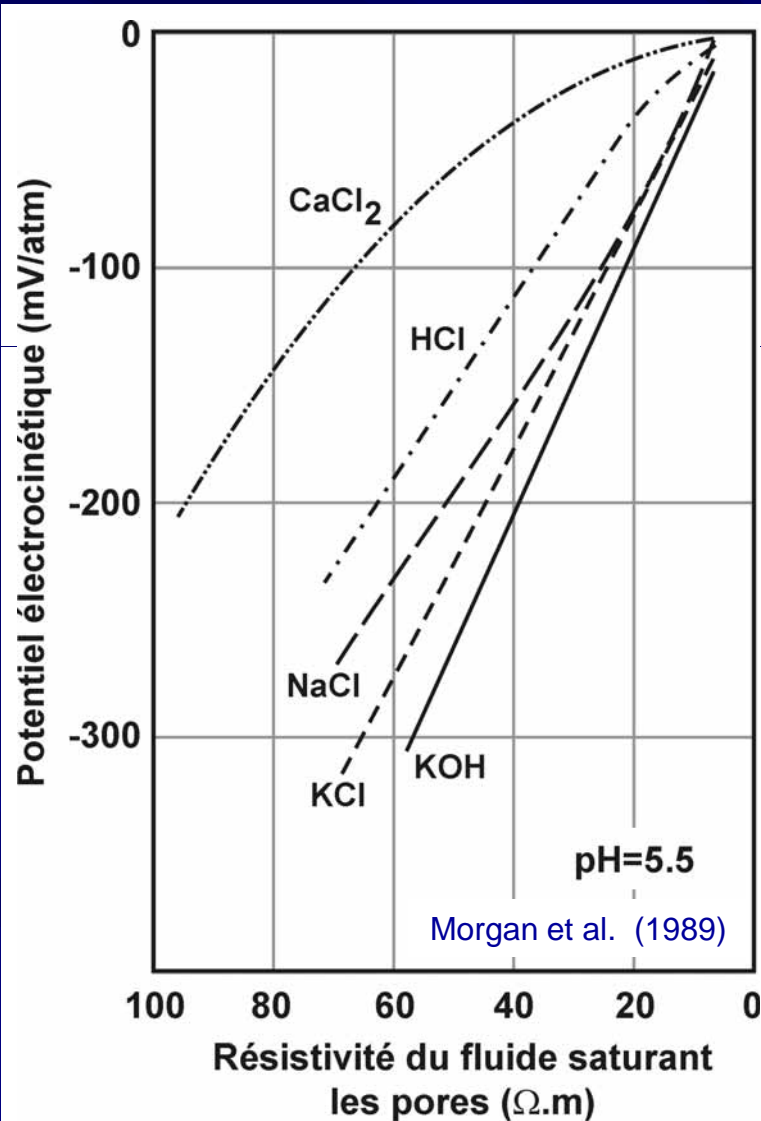
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Pore fluid chemistry



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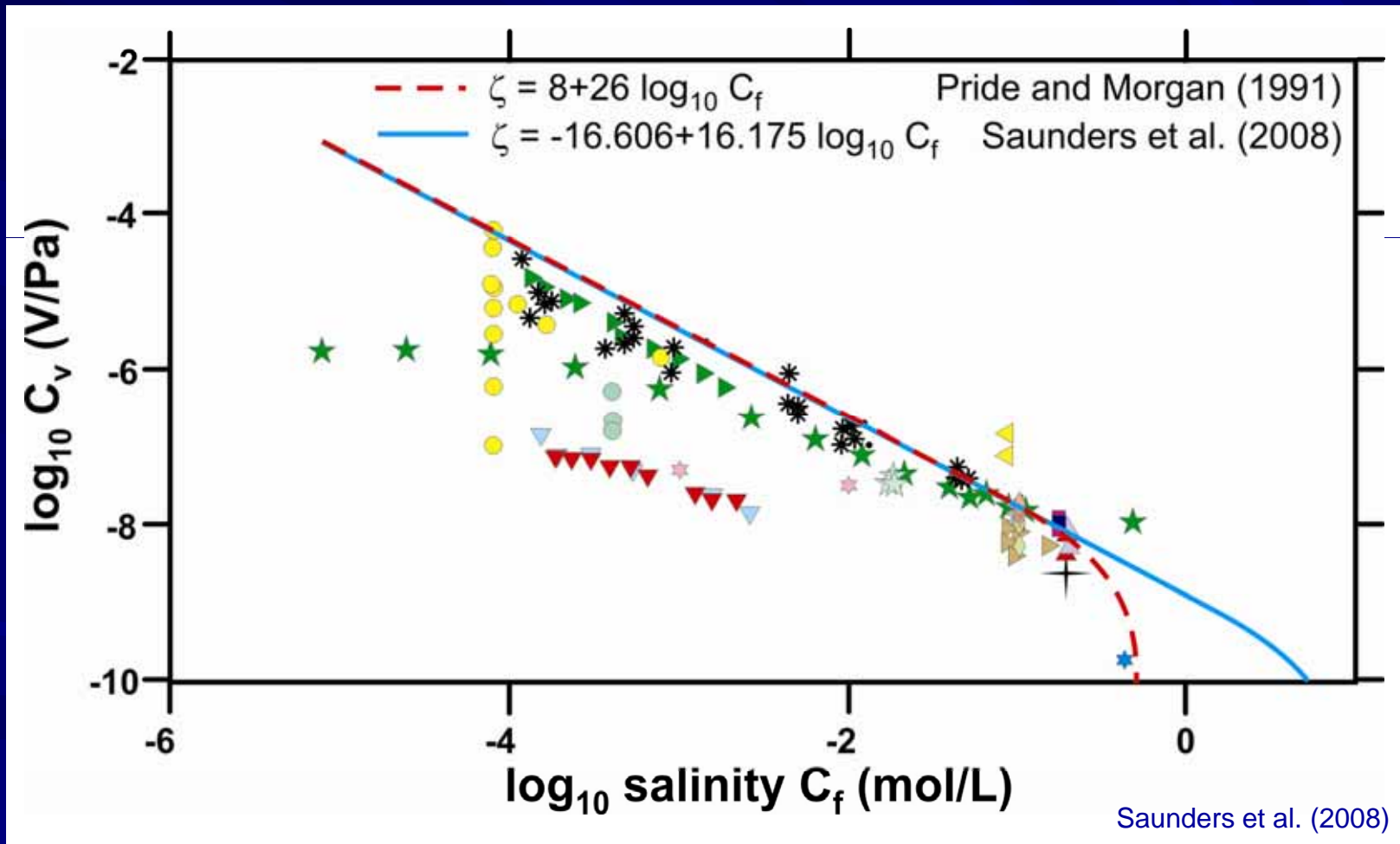
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Pore fluid salinity I



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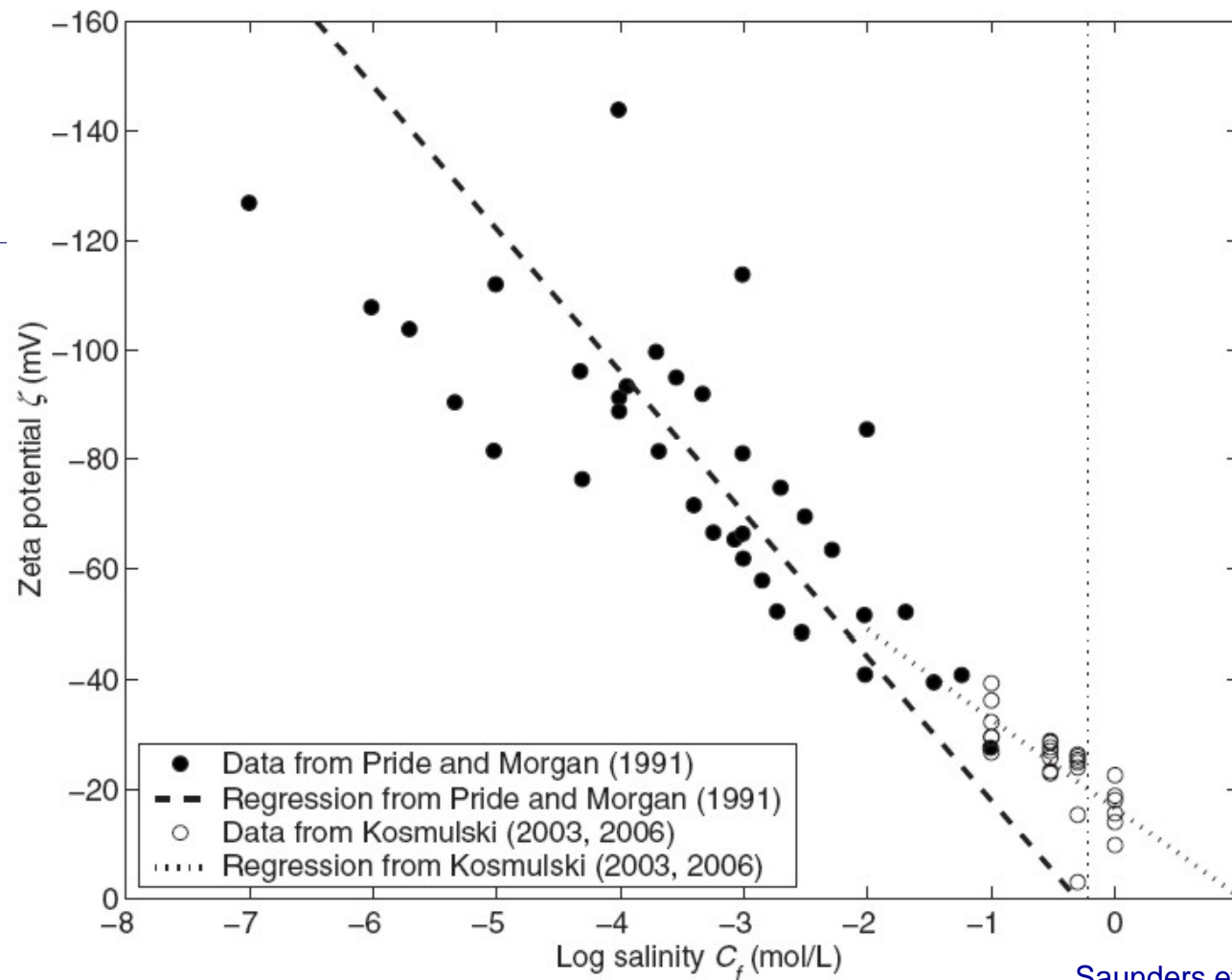
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Pore fluid salinity II



Saunders et al. (2008)



