



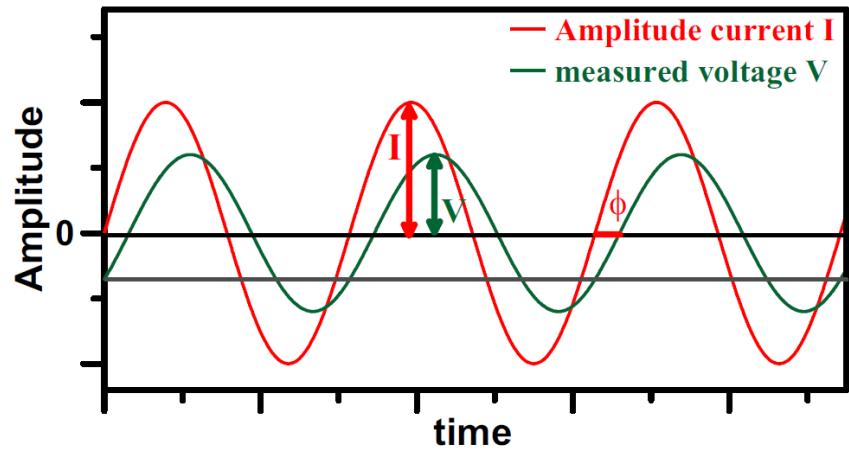
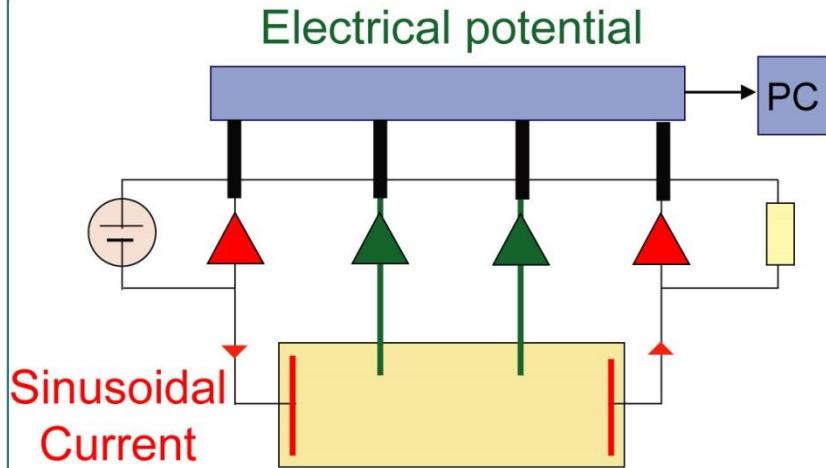
Modeling the evolution of spectral induced polarization during calcite precipitation on glass beads

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Complex conductivity in frequency or spectral induced polarization (SIP)

- > Sinusoidal electrical current injected.
Electrical potential difference measured.

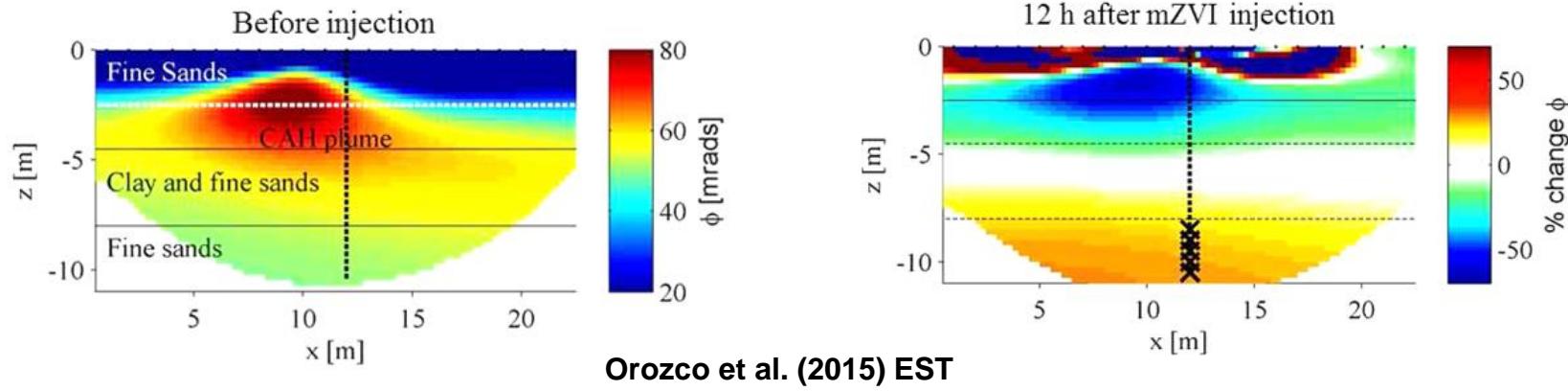


Thesis A. Ghorbani (2007)
Pierre and Marie Curie University

- > Phase shift between imposed current and measured voltage.
- > Method sensitive to conduction and polarization currents at the solid/water interface and inside conductive metals.

