Colorado School of Mines
Department of Geophysics

André Revil

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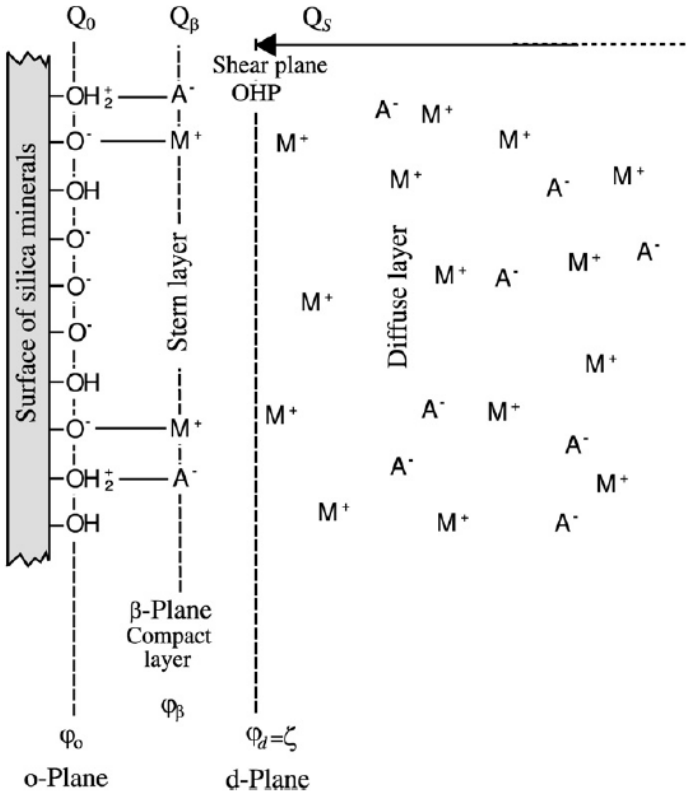
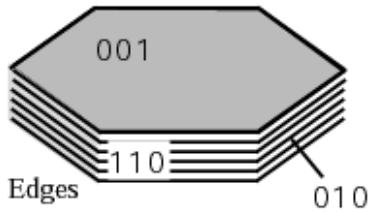
Cross-coupled flows in porous media