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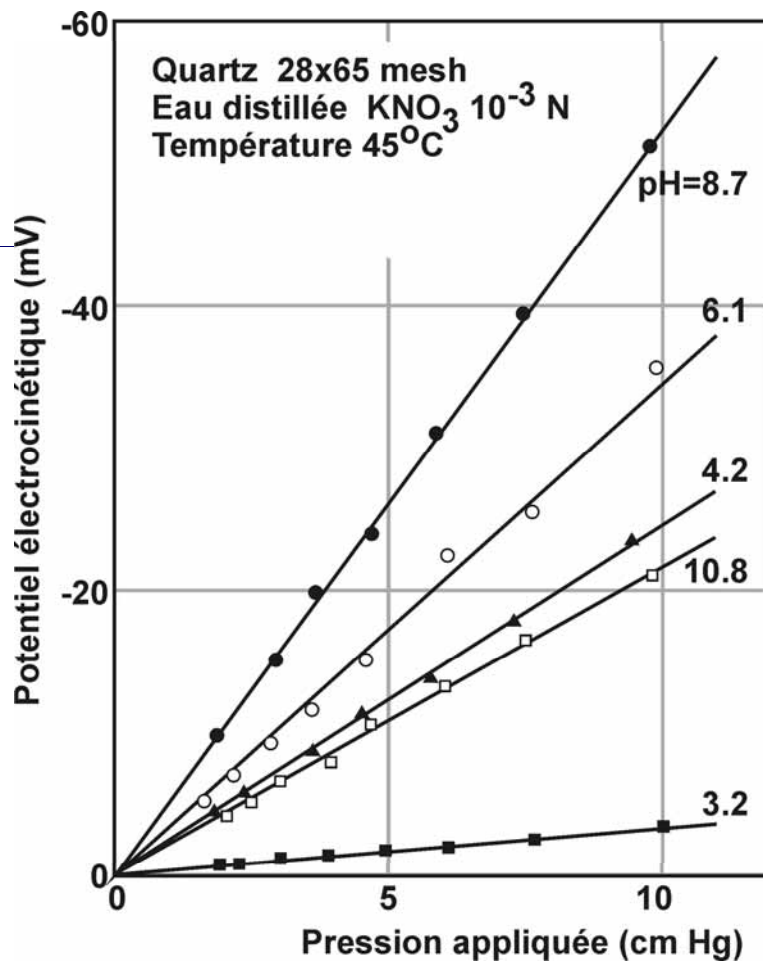
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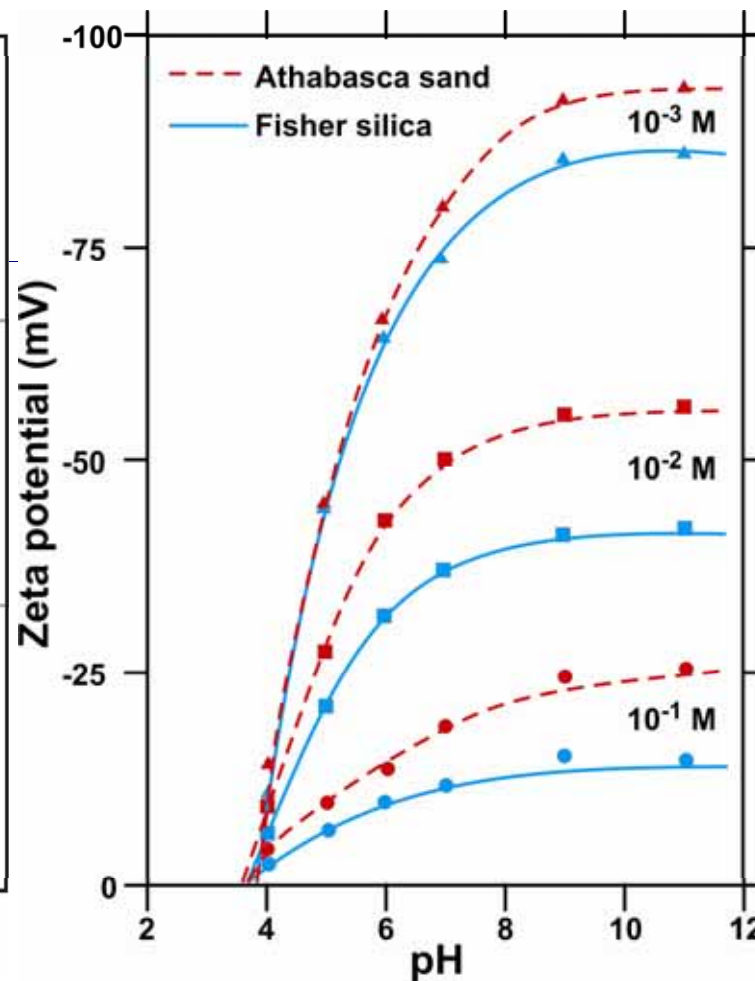
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Laboratory determinations

Pore fluid pH I



Ishido et Mizutani (1981)



Cerda & Non-Chhom (1989)



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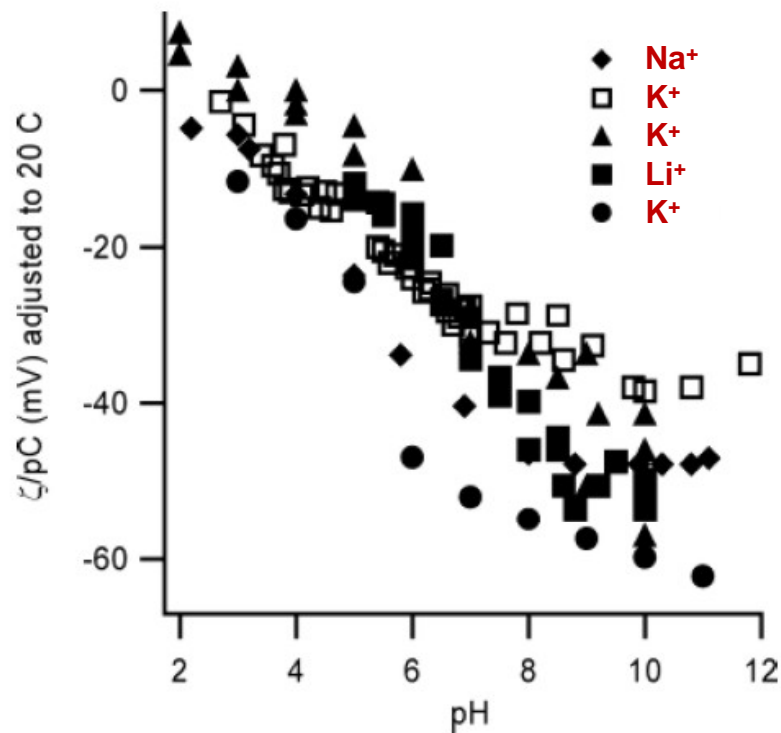
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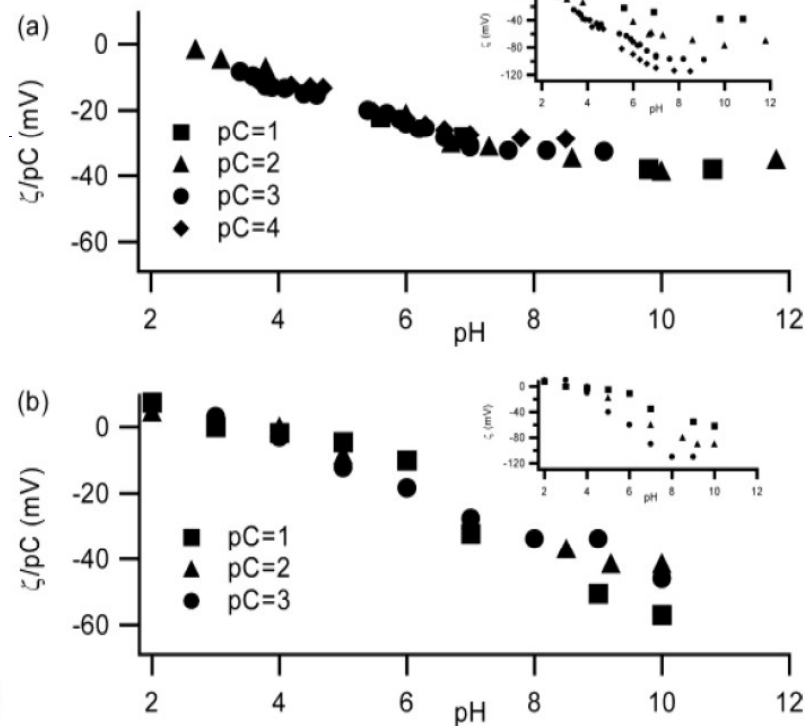
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Pore fluid pH II

Scales et al. (1992)
Kosmulski & Matijevic (1992)
Kirby & Hasselbrink (2004)



pH dependence of temperature-corrected (20°C), normalized zeta potential



Zeta potential measured as a function of pH and counterion concentration



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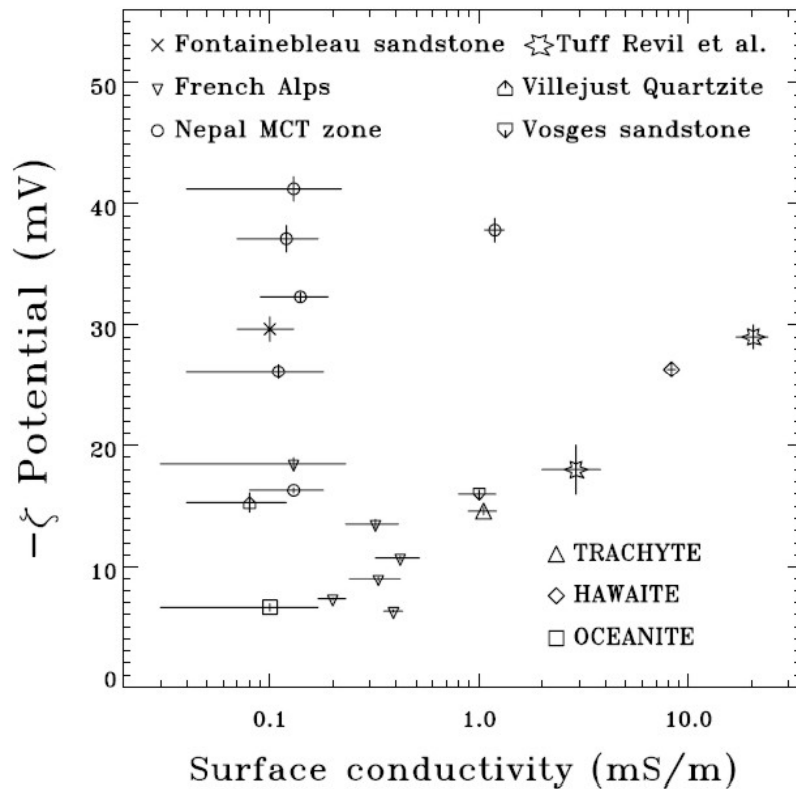
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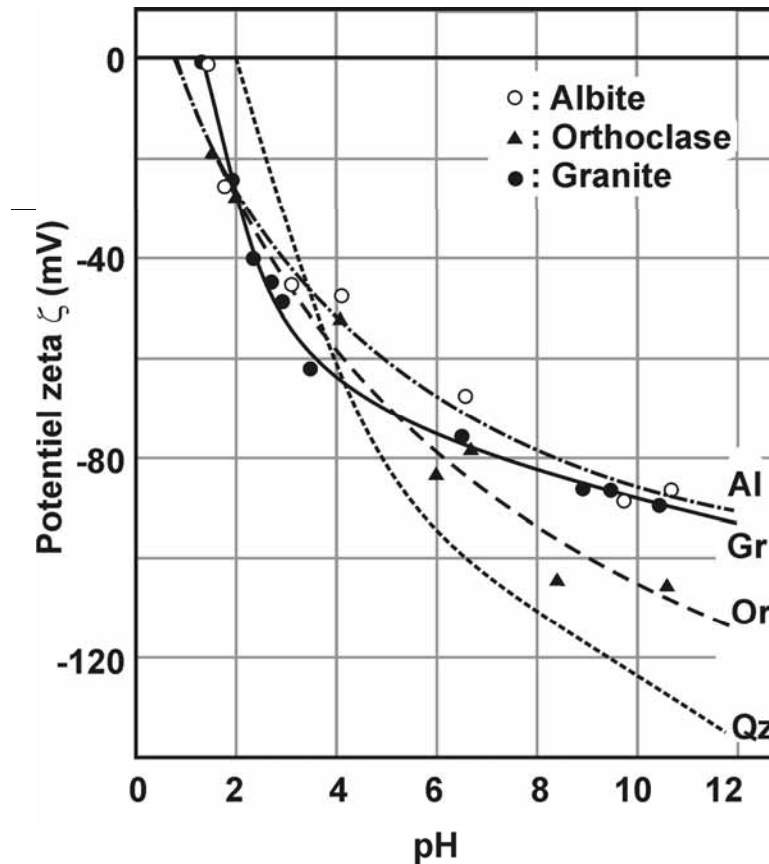
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Mineralogy I



Perrier and Froidefond (2003)



Ishido et Mizutani (1981)