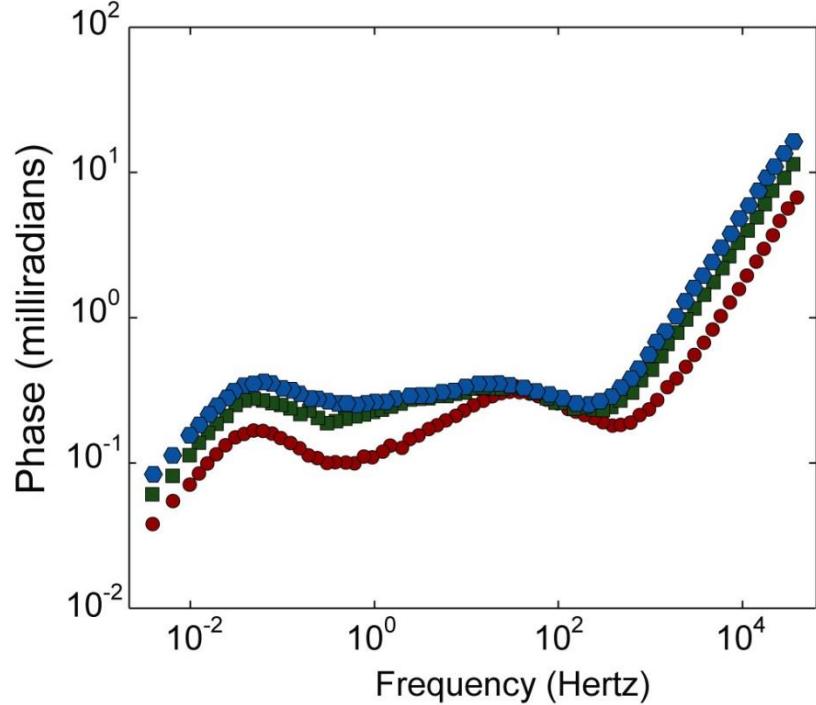
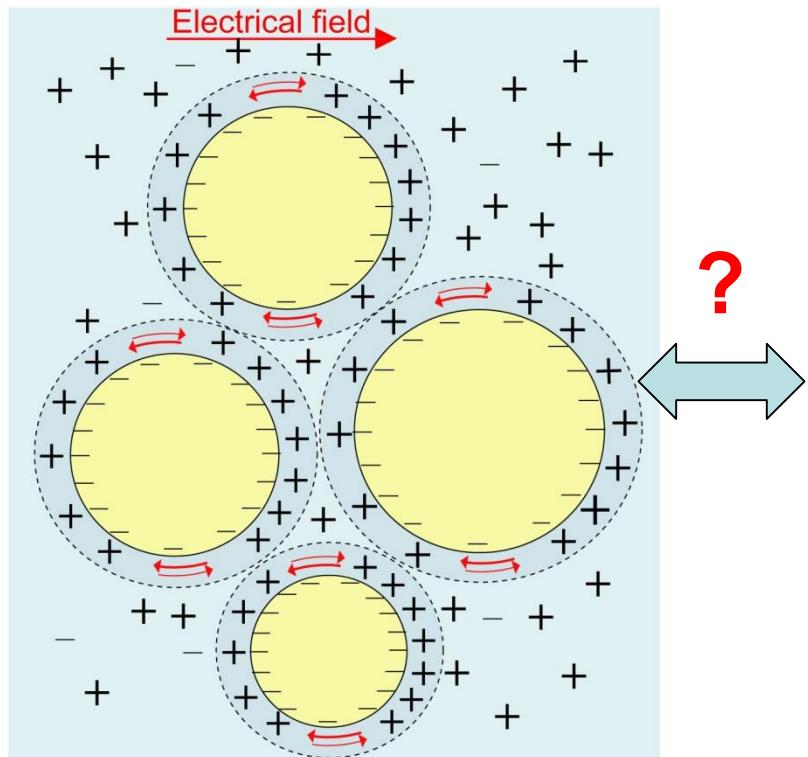
Complex conductivity (CC)

- > Method developed initially for the mining exploration because of its sensitivity to conduction and polarization currents in conductive metals.
- > High increase of the accuracy of CC measurements, inversion and interpretation during the last decades.
 - ➡ Application of the CC method in hydrogeophysics to estimate for instance the transport properties of porous media for environmental and hydrogeological investigations.
- > Example: monitoring remediation of groundwaters contaminated by organic pollutants using zero valent iron microparticles.



Grain polarization model

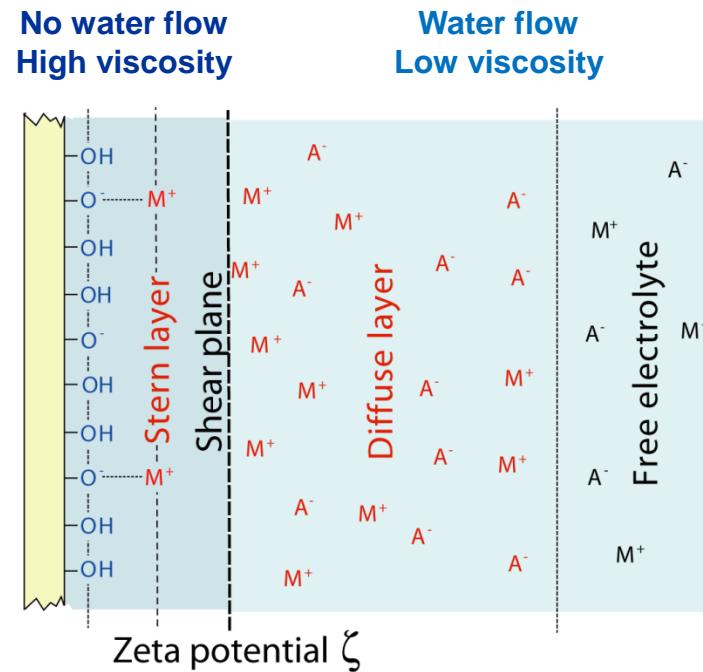
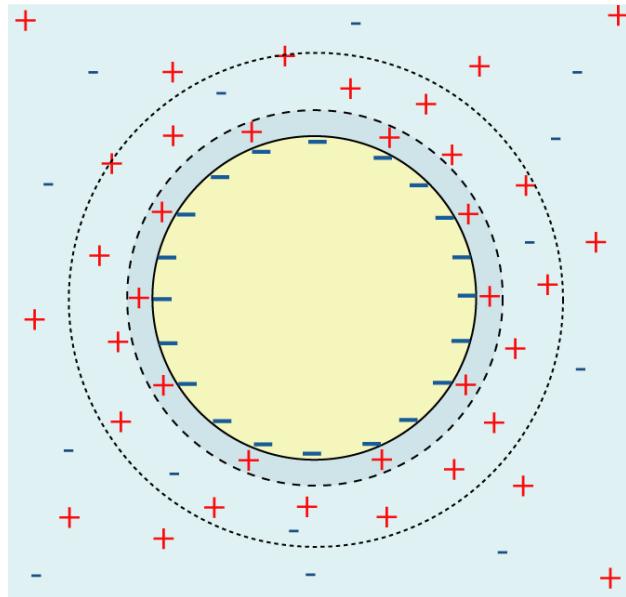
- However, frequency behavior of SIP spectra still not exactly known.