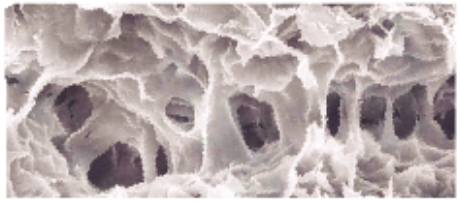


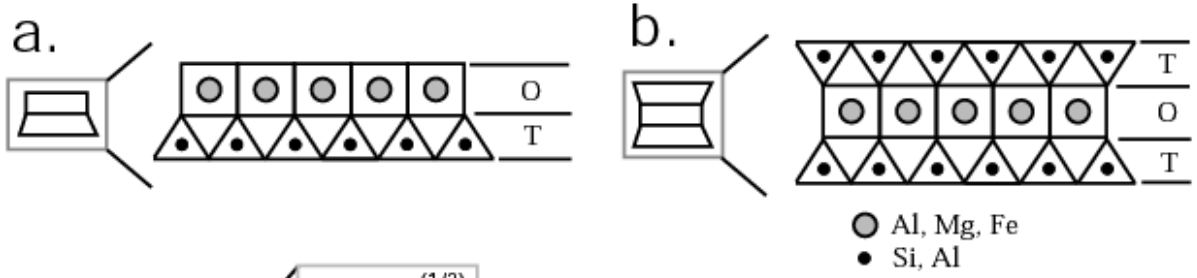
Clay minerals

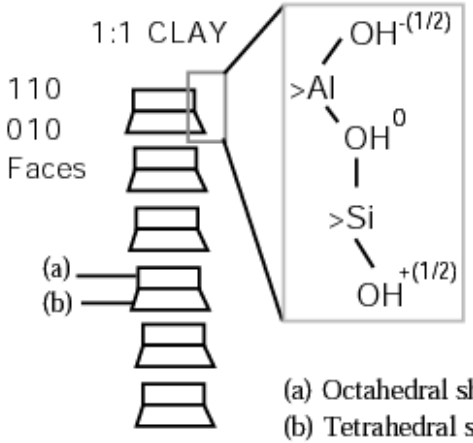
Kaolinite



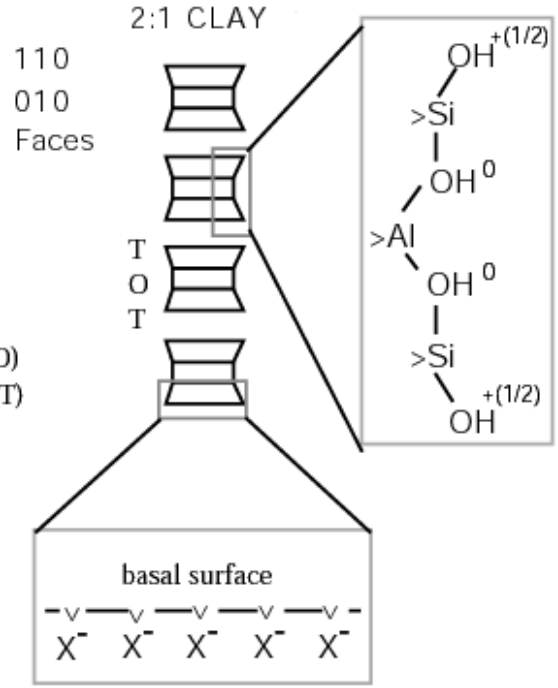
Smectite

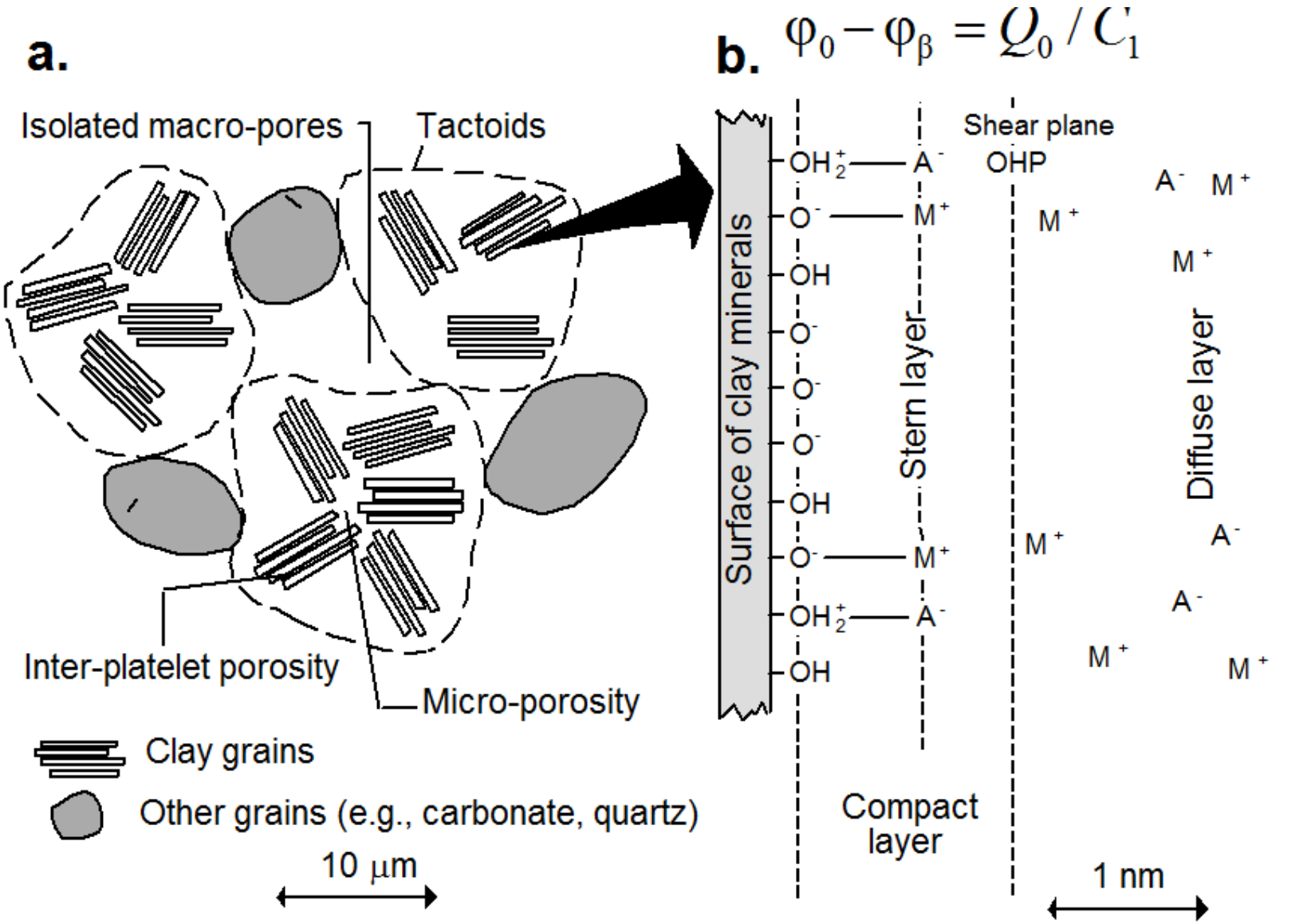






(a) Octahedral sheet (O)
(b) Tetrahedral sheet (T)