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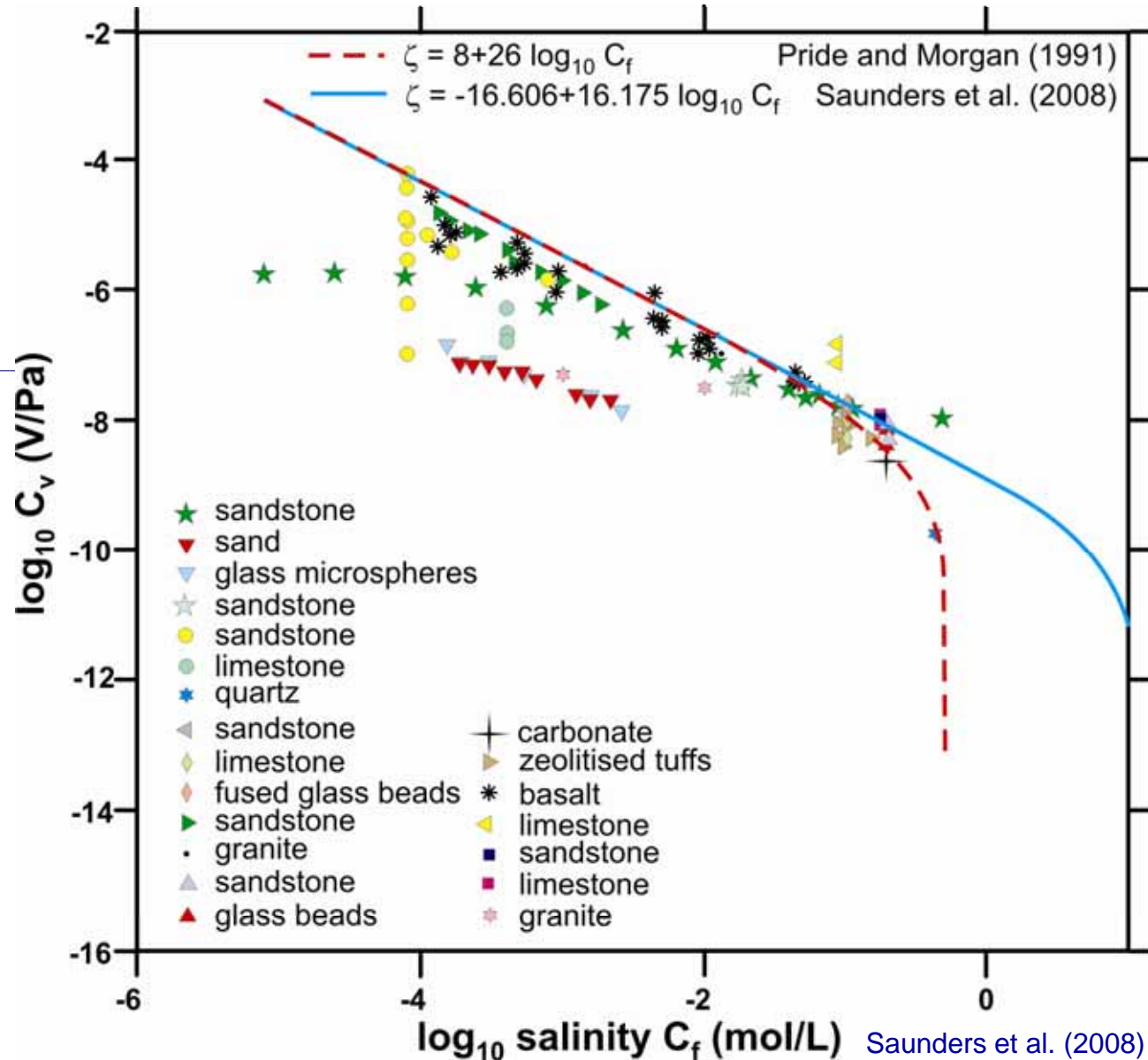
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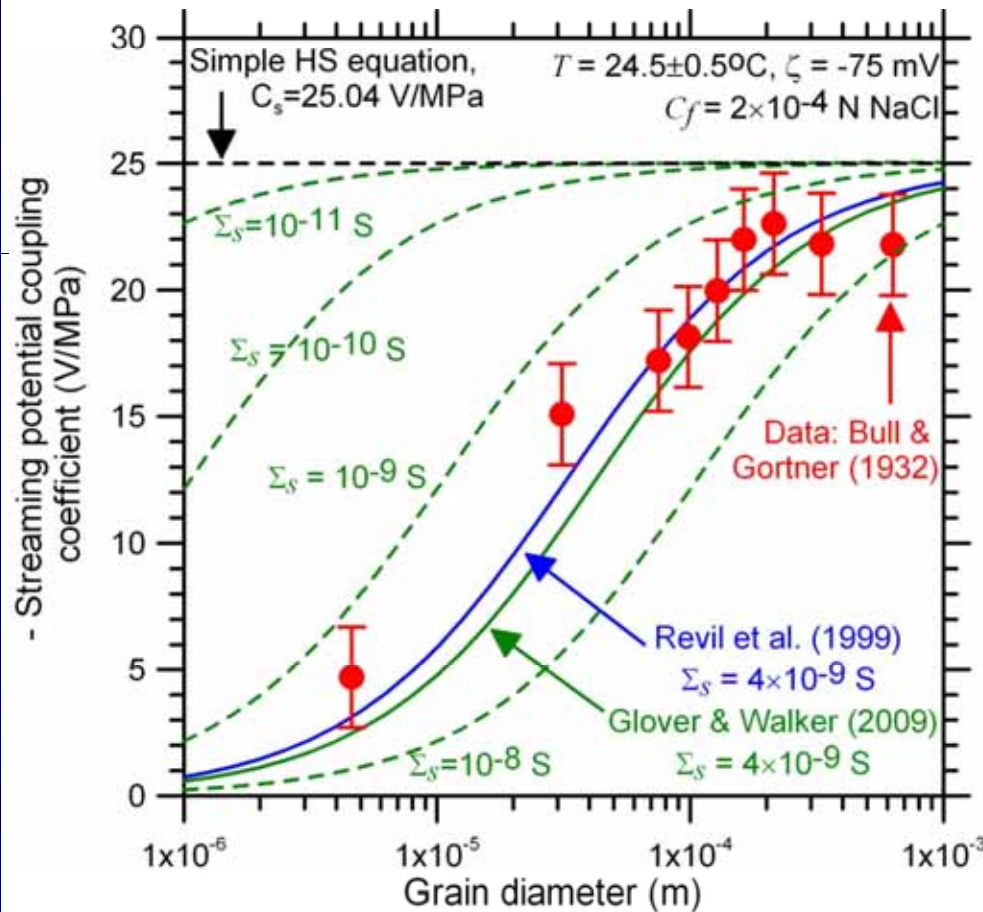
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Grain size



$$C_s = - \frac{d \varepsilon_f \zeta}{\eta_f (d \sigma_f + 6 \Sigma_s (F - 1))'}$$

$$\Lambda = \frac{d}{3(F - 1)} \quad \text{Revil et al. (1999)}$$

$$C_s = - \frac{d \varepsilon_f \zeta}{\eta_f (d \sigma_f + 4 \Sigma_s m F)'}$$

$$\Lambda = \frac{d}{2mF} \quad \text{Glover et al. (2006)}$$

$$C_s = - \frac{r \varepsilon_f \zeta \sqrt{a}}{\eta_f (r \sigma_f \sqrt{a} + 4 \Sigma_s \sqrt{2})'}$$

$$\Lambda = r \sqrt{\frac{a}{8}} \quad \text{Glover and Walker (2009)}$$



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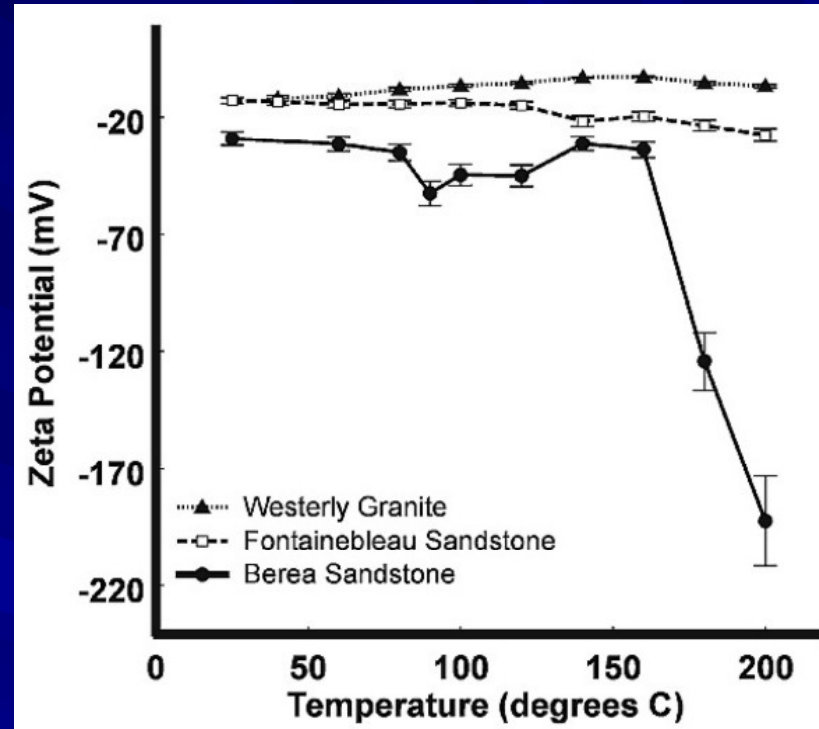
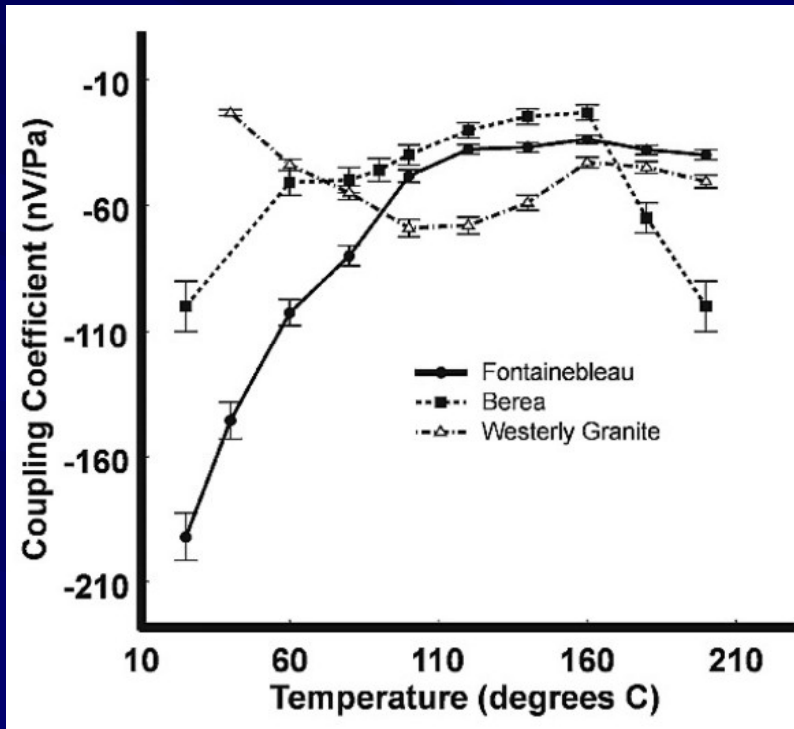
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Temperature

Reppert and Morgan (2003)



The coupling coefficient varies significantly, but erratically with temperature

Stability is the main experimental problem

The calculated zeta potential may be a function of temperature

However, its form is controlled by the effect of temperature on the fluid conductivity

$$\zeta = \frac{\Delta V}{\Delta P} \frac{\eta_f \sigma_f^*}{\epsilon_f} = \frac{C_s \eta_f \sigma_f^*}{\epsilon_f}$$



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Saturation I

$$J_i = -\sigma \sigma_{ri} C C_{ri} \nabla P_i$$

$$\sigma_{ri} = S_i^n$$

$$C_{ri} = ?$$

Many attempts at finding a solution

$$C_r = \frac{1}{S_w^{n+1}} \left(\frac{S_w - S_w^r}{1 - S_w^r} \right)^{(2+3\lambda)/\lambda}$$

Revil et al. (2007)

$$C_r = \frac{Q_w k_{rw}}{\mu_w \sigma_r} \quad \text{where} \quad C = \frac{k}{\sigma}$$

Jackson (2008)