- Necessity to develop mechanistic SIP models describing key transport phenomena at the pore scale responsible for the measured SIP response.
- Grain polarization model applied to calcite precipitation in porous media.

Electrical double layer around calcite

- > Surface charge of the calcite particle in water due to:
 - calcium surface sites $\text{>} \text{Ca-OH}^{-0.5}$
 - carbonate surface sites $\text{>} \text{CO}_3^{-0.5}$
- > Surface charge compensated by:
 - adsorbed counter-ions at the Stern,
 - adsorbed counter-ions and co-ions in the diffuse layer.
- > Assumed shear plane at the beginning of the diffuse layer.



Triple layer model (TLM) of calcite (1)

> Stoichiometric matrix of aqueous and surface reactions

Product species	H^+	Cl^-	Na^+	Ca^{2+}	HCO_3^-	$>\text{CaOH}^{-0.5}$	$>\text{CO}_3^{-0.5}$	$e^{\frac{-e\Phi_0}{k_b T}}$	$e^{\frac{-e\Phi_\beta}{k_b T}}$	$\log_{10} K$
CO_3^{2-}	-1	0	0	0	1	0	0	0	0	-10.33
H_2CO_3	1	0	0	0	1	0	0	0	0	6.35
CaHCO_3^+	0	0	0	1	1	0	0	0	0	1.11
$\text{CaCO}_3(\text{aq})$	-1	0	0	1	1	0	0	0	0	-7.10
CaOH^+	-1	0	0	1	0	0	0	0	0	-12.78
$>\text{CaOH}_2^{+0.5}$	1	0	0	0	0	1	0	1	0	0.50
$>\text{CaOH}_2^{+0.5} \cdots \text{Cl}^-$	1	1	0	0	0	1	0	1	-1	0.45
$>\text{CaOH}^{-0.5} \cdots \text{Na}^+$	0	0	1	0	0	1	0	0	1	0.56
$>\text{CaOH}^{-0.5} \cdots \text{Ca}^{2+}$	0	0	0	1	0	1	0	0	2	1.68
$>\text{CaOH}_2^{+0.5} \cdots \text{HCO}_3^-$	1	0	0	0	1	1	0	1	-1	0.54
$>\text{CaOH}_2^{+0.5} \cdots \text{CO}_3^{2-}$	0	0	0	0	1	1	0	1	-2	-6.57
$>\text{CO}_3\text{H}^{+0.5}$	1	0	0	0	0	0	1	1	0	-20
$>\text{CO}_3^{-0.5} \cdots \text{Na}^+$	0	0	1	0	0	0	1	0	1	0.56
$>\text{CO}_3^{-0.5} \cdots \text{Ca}^{2+}$	0	0	0	1	0	0	1	0	2	1.68

Li, Leroy et al. (2016), Influence of surface conductivity on the apparent zeta potential of calcite,
Journal of Colloid and Interface Science

Triple layer model of calcite (2)

> Parameters

- total surface site density,
- equilibrium constants of adsorption,
- capacitance C_1 .

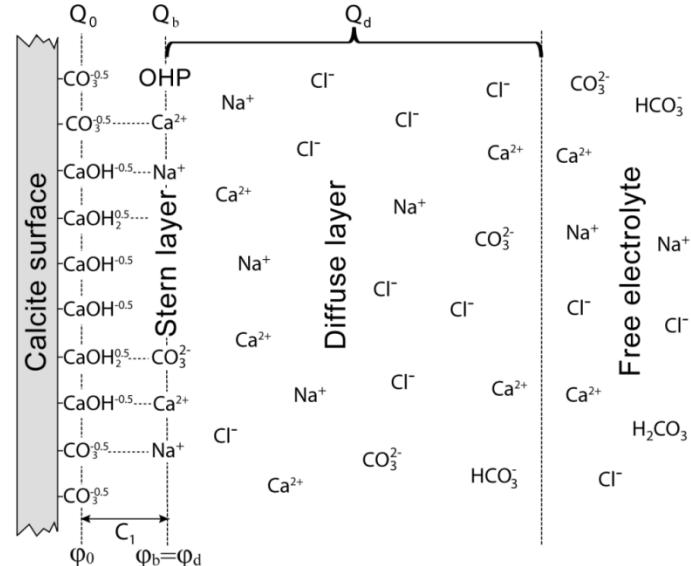
> Measured data

- surface charge densities Q_0 ,
- sorption isotherms,
- electrophoresis, streaming potential.

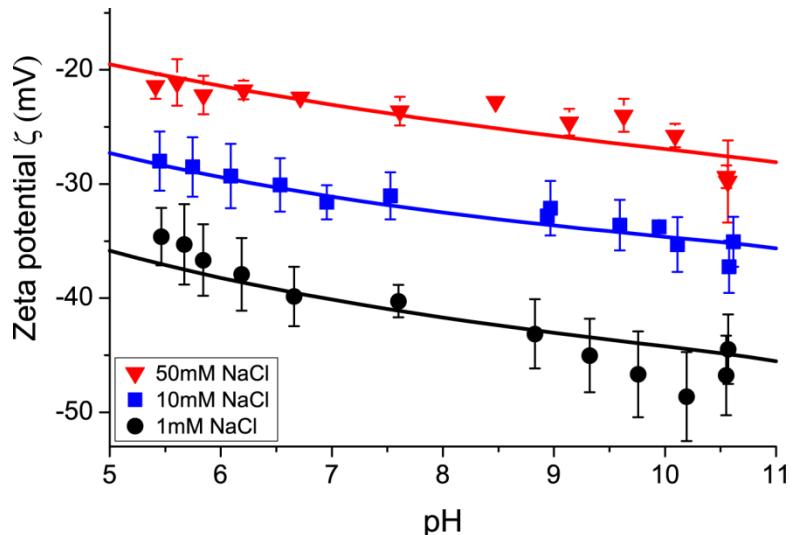
> Output data

- electrical potentials, zeta potential,
- surface site densities of adsorbed ions,
- surface charge densities of the Stern and diffuse layer.