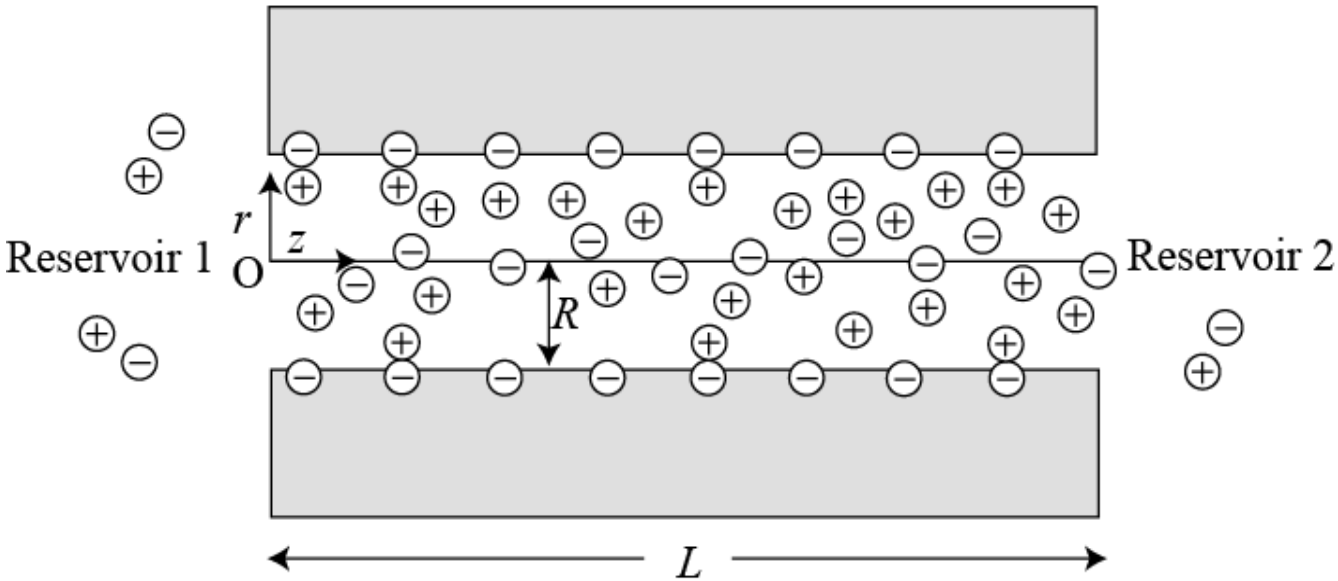




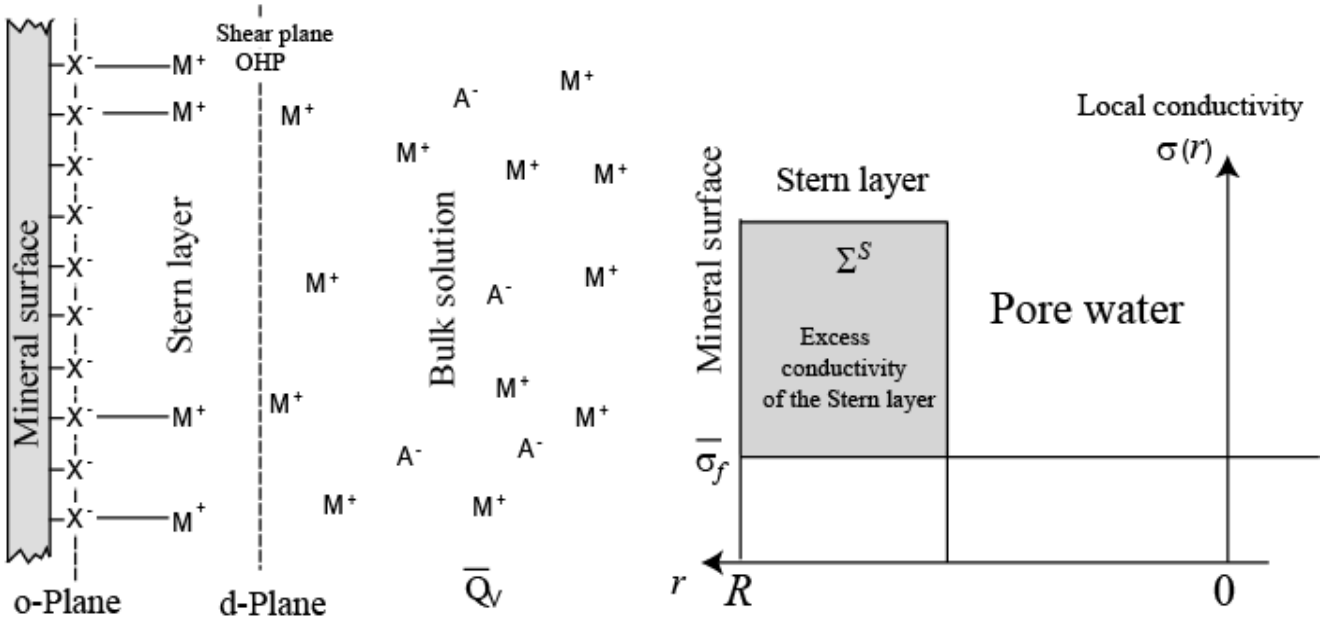
Stern and diffuse layers

Flow in nanopores

a. Sketch of the charged capillary



b. Sketch of the electrical double layer **c. Excess conductivity**



Local equations: 1. The Stokes equation

$$-\bar{C}_w \nabla \mu_w - \bar{C}_{(+)} \nabla \mu_{(+)} - \bar{C}_{(-)} \nabla \mu_{(-)} + \mathbf{F} + \eta \nabla^2 \mathbf{v} = 0$$

$$-\nabla (p - \pi) + \eta \nabla^2 \mathbf{v} + \mathbf{F} - \bar{c}_{(+)} \nabla \mu_{(+)} - \bar{c}_{(-)} \nabla \mu_{(-)} = 0$$

$$\mathbf{F} = \bar{q}_V \mathbf{E}$$ **Bulk force**

$$\mathbf{E} = -\nabla \psi$$ **Quasi-static approximation**

$$\nabla (p - \pi) + \bar{c}_{(+)} \nabla \tilde{\mu}_{(+)} + \bar{c}_{(-)} \nabla \tilde{\mu}_{(-)} = \eta \nabla^2 \mathbf{v}$$

Local Stokes equation with the electrochemical potentials defined as

$$\tilde{\mu}_{(\pm)} = \mu^0_{(\pm)} + k_b T \ln C_{(\pm)} \pm e\psi$$

A note on the osmotic pressure

In the reservoirs

$$\pi = -k_b T \ln C_w$$

$$\mu_w = \mu_w^0 + \Omega_w p + k_b T \ln C_w$$

In the pore space

$$\bar{\pi} = -k_b T \ln \bar{C}_w$$

$$\bar{\mu}_w = \mu_w^0 + \Omega_w \bar{p} + k_b T \ln \bar{C}_w$$

Local equilibrium condition

$$\bar{\mu}_w = \mu_w$$

$$\bar{p} = p - (\pi - \bar{\pi})$$

Osmotic pressure difference

$$\delta\pi = \pi - \bar{\pi} = -\frac{k_b T}{\Omega_w} \ln\left(\frac{C_w}{\bar{C}_w}\right)$$

$$\delta\pi \approx -k_b T \left(\bar{C}_{(+)} + \bar{C}_{(-)} - 2C_f\right)$$

van't Hoff [1888] equation

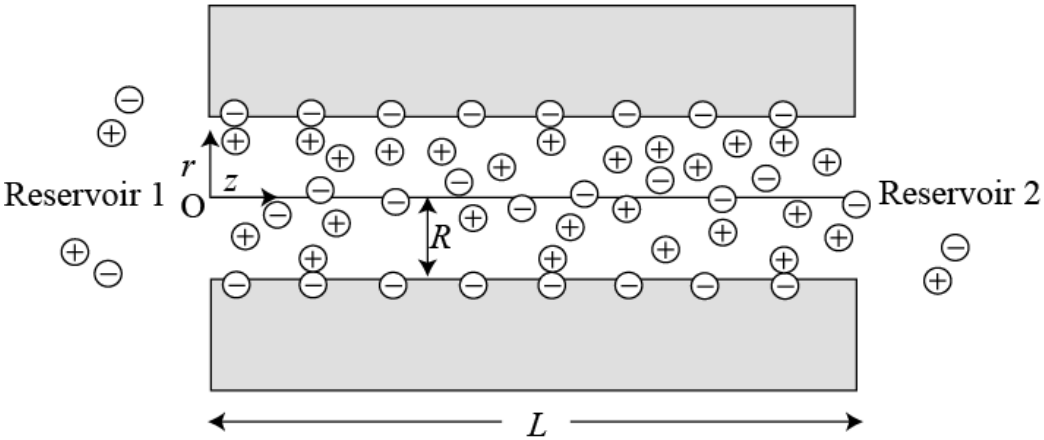
$$\pi = 2C_f k_b T$$

$$\bar{\pi} = k_b T \left(\bar{C}_{(+)} + \bar{C}_{(-)}\right)$$

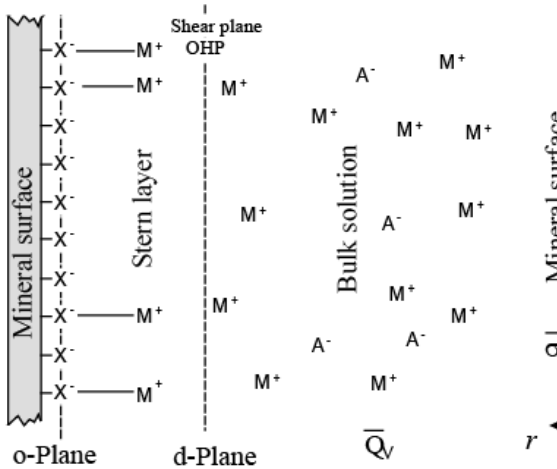
$$\mathbf{v} = \mathbf{v}_m + \mathbf{v}_e + \mathbf{v}_c$$