Jackson (2008)

$$C_r = S_w^{n+2} \left(\frac{S_w - S_w^r}{1 - S_w^r} \right)^{1/\lambda}$$

Glover (2009)

$$C_r = \frac{\frac{Q_w}{\mu_w} k_{rw} + \frac{Q_o}{\mu_o} k_{ro}}{\sigma_r}$$



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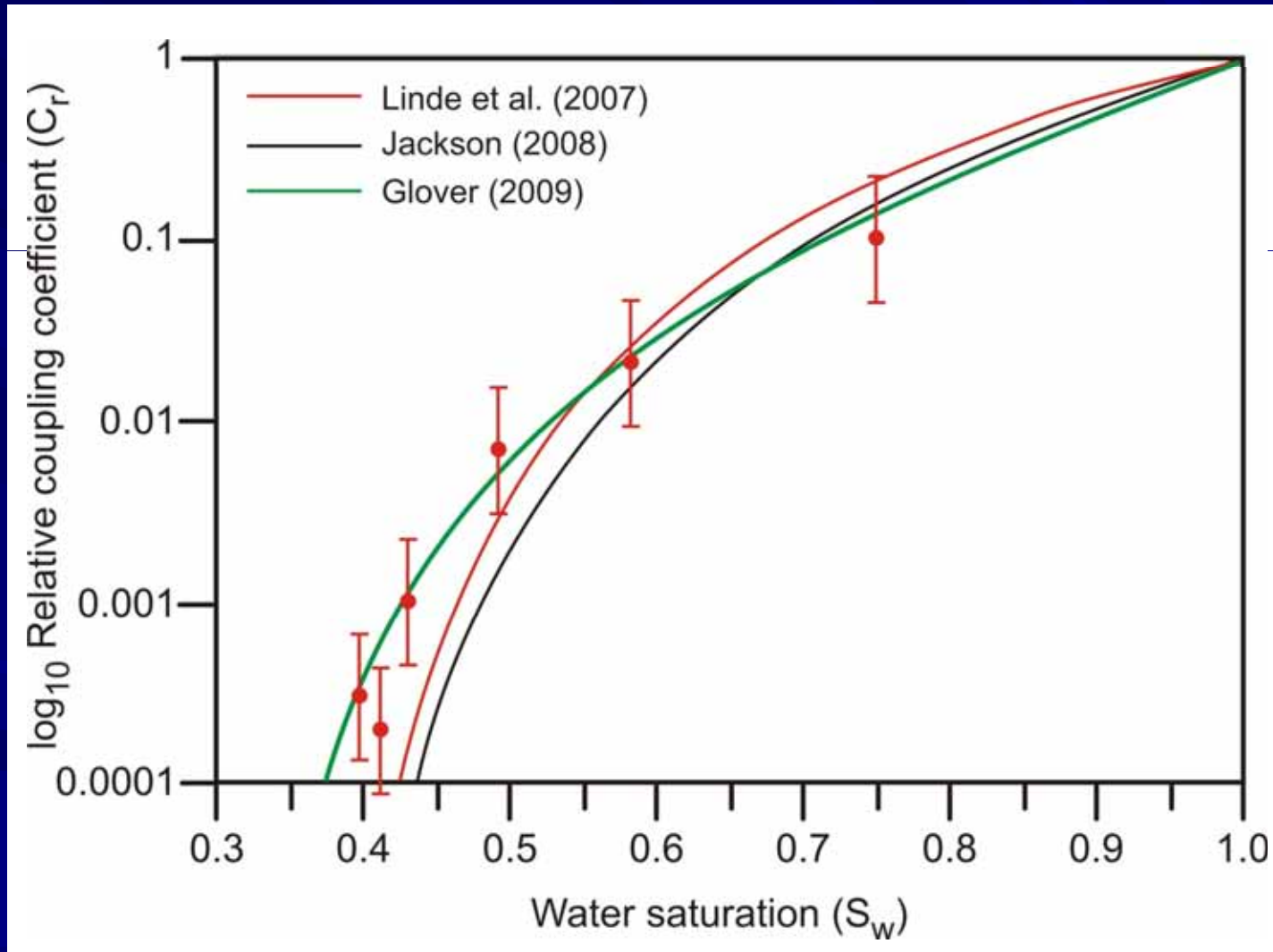
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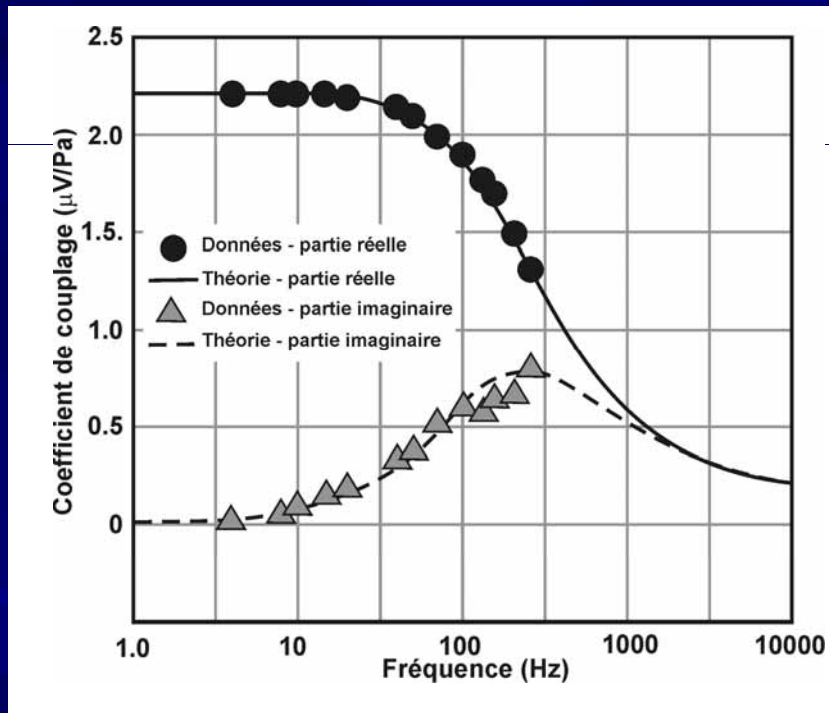
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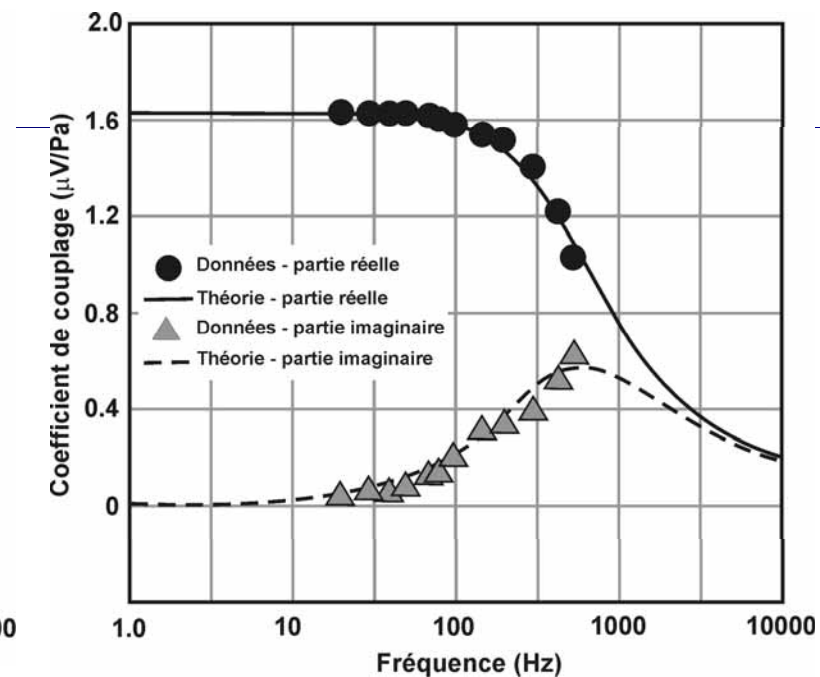
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Frequency (AC measurements) I

No reliable data exists for rocks in the public domain
Here is the best data made on silica filters



Filter A (72.5-87 μm). Modelled transition frequency (269 Hz) corresponds to a pore radius of 65 μm .



Filter B (35-50 μm). Modelled transition frequency (710 Hz) corresponds to a pore radius of 40 μm .



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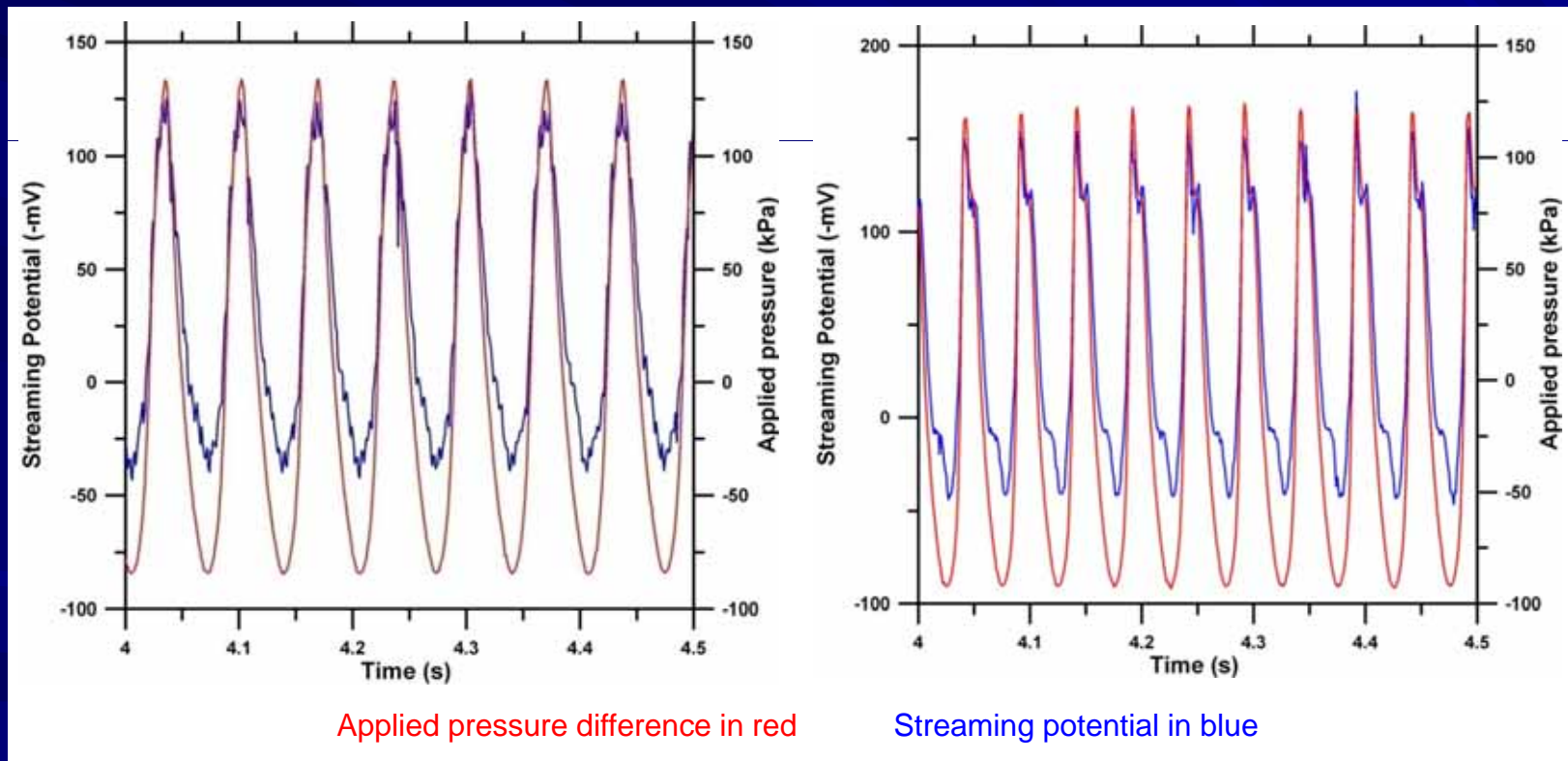
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Frequency (AC measurements) II

First data available for ottawa sand using the Université Laval Petrophysics AC cell Mk 2



15 Hz – some improvement of S/N ratio required

20 Hz – Problems with cavitation. Calculations have been carried out to avoid this phenomenon.



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- **Hydrocarbon exploration & production**
- **Water reservoir management**
- **Remediation of polluted soils**
- **Permafrost monitoring**
- **Acid mine drainage monitoring**
- **Volcano prediction**
- **Earthquake prediction**
- **Synthetic earthquakes**
- **Geothermal HDR reservoir monitoring**
- **Monitoring of CO₂ sequestering**
- **Soil stabilisation**