➡ Computed excess of charge controlling the SIP response.



Assumption: $\phi_d = \zeta$



Grain polarization model of Leroy et al. (2008)

> Assumptions

- continuous diffuse layer and discontinuous Stern layer.

> Application of a sinusoidal electrical field

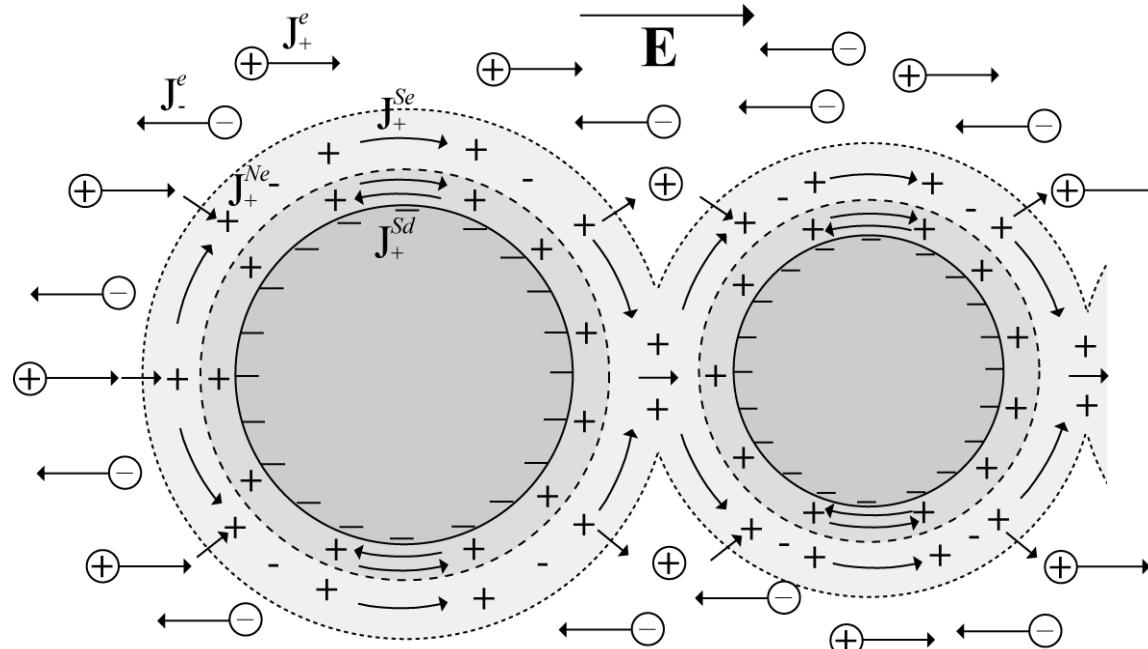
- electromigration in the diffuse layer

→ DC surface conductivity of the diffuse layer.

Leroy et al. (2008),
Complex conductivity of water-saturated packs of glass beads,
Journal of Colloid and Interface Science

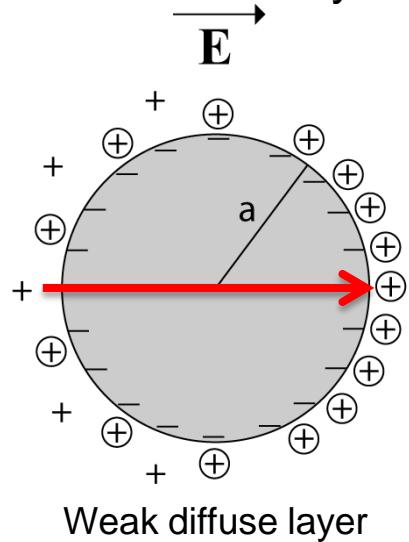
- electromigration and diffusion in the Stern layer

→ polarization, AC surface conductivity of the Stern layer.

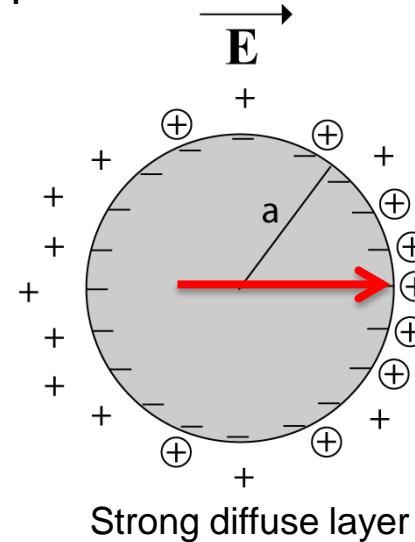


Improvement of the grain polarization model of Leroy et al. (2008)

- Multivalent and monovalent ions adsorbed at the Stern layer
- Effects of the diffuse layer on Stern layer polarization



Weak diffuse layer



Strong diffuse layer

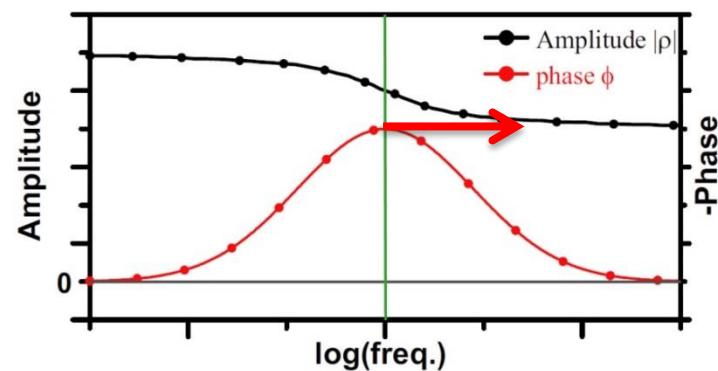
- ➡ decrease of the relaxation time τ of the polarization of the Stern layer
- ➡ increase of the associated characteristic frequency f

$$\tau = a^2 / 2 D_s M \quad f = 1 / \tau \quad \omega = 2 \pi f$$

D_s : diffusion coefficient of
the counter-ions in the Stern layer

M : effects of the diffuse layer
on Stern layer polarization ($M \geq 1$)