Total velocity = Mechanical + electroosmotic + chemio-osmotic

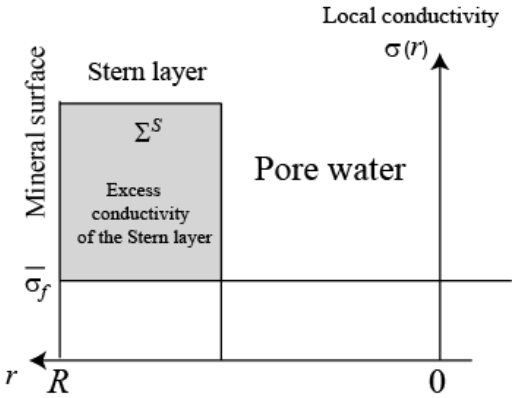
a. Sketch of the charged capillary



b. Sketch of the electrical double layer



c. Excess conductivity

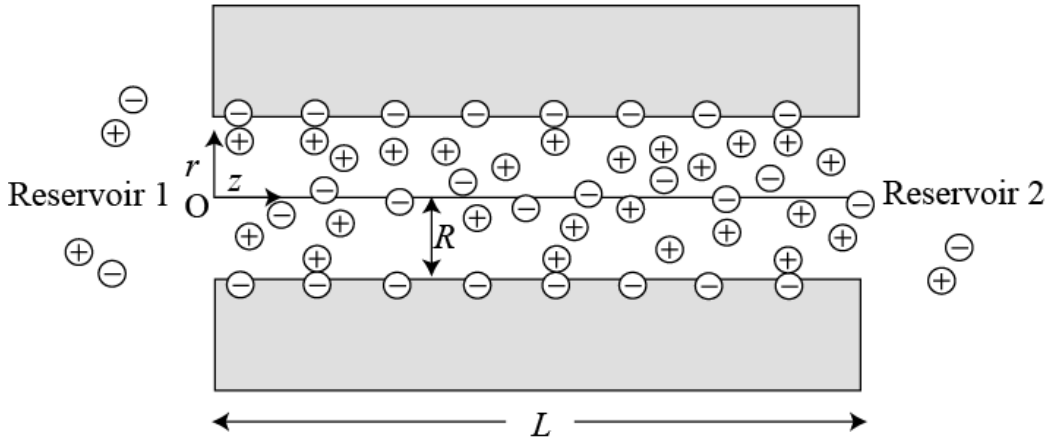


Local equations: 2. The Nernst-Planck equation

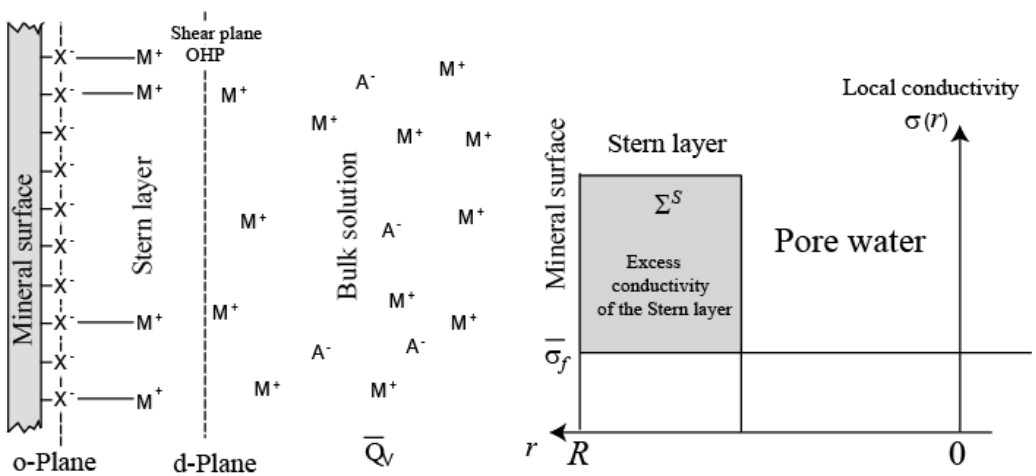
$$\mathbf{j}_{(\pm)} = -b_{(\pm)}\bar{c}_{(\pm)}\nabla\tilde{\mu}_{(\pm)} - b^{S}_{(\pm)}\Gamma_{(\pm)}\nabla\tilde{\mu}^{S}_{(\pm)}\delta(r-R) + \bar{c}_{(\pm)}\mathbf{v}_m$$

$$\nabla\tilde{\mu}^{S}_{(\pm)} = \nabla\tilde{\mu}_{(\pm)}$$

a. Sketch of the charged capillary



b. Sketch of the electrical double layer **c. Excess conductivity**



A note on the surface transport

$$>\mathrm{SO}^- + \mathrm{M}^+ \overset{K_{(+)}}{\Leftrightarrow} >\mathrm{SO}^-\mathrm{M}^+$$

$$>\mathrm{SOH}_2^+ + \mathrm{A}^- \overset{K_{(-)}}{\Leftrightarrow} >\mathrm{SOH}_2^+\mathrm{A}^-$$

$$K_{(+)} = \frac{\Gamma_{(+)}}{\Gamma^0_{(-)} C_{(+)} \exp\left(-\frac{e\varphi_d}{k_b T}\right)}$$

$$K_{(-)} = \frac{\Gamma_{(-)}}{\Gamma^0_{(+)} C_{(-)} \exp\left(\frac{e\varphi_d}{k_b T}\right)}$$

Surface flux densities

$$\mathbf{j}_{(\pm)} = -b^S_{(\pm)} \Gamma_{(\pm)} \nabla_S \tilde{\mu}^S_{(\pm)}$$

$$\mathbf{j}_{(\pm)} = -b^S_{(\pm)} \Gamma_{(\pm)} (\pm e) \nabla_S \psi - k_b T b^S_{(\pm)} \Gamma_{(\pm)} \nabla_S \ln \Gamma_{(\pm)}$$

This implies:

$$\nabla_S \ln \Gamma_{(\pm)} = \nabla_S \ln C_{(\pm)}$$

In conclusion:

$$\mathbf{j}_{(\pm)} = -b^S_{(\pm)} \Gamma_{(\pm)} (\pm e) \nabla \psi - k_b T b^S_{(\pm)} \Gamma_{(\pm)} \nabla \ln C_{(\pm)}$$

$$\mathbf{j}_{(\pm)} = -b^S_{(\pm)} \Gamma_{(\pm)} \nabla \tilde{\mu}_{(\pm)}$$

3. Inclusion of the pore size distribution in the upscaling process

$g(R)$ probability density to have a capillary with a radius comprised between R and $R + dR$.

(e.g., through NMR calculations)

$$\int_0^\infty g(R)dR = 1$$

Raw moments of the probability distribution

$$\Pi_n = \int_0^\infty R^n g(R)dR$$

For instance $$\Pi_{-1} = \int_0^\infty R^{-1} g(R)dR = \int_0^\infty g(R)d\ln R$$

$$\Pi_0 = \int_0^\infty g(R)dR = 1$$

$$\Pi_1 = \int_0^\infty R\ g(R)dR$$

For a bundle of capillaries, the porosity, the excess of charge and the mean concentrations in the bulk pore space

,

$$\phi = \frac{n\pi}{A}\Pi_2$$

$$\bar{Q}_V = -2Q_S\Pi_{-1}$$

$$\bar{C}_{(\pm)} = C_f\left(\sqrt{1+\Theta^2} \pm \Theta\right)$$

with the dimensionless parameter Θ defined by,

$$\boxed{\Theta \equiv \frac{Q_S}{eC_f}\Pi_{-1}}$$

$$\Theta \equiv \frac{10^{-3}(1-f_Q)}{2C_f}\rho_g\left(\frac{1-\phi}{\phi}\right)\mathrm{CEC}$$