...many others



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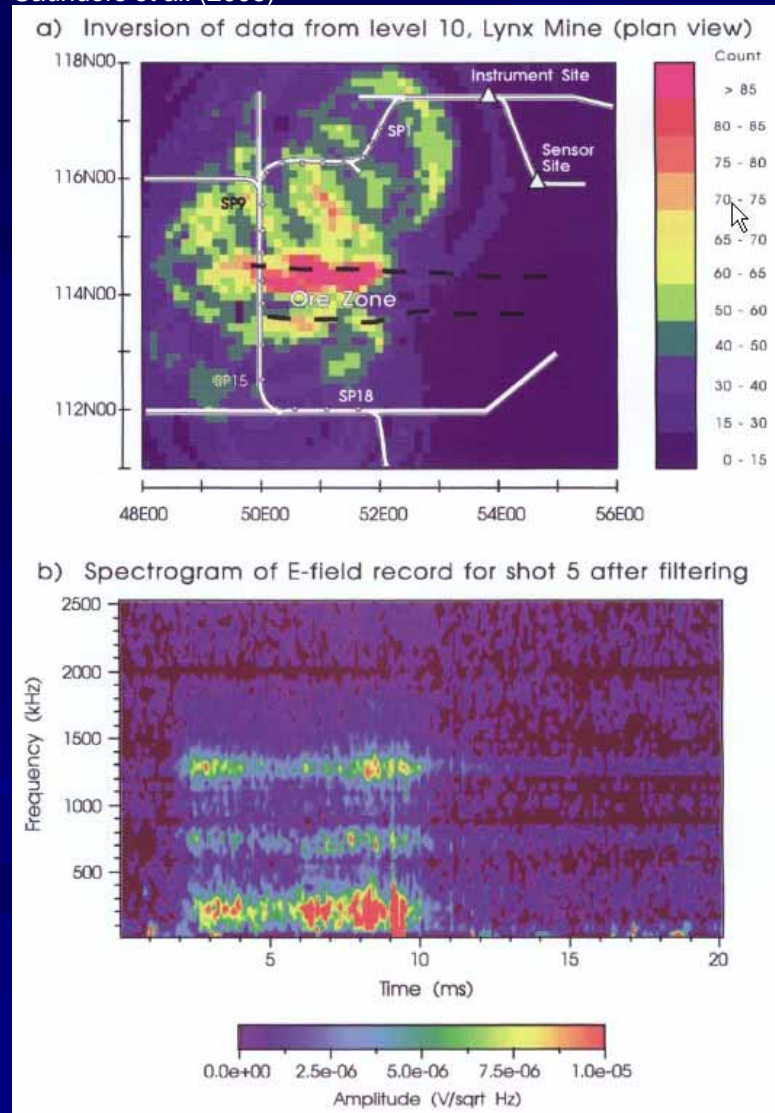
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Hydrocarbon exploration & production I

Saunders et al. (2008)



There are many impressive examples of the use of seismoelectric and electro-kinetic prospection of hydrocarbon reservoirs

All are impossible to publish!!!

Here is an application to mining instead – the discovery of zinc ore by electroseismics



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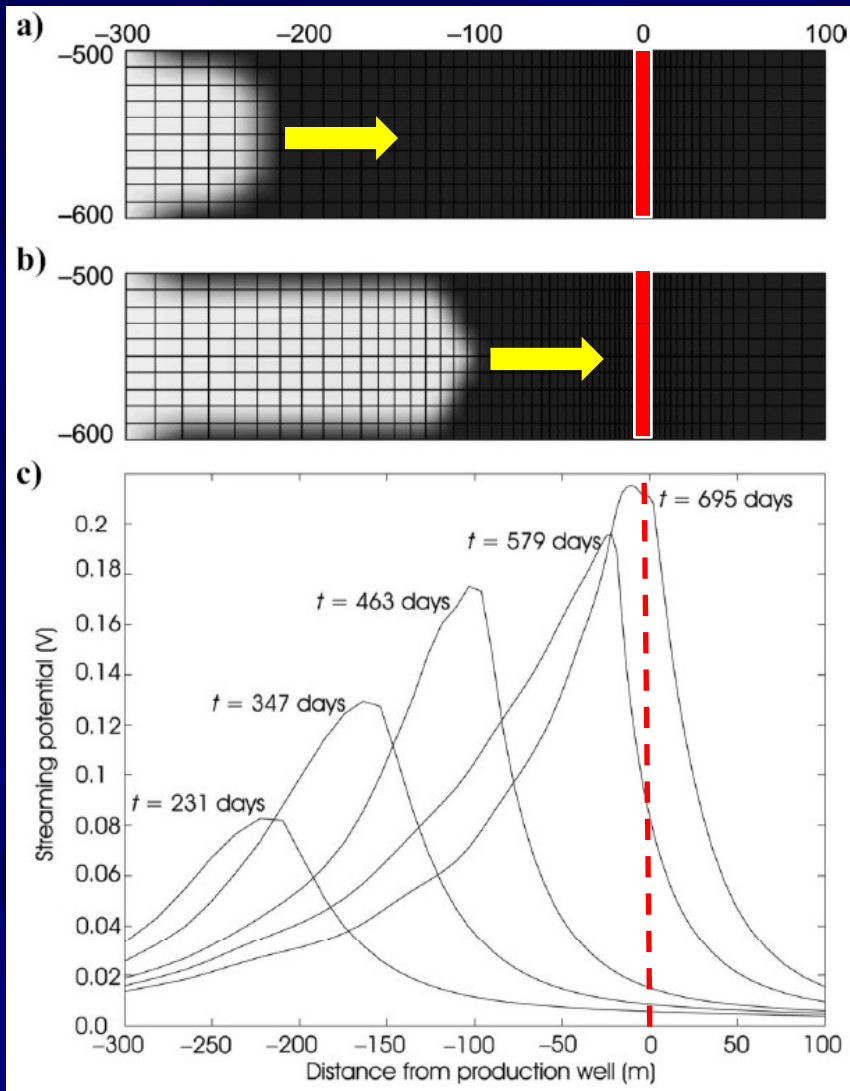
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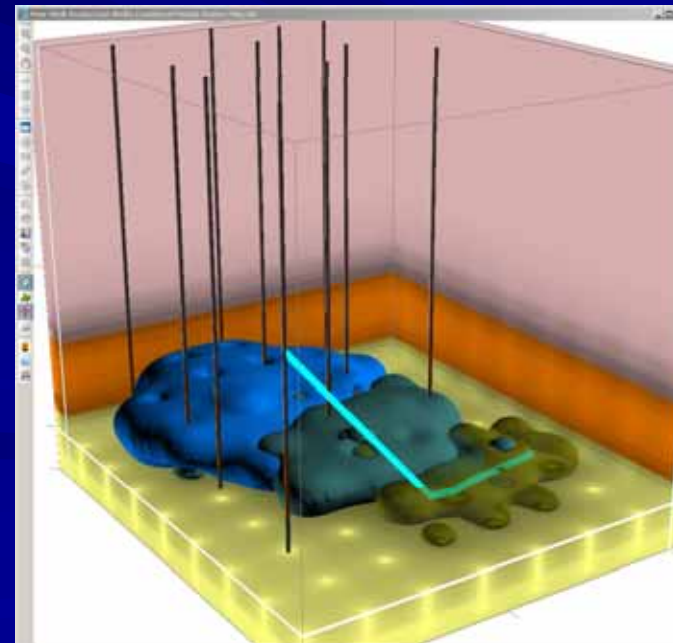
Hydrocarbon exploration & production II

Saunders et al. (2008)



As water approaches the borehole it may be predicted by measuring the increasing streaming potential

The well can be shut to improve the reservoir production



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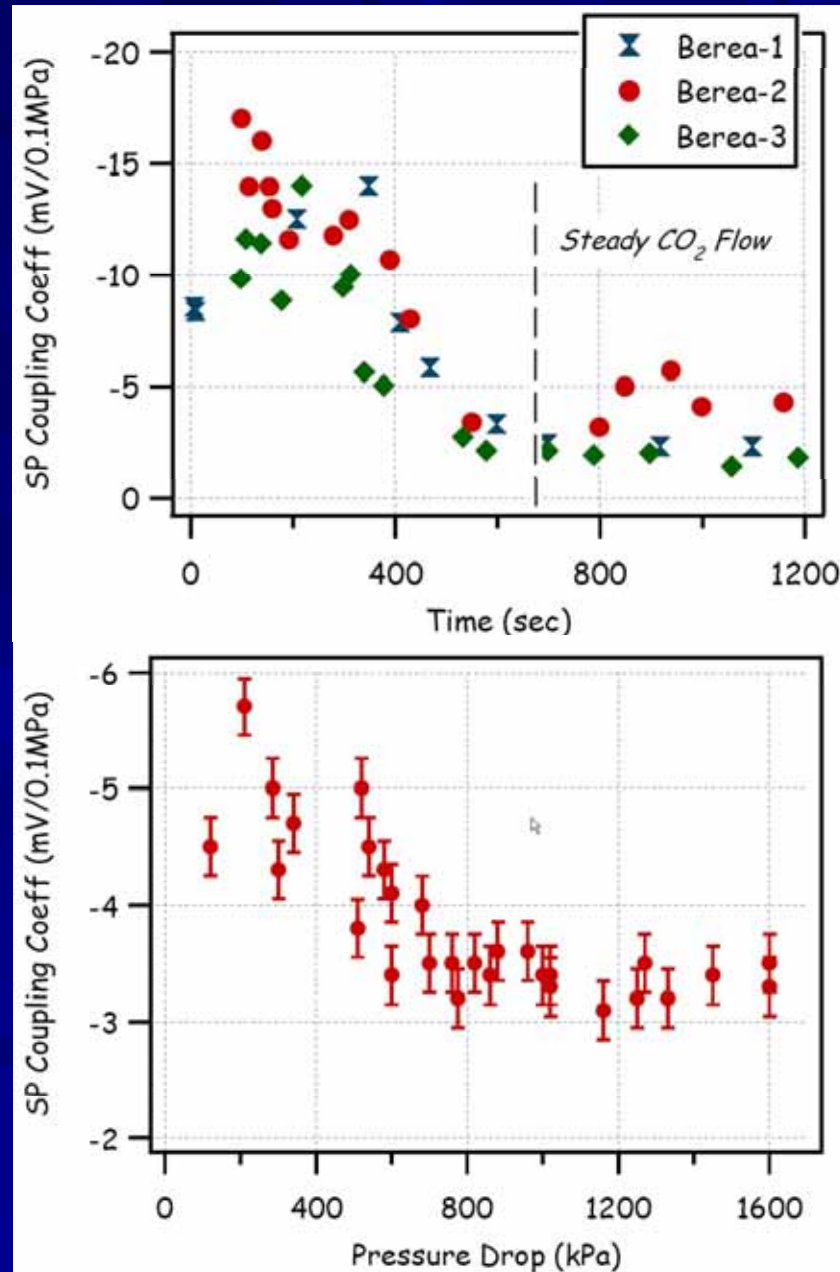
CO₂ Sequestration

Injection of CO₂ produces a dramatic decrease in the coupling coefficient

-300 mV/MPa \longrightarrow -30 mV/MPa

These differences would be easily detectable by measuring surface SP

- ❖ Progressive injection of a reservoir with CO₂ could be monitored
- ❖ CO₂ leaking from a sequestration reservoir may also be detected before it appears at the surface



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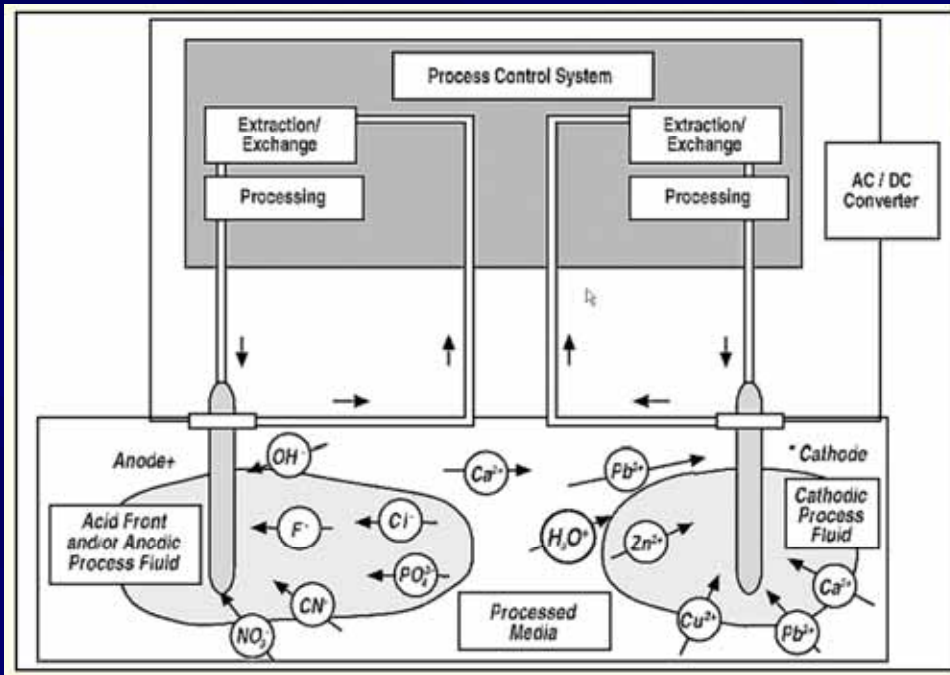
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Remediation of polluted soils