ω : angular frequency



Grain polarization model – theory (1)

1. TLM  electrical potential at the onset of the diffuse layer φ_d
 surface charge density of the Stern layer Q_b
 ions surface site densities in the diffuse layer Γ_i^d

2. Specific surface conductivities of the Stern and diffuse layer

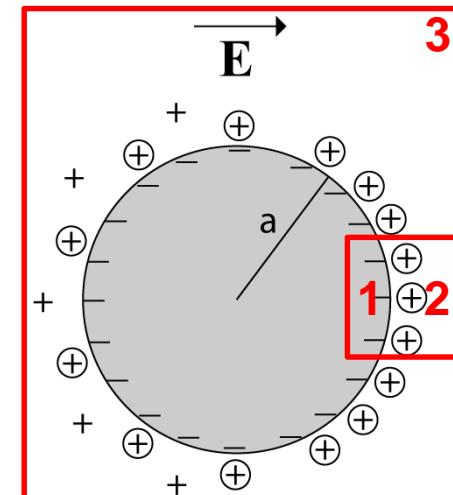
$$\Sigma_s^b = \pm \beta_b Q_b \quad \Sigma_s^d = \sum_{i=1}^N e z_i B_i^d \Gamma_i^d \quad \begin{aligned} \beta_b &: \text{ions surface mobility in the Stern layer} \\ B_i^d &: \text{ions effective mobility in the diffuse layer} \\ &\quad (\text{electromigration+electroosmosis}) \end{aligned}$$

3. Complex surface conductivity of the particle

$$\sigma_s^*(d, \omega) = \sigma_s(d, \omega) + i \omega \epsilon_s \quad \epsilon_s: \text{dielectric permittivity of the particle (constant)}$$

$$\sigma_s^*(d, \omega) = \frac{4}{d} \left\{ \sum_s^b \left[\frac{i \omega \tau_b(d)}{1 + i \omega \tau_b(d)} \right] + \sum_s^d \right\} + i \omega \alpha \rho_s \epsilon_0$$

$$\tau_b = \frac{1}{f_b} = \frac{a^2}{2 D_b M} = \frac{d^2}{8 D_b M} = \frac{d^2 |q|}{8 k_B T \beta_b M}$$



Grain polarization model – theory (2)

4. Superposition principle: complex conductivity of particles of different sizes

$$\sigma_s^* = \sum_{i=1}^Q f(d_i) \sigma_s^*(d_i, \omega)$$

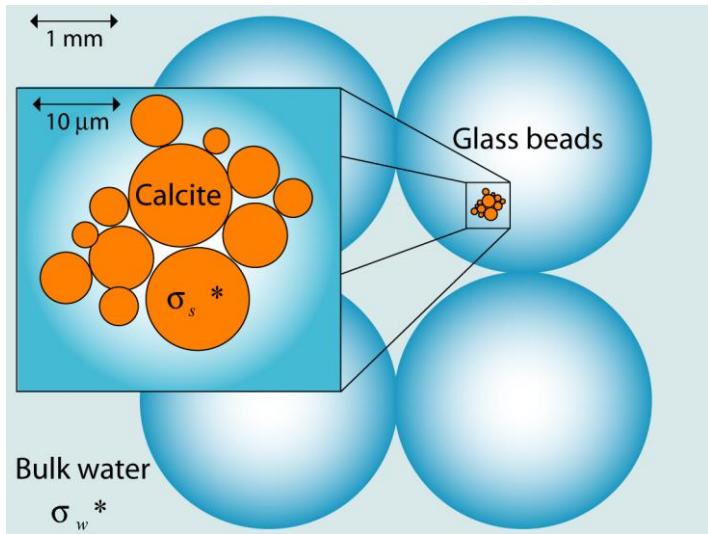
$f(d_i)$: particle size distribution

5. Differential effective medium theory: porous medium complex conductivity

$$\sigma^* = \frac{\sigma_w^*}{F} \left(\frac{1 - \sigma_s^* / \sigma_w^*}{1 - \sigma_s^* / \sigma^*} \right)^m$$