Key dimensionless variable of the problem

Methodology

1) Local equation and external and internal bounadry conditions

2) Surface average to get the total flux of a single capillary

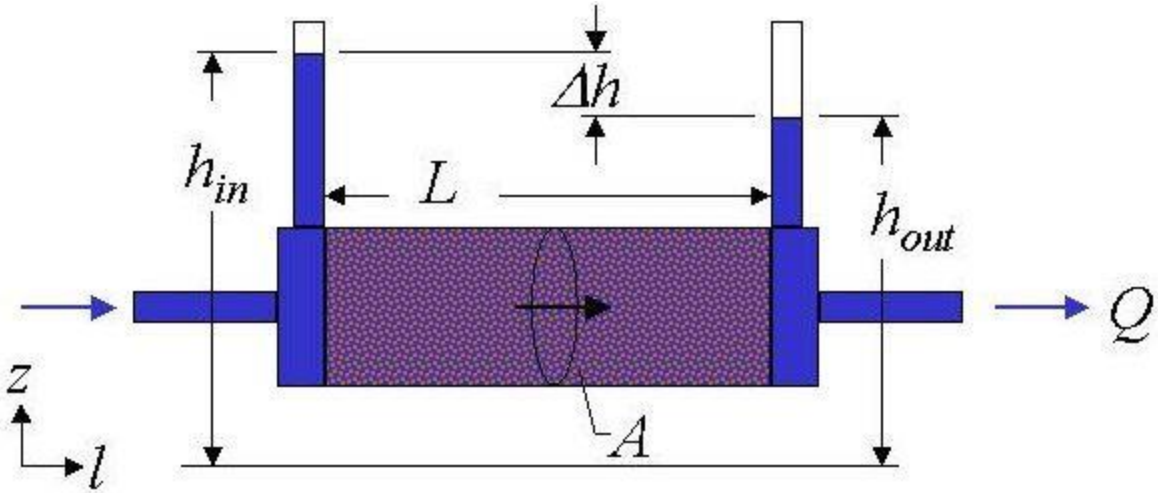
3) Collection of *n* capillaries: total flux

4) Getting the flux density by dividing by the cross section area

Darcy is not dead ! Heros don't die, they become legends

H. Darcy, Les Fontaines Publiques de la Ville de Dijon, Dalmont, Paris (1856).

Henry Philibert Gaspard Darcy (June 10, 1803 – January 3, 1858) was a French engineer who made several important contributions to hydraulics .



Constitutive equation of flow in porous materials

4. Macroscopic constitutive equations

Extending Darcy's law

$$\begin{bmatrix} 2\mathbf{J}_d \\ \mathbf{J} \\ \mathbf{U} \end{bmatrix} = -\bar{\bar{\mathbf{M}}} \begin{bmatrix} \nabla \mu_f \\ \nabla \psi \\ \nabla (p - \pi) \end{bmatrix}$$

Matrix of material properties

$$\bar{\bar{\mathbf{M}}} = \begin{bmatrix} \dfrac{\sigma}{e^2} & \dfrac{1}{2}\left(\sigma_{(+)} - \sigma_{(-)}\right) & \dfrac{k}{\eta}\left(\bar{C}_{(+)} + \bar{C}_{(-)}\right) \\ \dfrac{1}{2}\left(\sigma_{(+)} - \sigma_{(-)}\right) & \sigma & \dfrac{k}{\eta}\bar{Q}_V \\ \dfrac{k}{\eta}\left(\bar{C}_{(+)} + \bar{C}_{(-)}\right) & \dfrac{k}{\eta}\bar{Q}_V & \dfrac{k}{\eta} \end{bmatrix}$$

Where the conductivity contributions are given by,

$$\sigma_{(\pm)} = \frac{1}{F}\left(e\beta_{(\pm)}\bar{C}_{(\pm)} + 2\Pi_{-1} e\beta^S_{(\pm)}\Gamma_{(\pm)}\right)$$