Electro-kinetic processes are used to

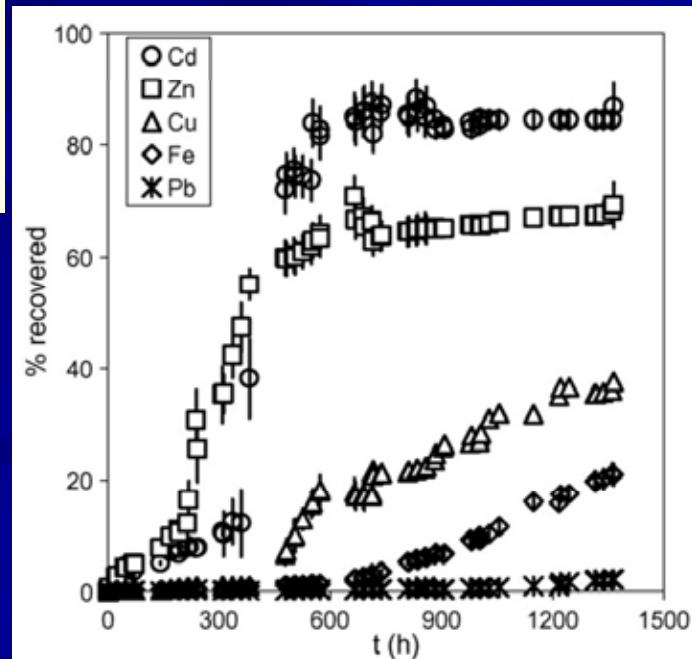
- Extract polluted fluids and ions, or
- Move polluted fluids into contact with bioremediation or other active agents

Active from ppt upwards

Electrolysis
Electro-osmosis
Electrophoresis

ions
water
colloids

Electro-kinetic water extraction
Is also used to strengthen soils



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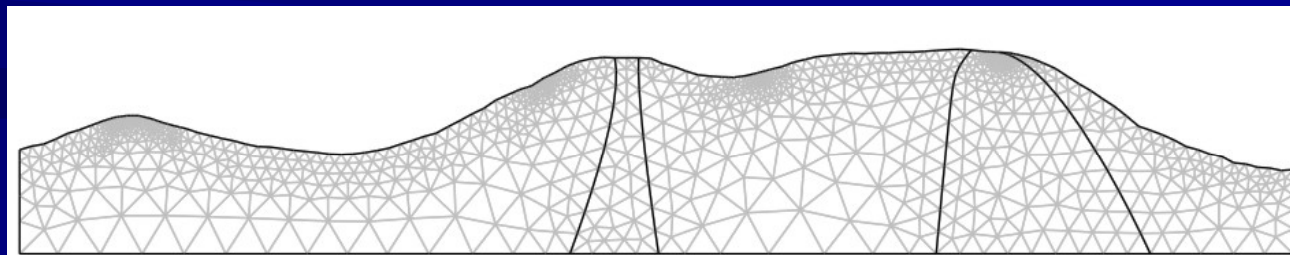
Volcano prediction I

© Google Earth

© John Freeman



First create a 2D finite element model
in Comsol Multiphysics



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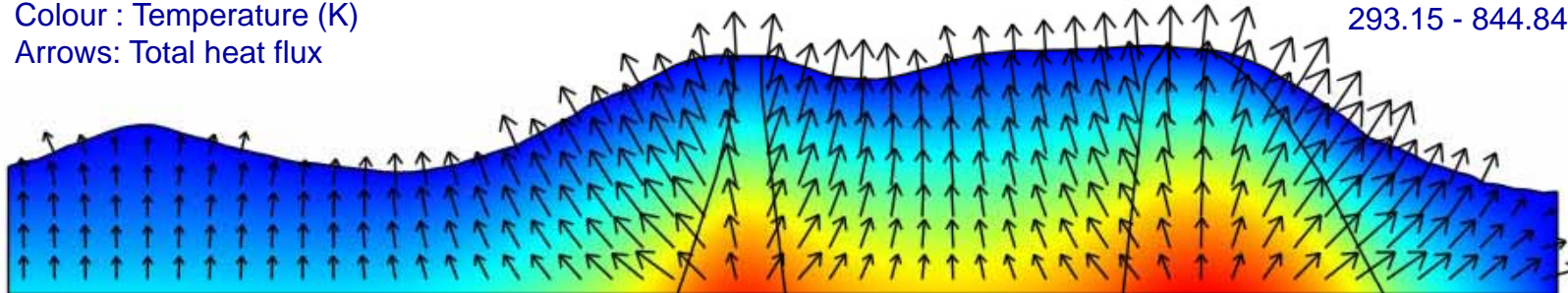
Volcano prediction II

First create a 2D finite element model
in Comsol Multiphysics

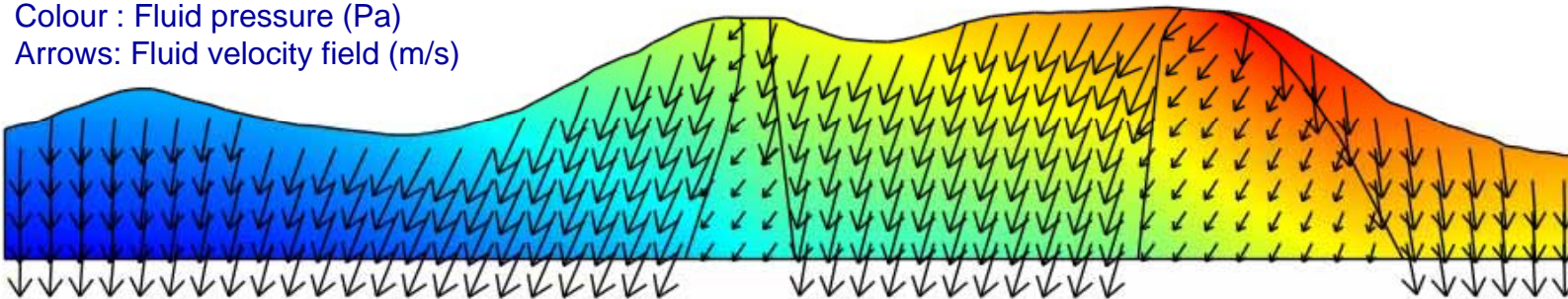
Courtesy of Emile Walker

Colour : Temperature (K)
Arrows: Total heat flux

293.15 - 844.846

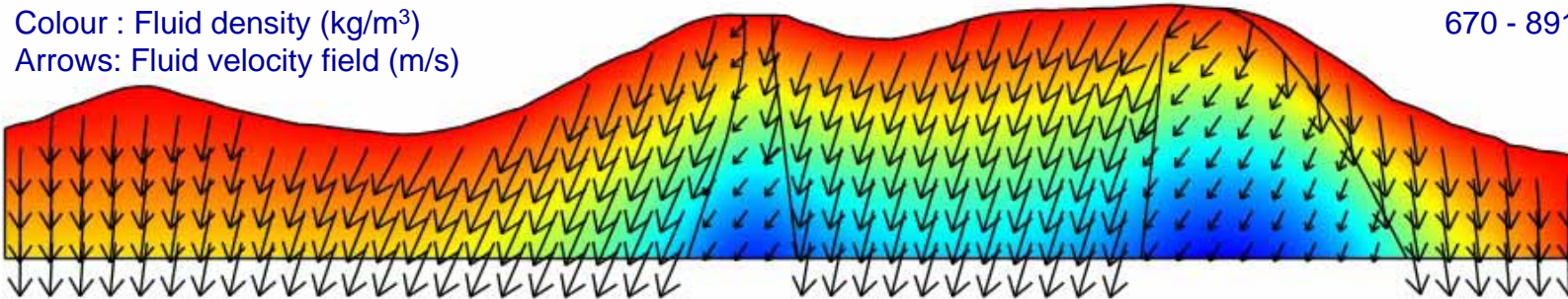


Colour : Fluid pressure (Pa)
Arrows: Fluid velocity field (m/s)



Colour : Fluid density (kg/m³)
Arrows: Fluid velocity field (m/s)

670 - 891



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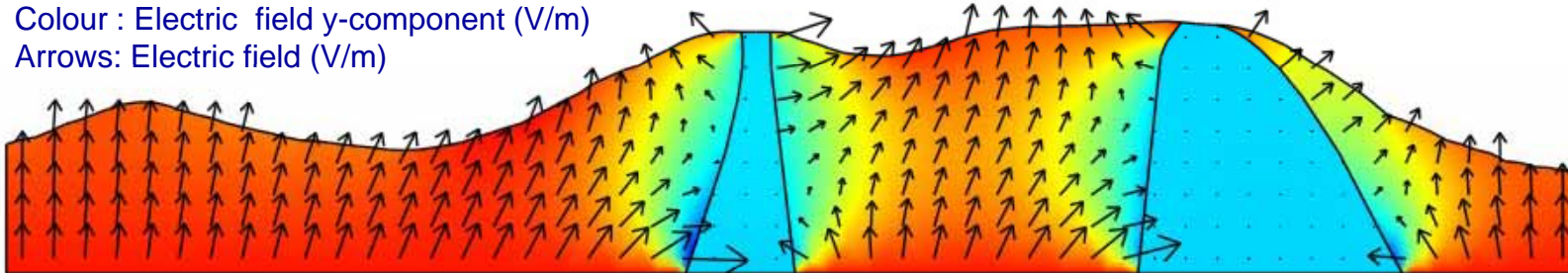
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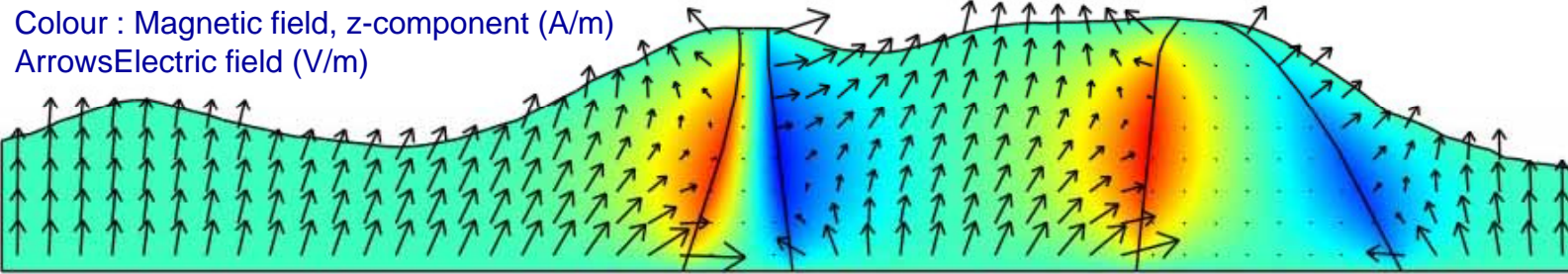
Volcano prediction III

Courtesy of Emile Walker

Colour : Electric field y-component (V/m)
Arrows: Electric field (V/m)



Colour : Magnetic field, z-component (A/m)
Arrows: Electric field (V/m)



Modelling is still at an early stage. Need to develop convective flow.
A map of the electric potential across the surface will then be compared to
The measured SP values.

Time dependent injection of magma will then be modelled
to see the SP values change with time.