$$\sigma_w^* = \sigma_w + i\omega \epsilon_w$$

$$F = \phi^{-m}$$



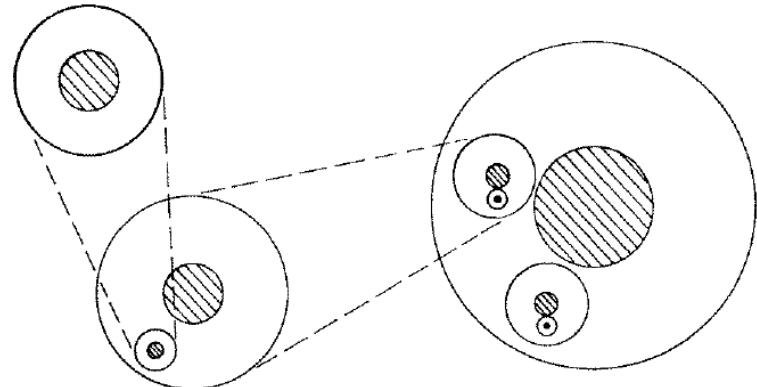
σ_w^* : water conductivity

ϵ_w : water dielectric permittivity

F: formation factor

ϕ : porosity

m: cementation exponent

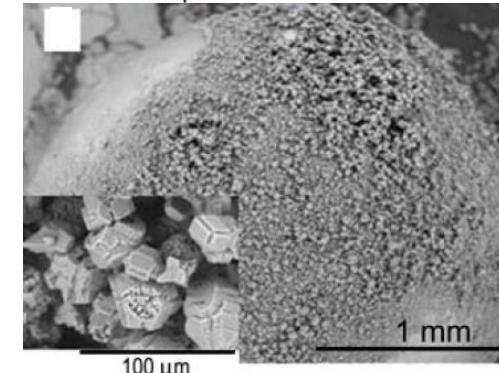
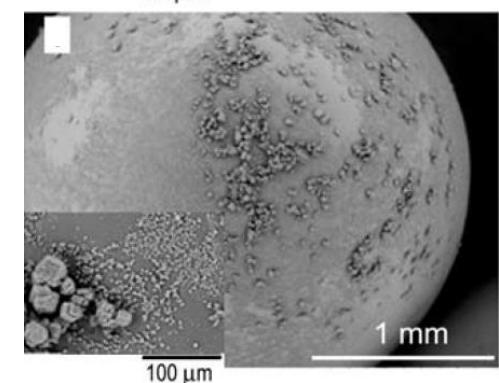
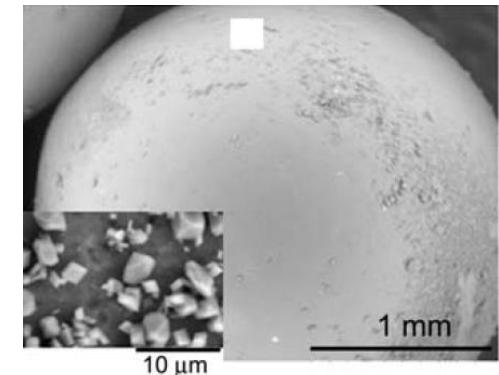
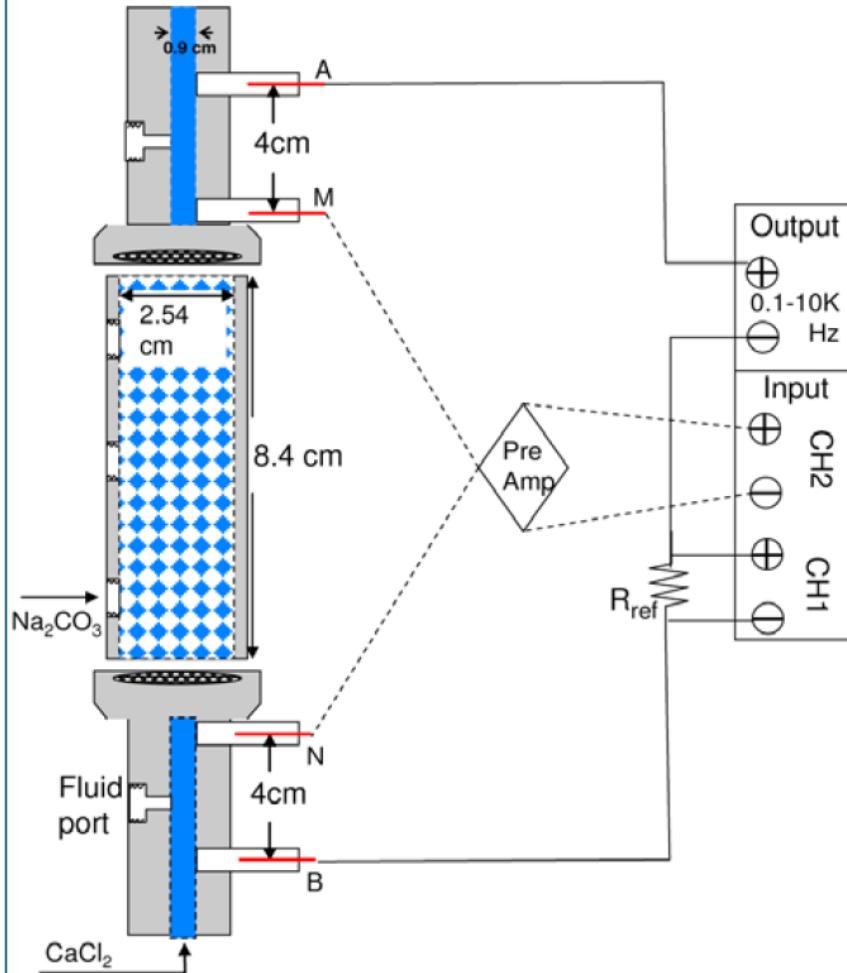


Self-similar model of rock

(from Sen et al. (1981), A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads, Geophysics)

Grain polarization model - comparison with experimental data (1)

> Spectral induced polarization (SIP) experiment of calcite precipitation



Wu et al. (2010),

On the complex conductivity signatures of calcite precipitation,
Journal of Geophysical Research: Biogeosciences.

Grain polarization model - comparison with experimental data (2)