5. Application to the Callovo-Oxfordian Argillite

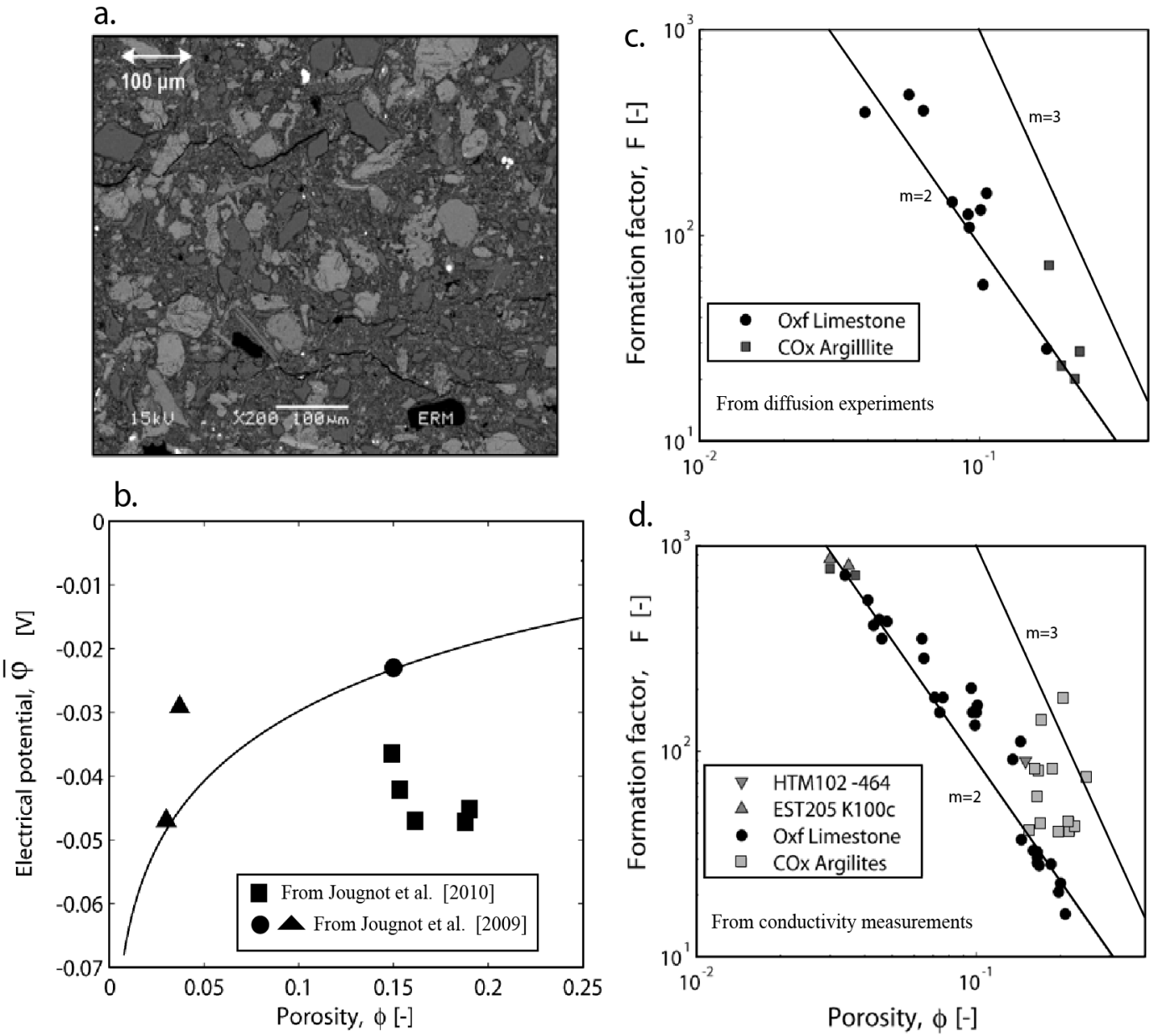
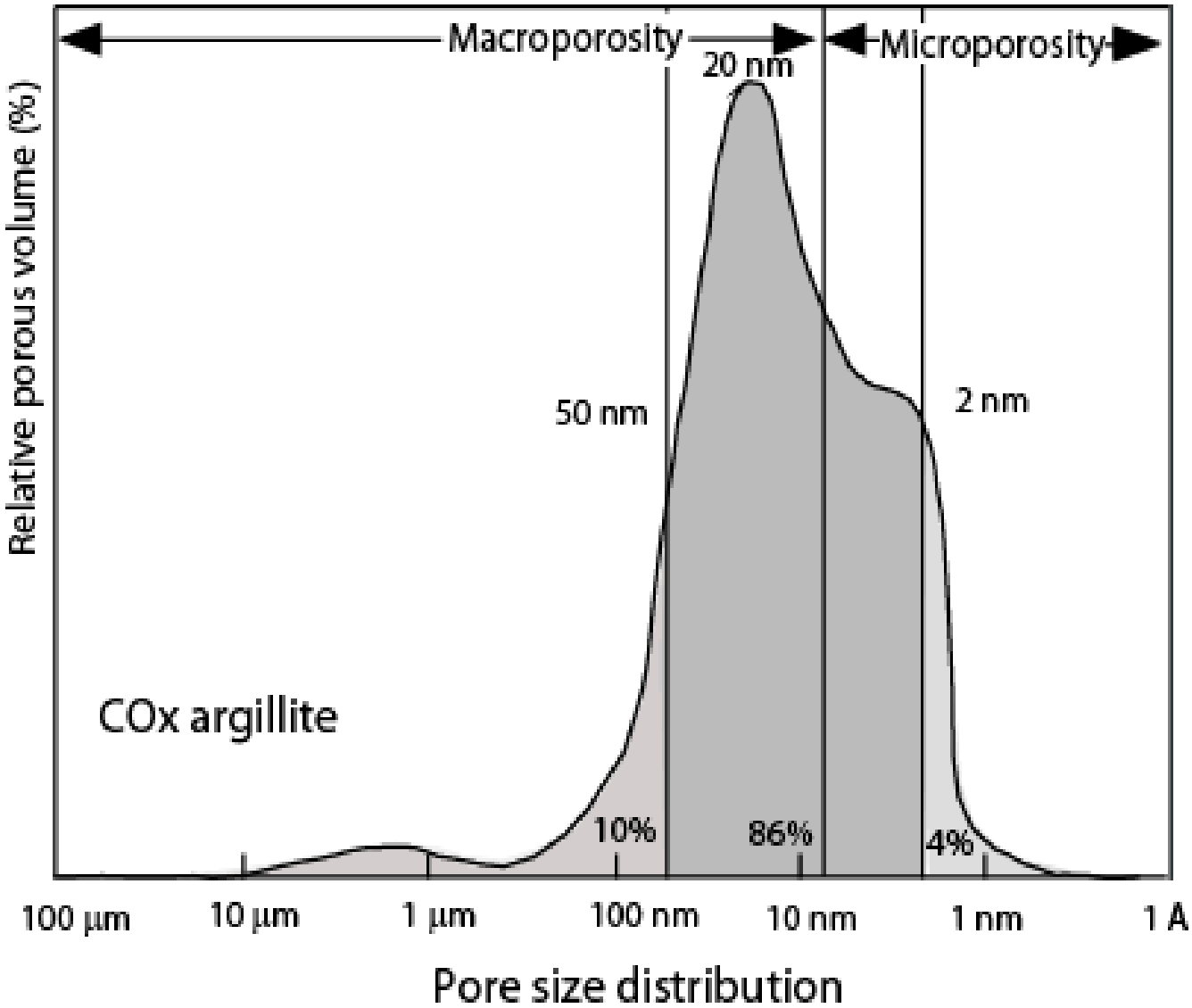


Table 1. Material Properties of the COx clay-rock.

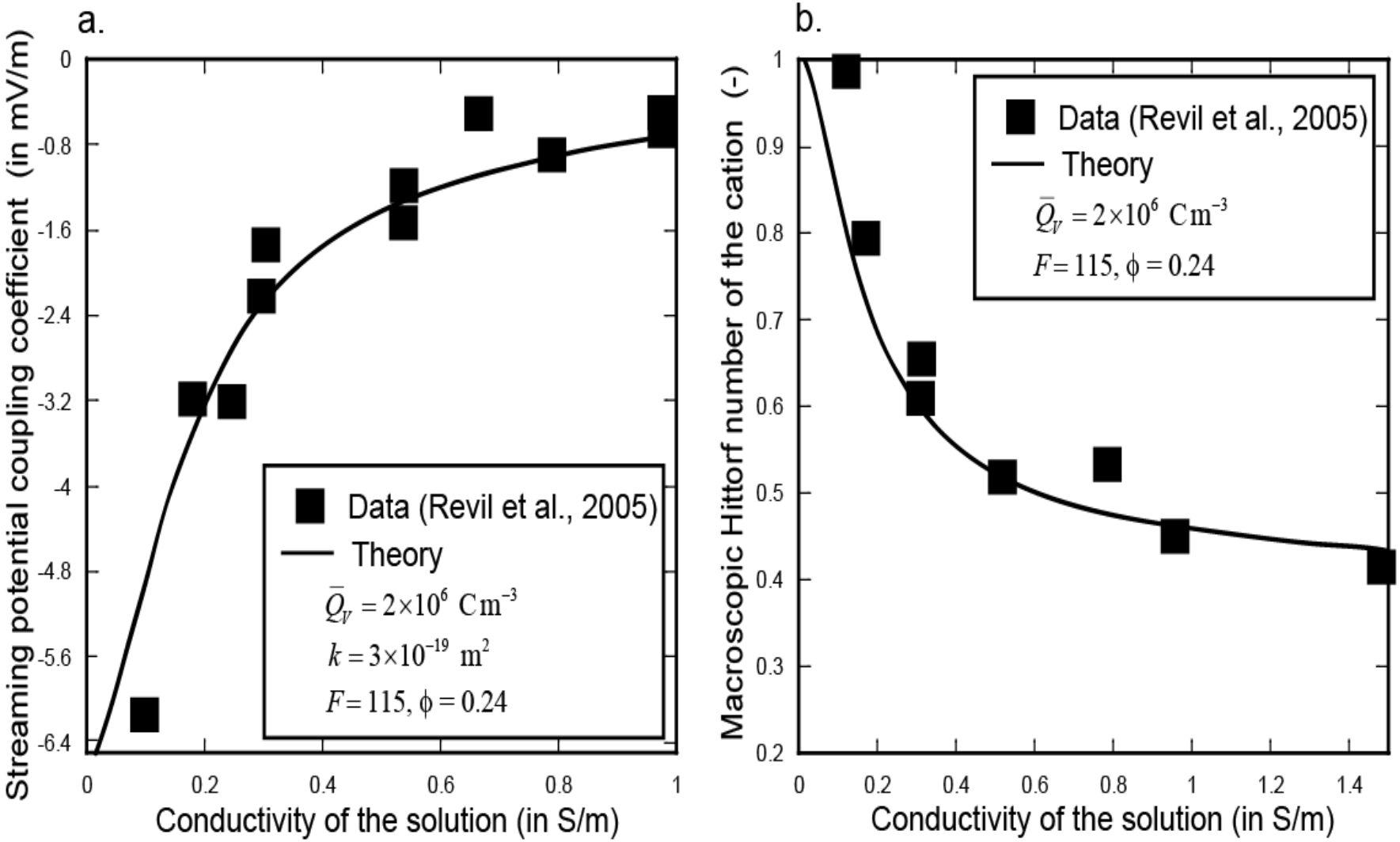
Symbol	Meaning	Value
$\bar{\varphi}$	Mean pore electrical potential	-40±10 mV (a)
m	Cementation exponent	2.5±0.5 (a),
ϕ	Connected porosity	0.15±0.08 (e)
log k	Log permeability	-20 ± 1 (b)
CEC	Cation exchange capacity	0.18±0.08 Mol kg^{-1} (c)
ρ_g	Grains mass density	2700±50 kg m^{-3} (c)
S_{sp}	Specific surface area	5×10^4 m^2 kg^{-1} (d)