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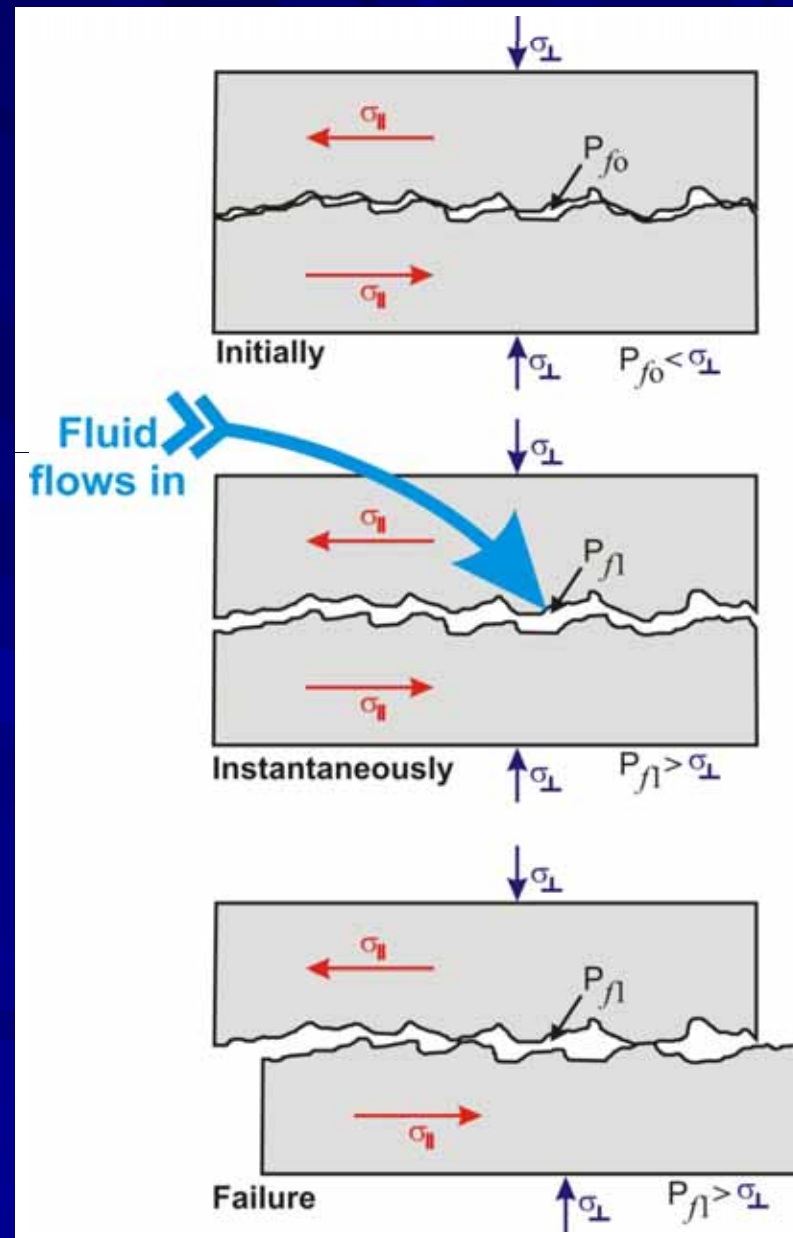
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Applications - Earthquake prediction I

- ❖ Initial fault is submitted to a shear stress
- ❖ However, it is locked
 - by its surface geometry and
 - by the effective stress perpendicular to the fault
- ❖ Fluid flowing into a fault increases the fluid pressure
- ❖ It decreases the effective stress on the fault
- ❖ Unlocks the fault for it to fail
- ❖ Lubricates the faulting process

What causes the fluid flow?
 What can the fluid flow cause?



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Earthquake prediction II

- ❖ The inflow may cause an electrical potential difference hence generating a streaming current and hence a magnetic field by electro-kinetic processes generating electro-magnetic and SP precursors $\Delta P \rightarrow \Delta V$
- ❖ The fluid flow can be caused by electrical potential differences within the crust associated with natural telluric currents induced by ionospheric currents by electro-osmosis $\Delta V \rightarrow \Delta P$
- ❖ The fluid flow may be caused by elastic waves set in motion by other earthquakes

Understanding these links may lead to improvement in our ability to predict the time of earthquakes



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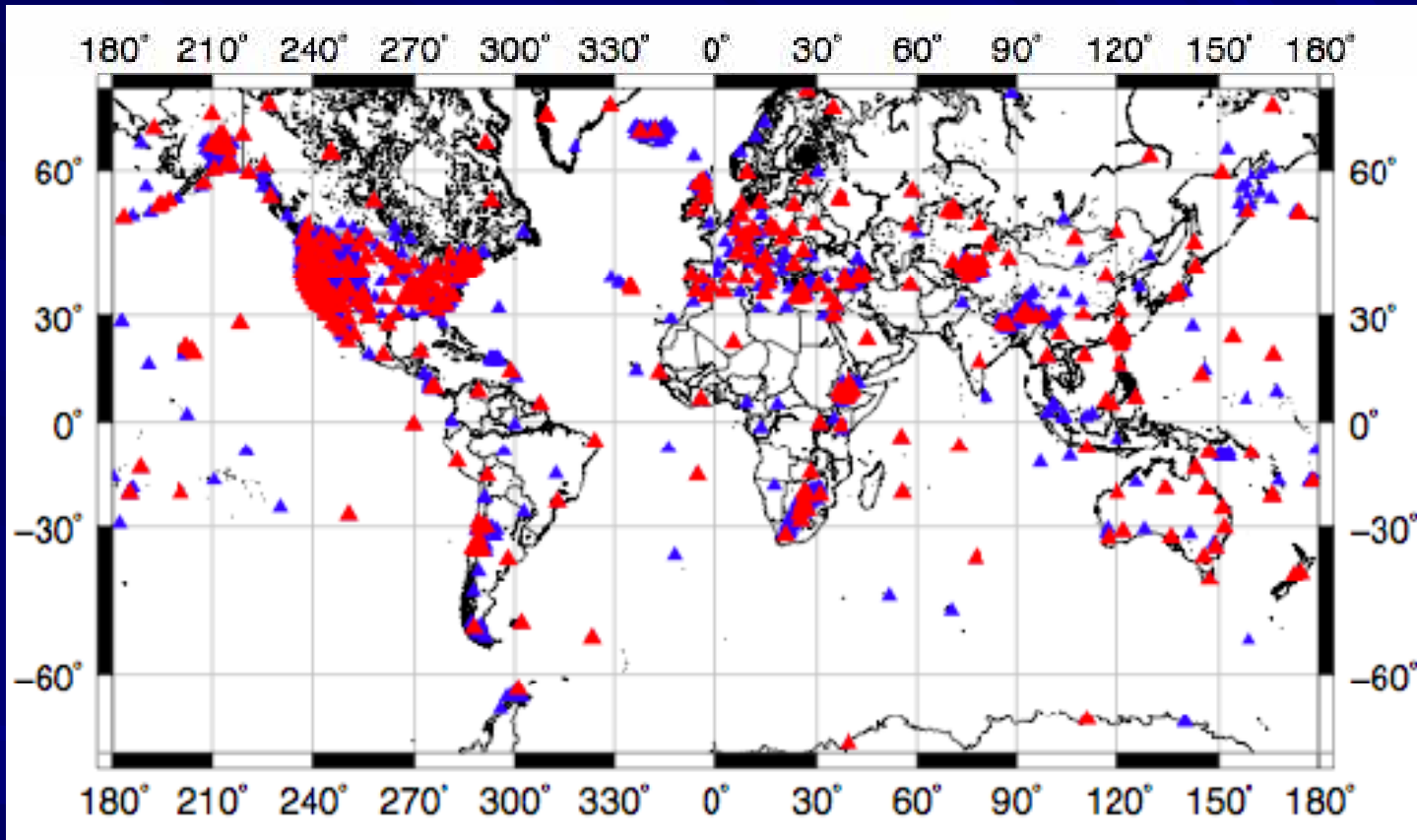
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Earthquake prediction III



Red seismic stations received arrivals from small local earthquakes that was triggered by a large distant earthquake (those in blue did not)
Independent of tectonic province – mediated by surface waves!



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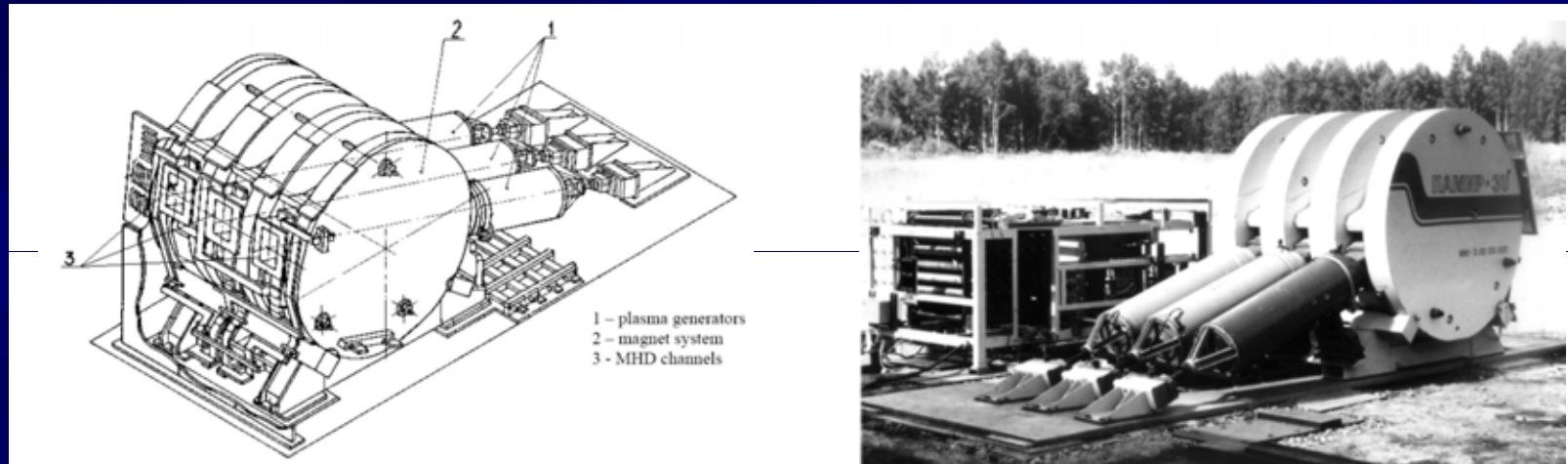
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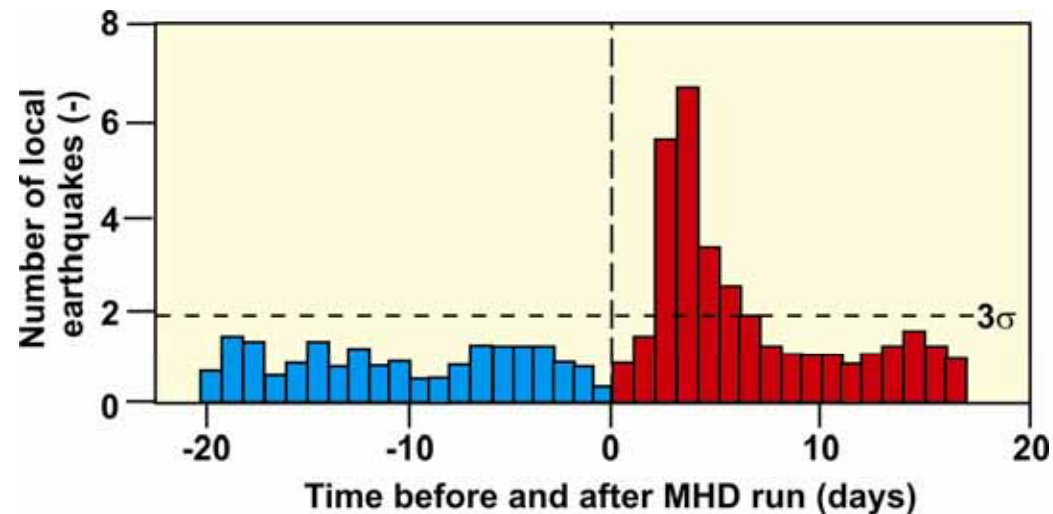
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Synthetic earthquakes I

MHD Generators – The Earthquake machine



Weight 18,000 kg
 Maximum power 15 MW
 Runtime 2 & 7 seconds
 Output 1.5 kA at 1350 V