> Measured sample complex conductivities

$$\sigma^*(\omega) = I(\omega)/(\Delta V(\omega) \times k)$$

$$\sigma^*(\omega) = \sigma' + i\sigma'' = |\sigma| e^{i\phi}$$

$$|\sigma| = (\sigma'^2 + \sigma''^2)^{0.5}$$

$$\phi = \tan^{-1}(\sigma''/\sigma') \approx \sigma''/\sigma'$$

σ' sensitive to conduction currents

$I(\omega)$: injected sinusoidal current

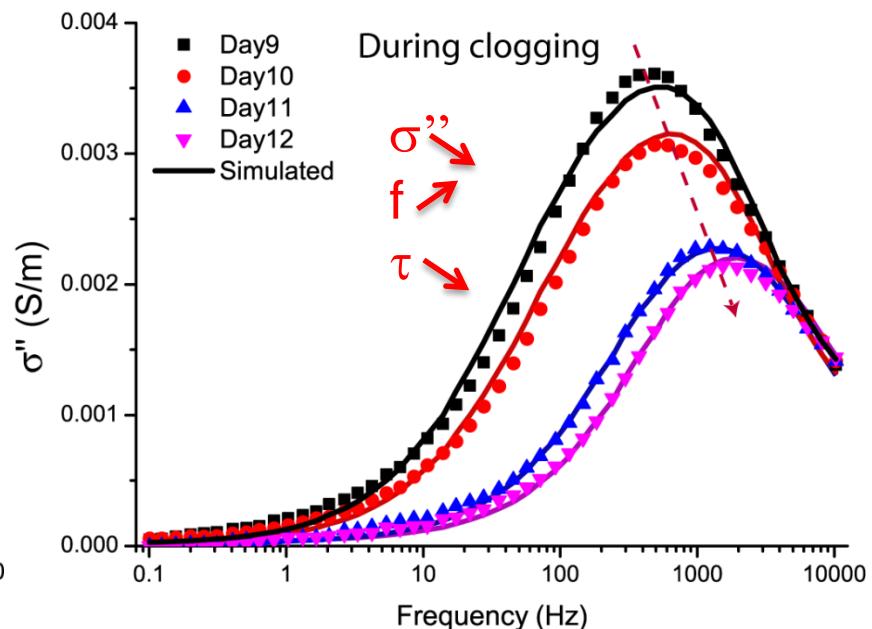
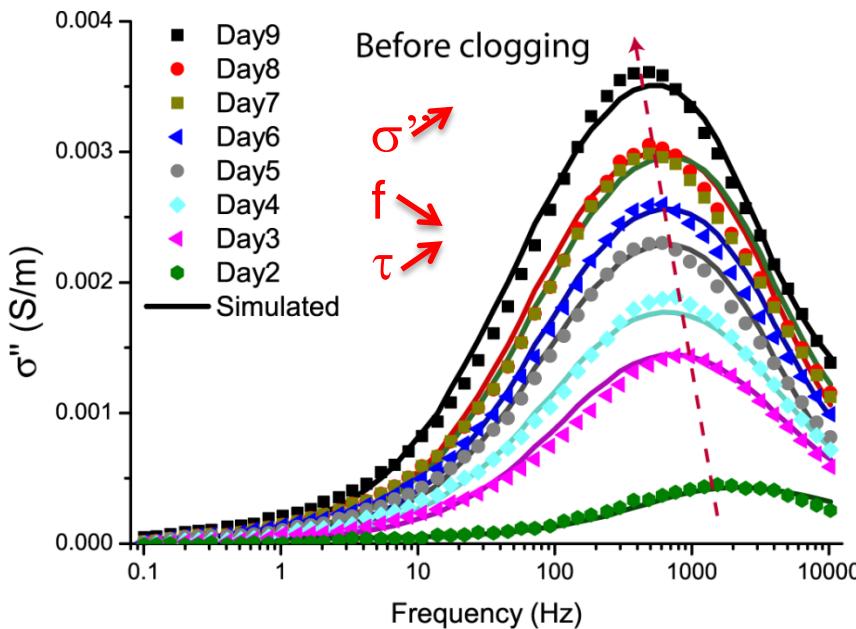
$\Delta V(\omega)$: measured electrical potential difference

k : geometric factor

ϕ : phase shift between measured electric potential difference and imposed current

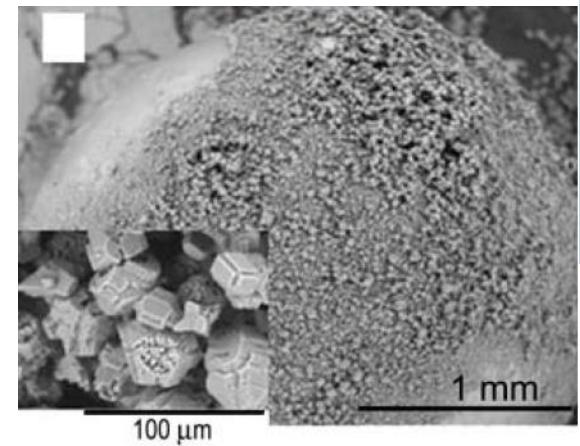
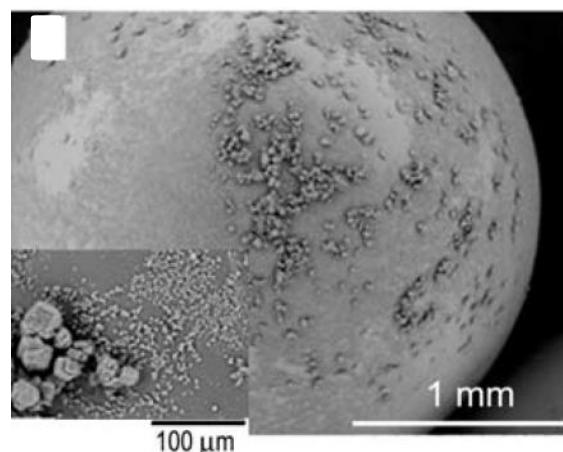
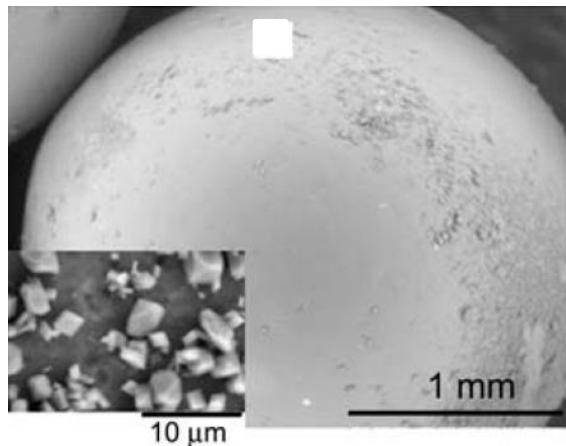
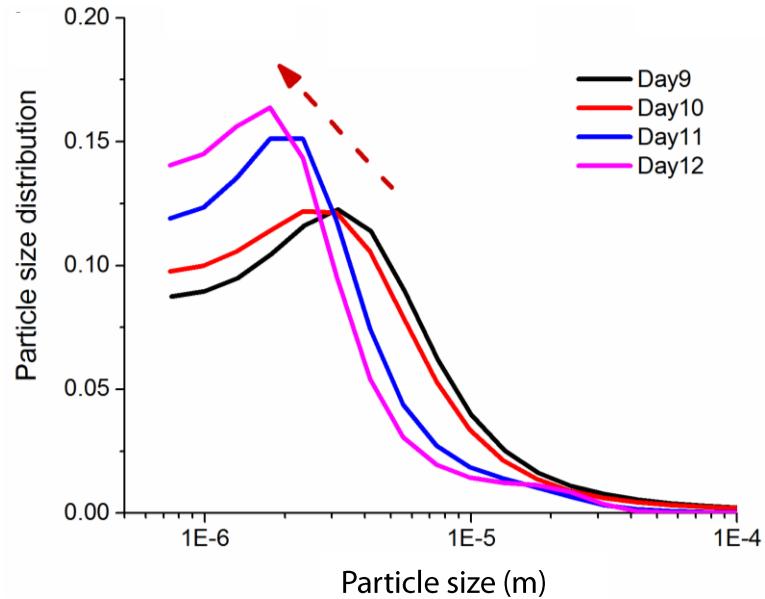
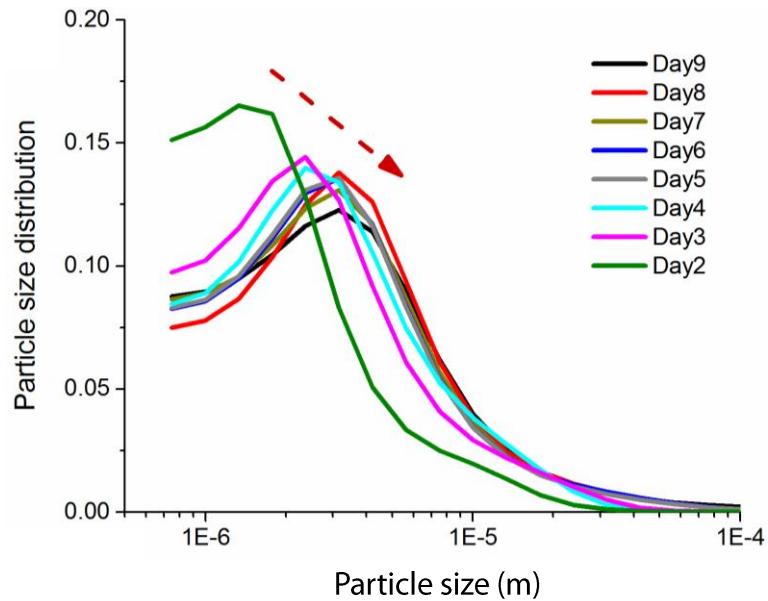
σ'' sensitive to polarization currents