(a) Jougnot et al. [2009].
(b) Distinguin and Lavanchy [2007] and Rousseau-Gueutin et al. [2010].
(c) Leroy et al. [2007].
(d) Gaucher et al. [2004]. The confidence interval is not known.
(e) Descostes et al. [2008].

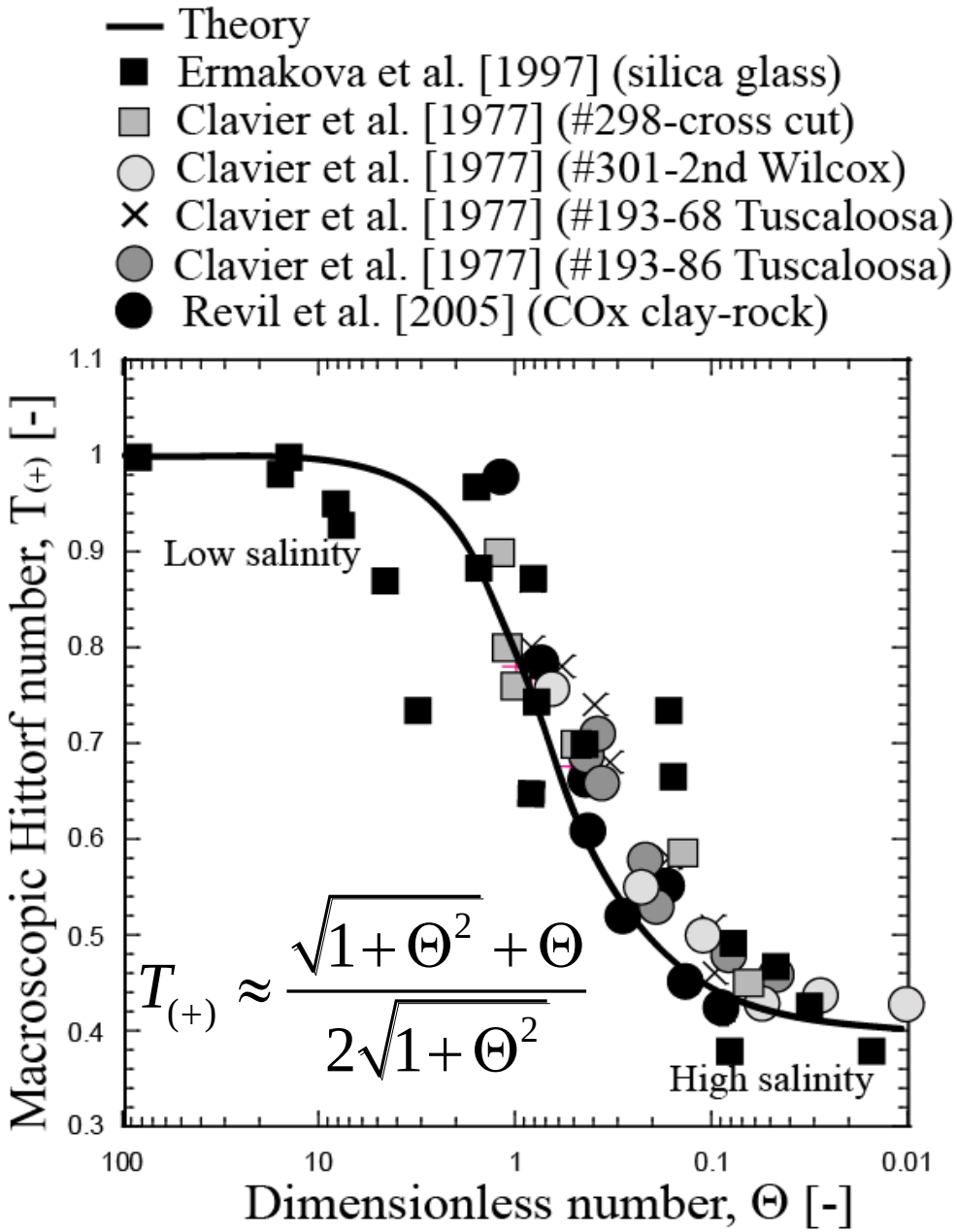
Pore size distribution



Prediction of the streaming coupling coefficient and Hittorf number

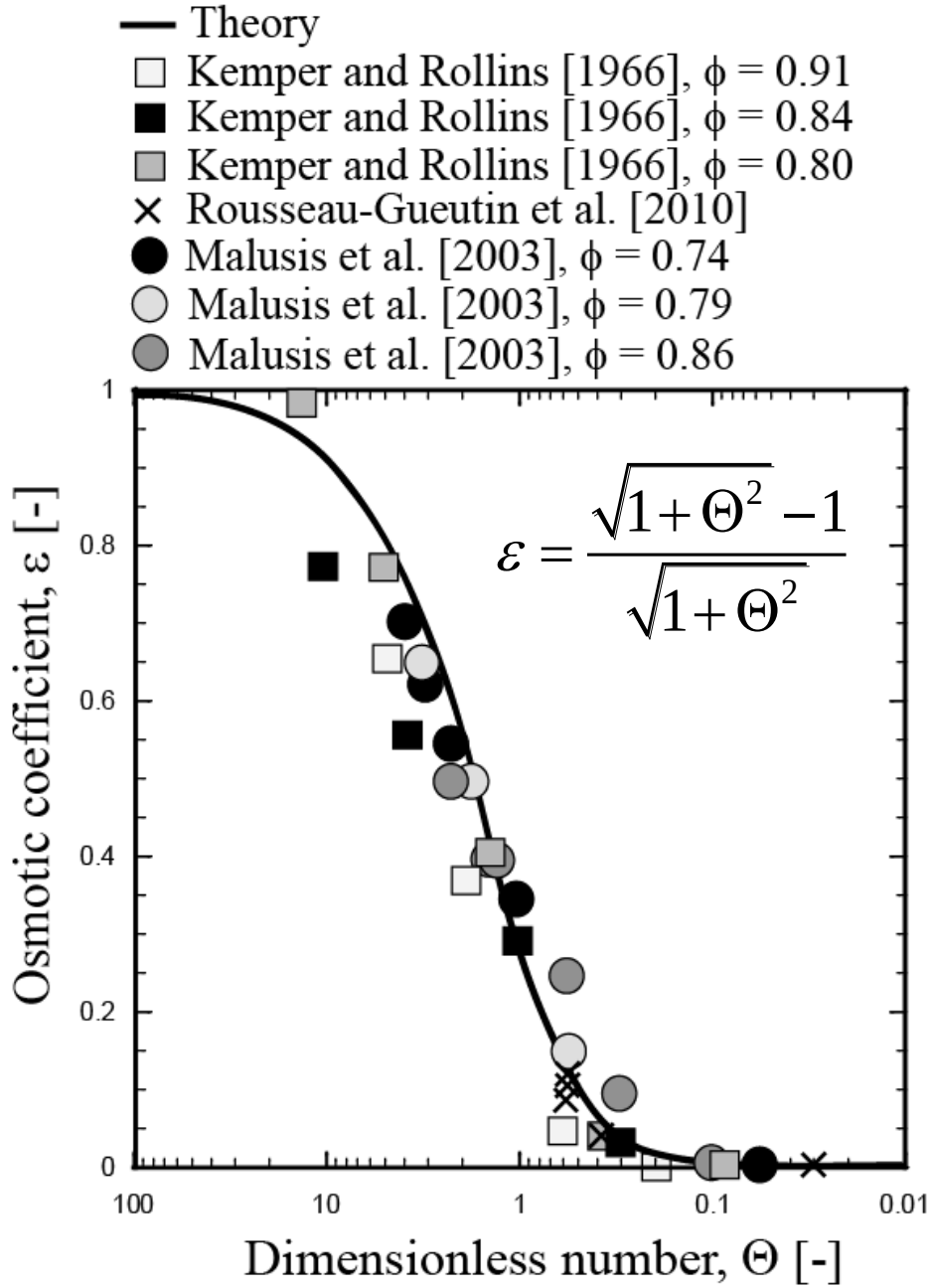


Prediction of the Hittorf number

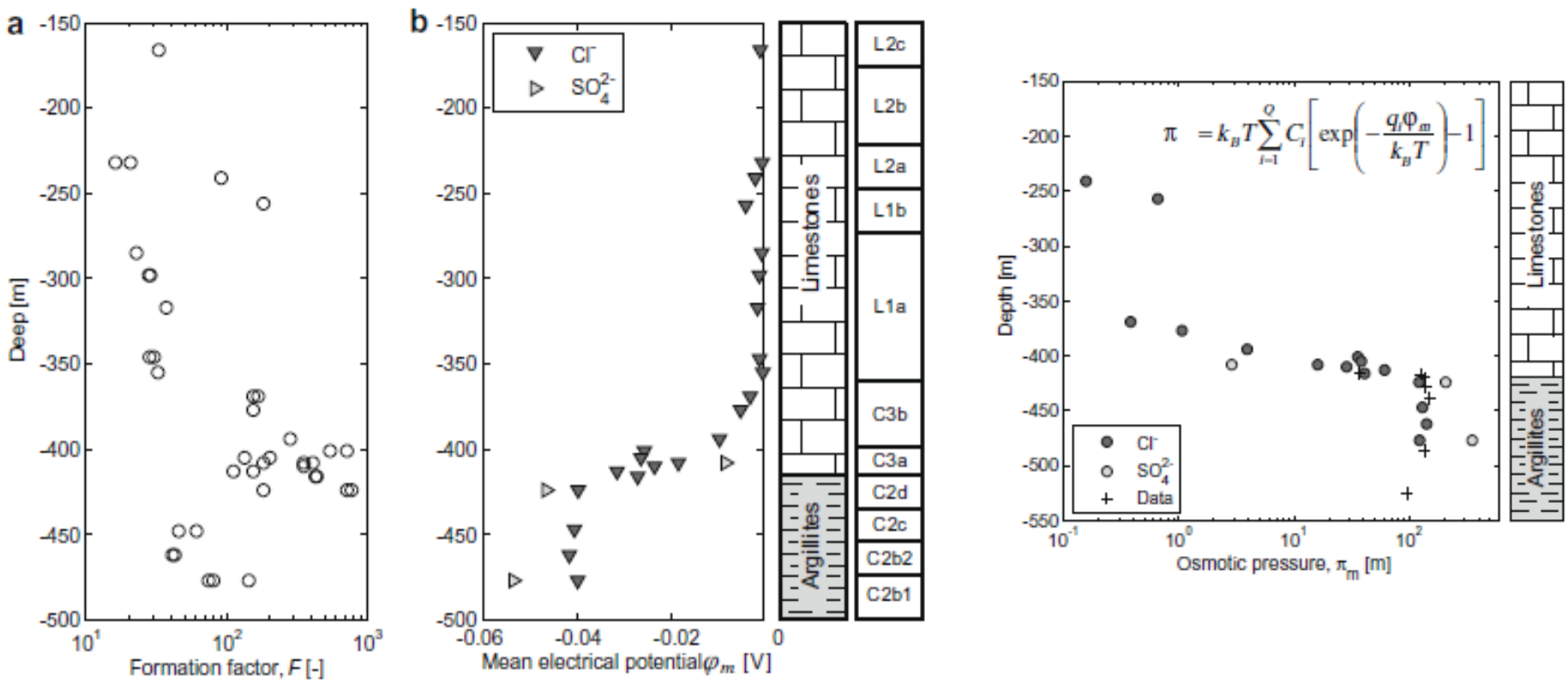


$$T_{(+)} \approx \frac{\sqrt{1+\Theta^2}+\Theta}{2\sqrt{1+\Theta^2}}$$

Prediction of the osmotic coefficient



Osmotic pressure in the field



Hydraulic and chemical pulse tests in a shut-in chamber imbedded in an argillaceous formation: Numerical and experimental approaches

P. Rousseau-Gueutin,[1,2,3] J. Gonçalvès,[1] M. Cruchaudet,[4] G. de Marsily,[1] and S. Violette[1]