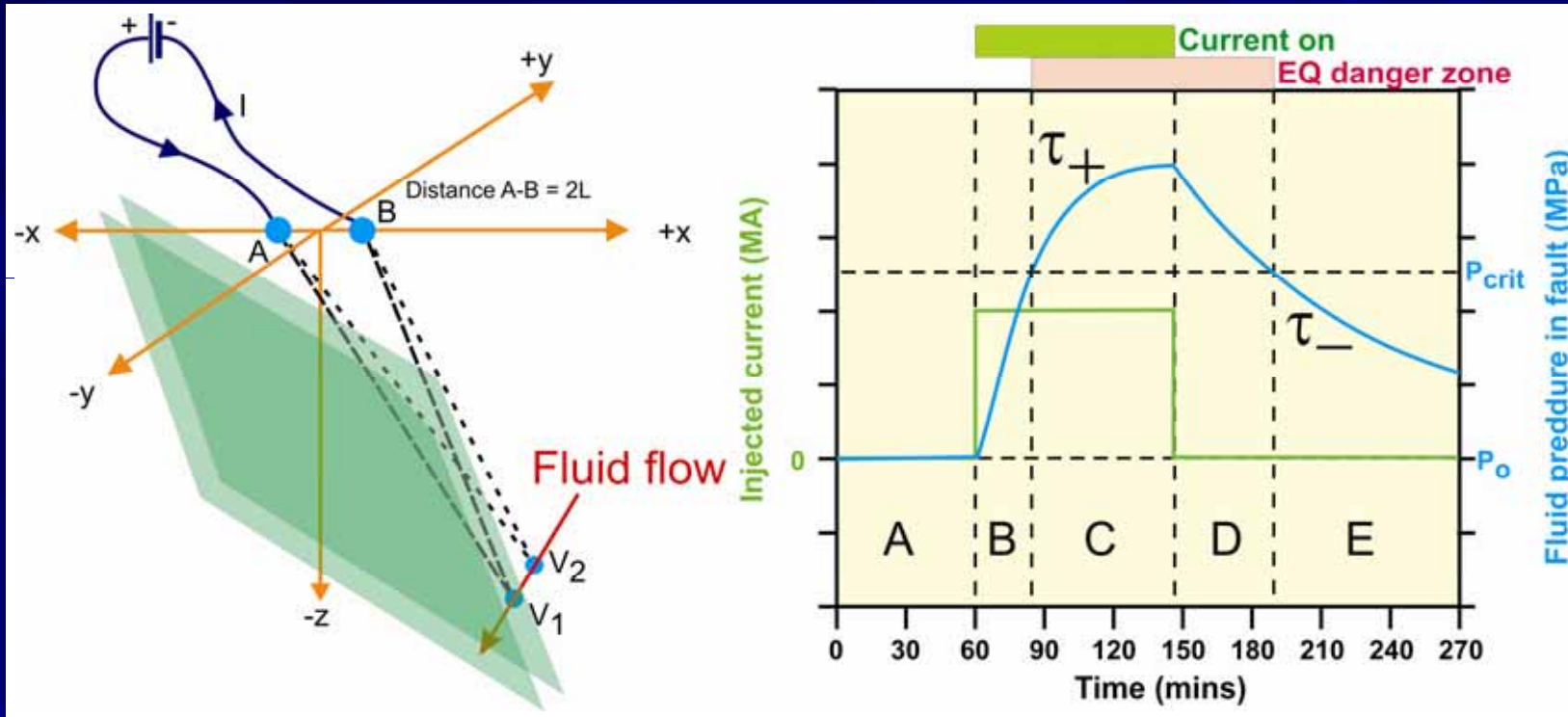



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Synthetic earthquakes II



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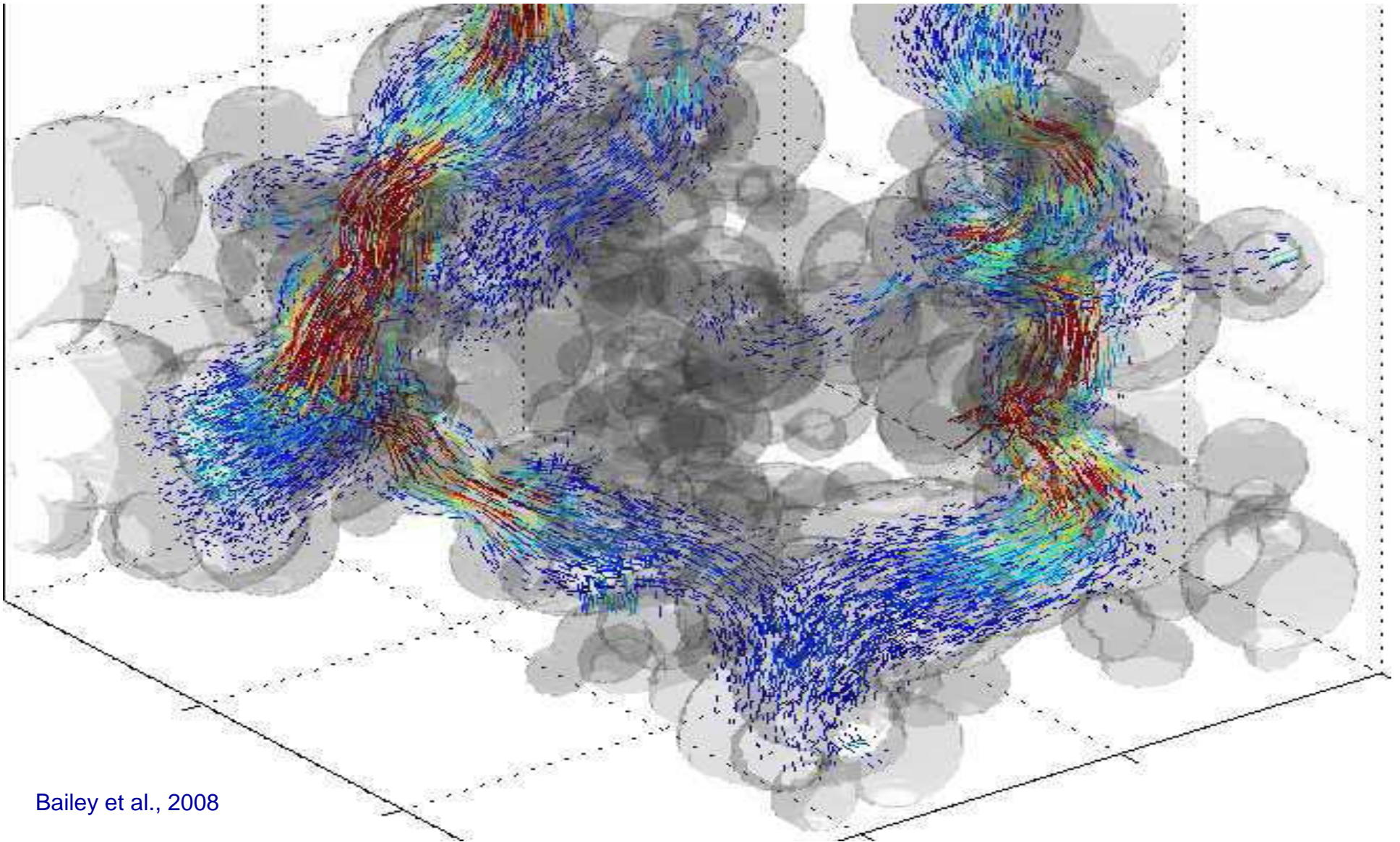
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Fluid flow into the fault reduces the effective pressure, triggering the earthquake

Pressure in the fault increases at one rate and decreases at another. Fracture fluid pressure may be over a critical level for several days after current injection

Conclusions



Bailey et al., 2008

Conclusions I

- ❖ The electro-kinetic and (seismo-electric) phenomena are well understood conceptually and qualitatively
- ❖ Unfortunately we do not have a sufficient database of measurements to fully understand quantitatively these phenomena in rocks
- ❖ Despite this fundamental lack both phenomena have been pressed into practical application



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Conclusions II

- ❖ However, high quality apparatus is being developed in a number of laboratories worldwide
- ❖ Future data should give us a better quantitative basis for the phenomena
- ❖ Applications for the phenomena are huge with a potential market amounting to billions of euros
- ❖ The properties as a function of frequency and saturation are particularly important



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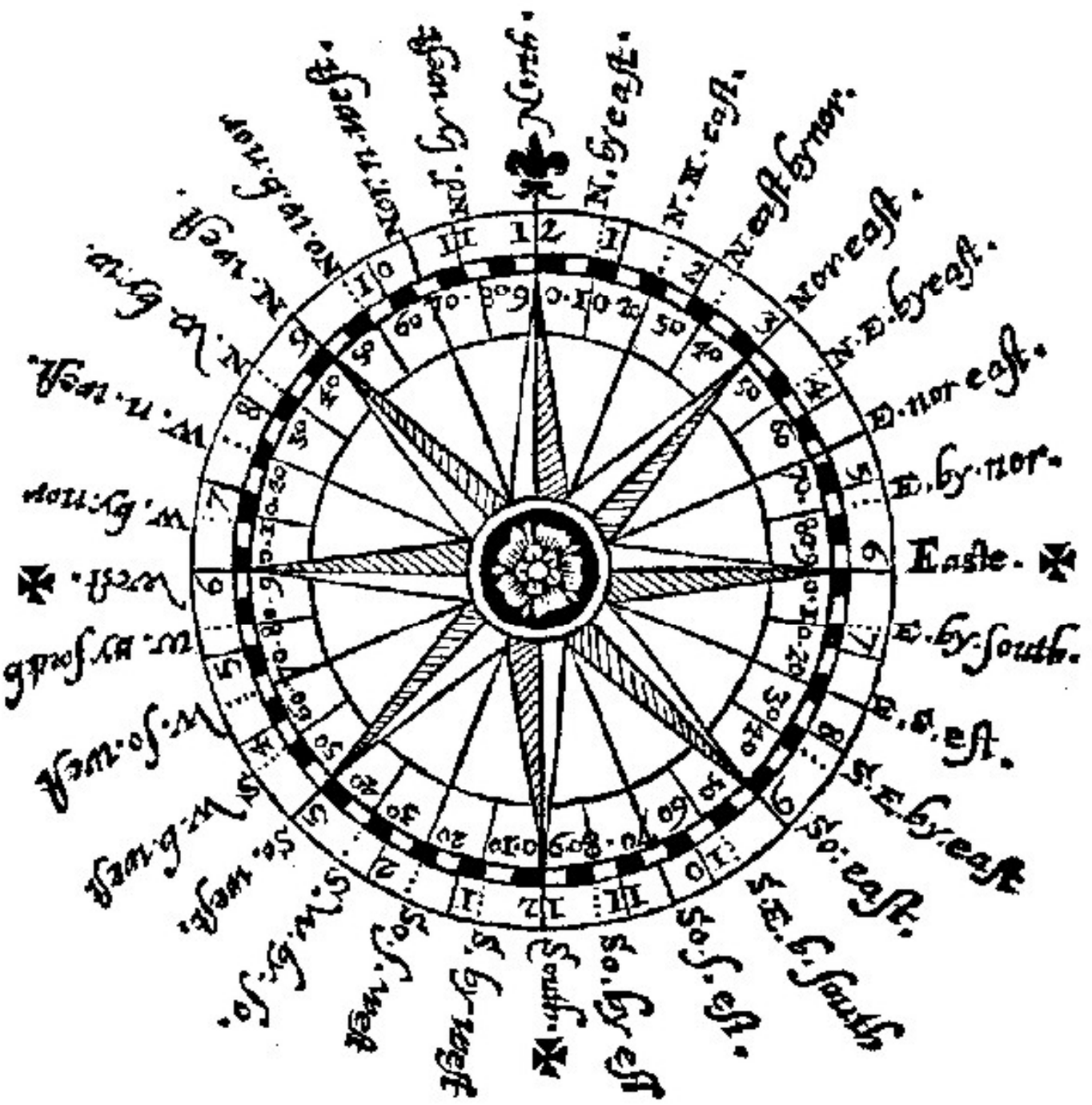
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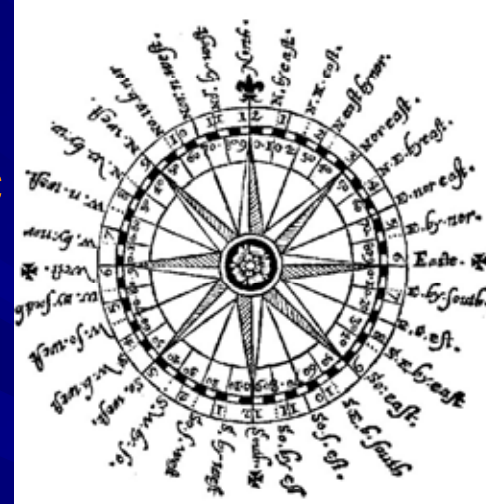
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Future directions

- Development of AC electrical theory in rocks
- Development of AC electro-kinetic and seismo-electric theory
- Better basic measurements made over a large range of rocks and parameters
- Particular importance given to AC measurements and saturation measurements
- Open research with industry
- Ensure applications use the latest developments and data



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