> Imaginary conductivity response of calcite precipitation



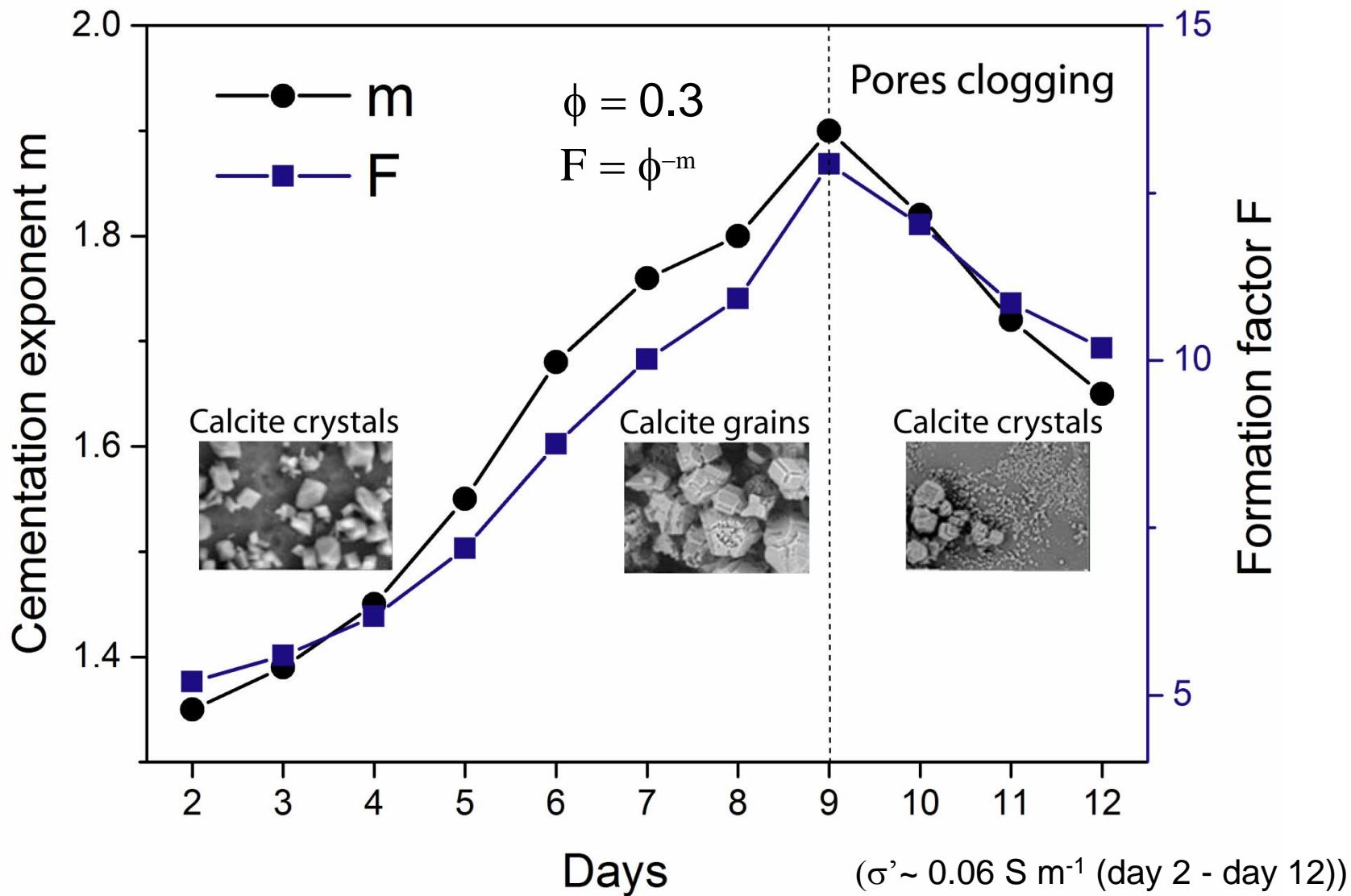
Grain polarization model - comparison with experimental data (3)

> Inverted particle size distribution



Grain polarization model - comparison with experimental data (4)

> Adjusted cementation exponent



Grain polarization model - comparison with experimental data (5)

> Modeled electrochemical properties of the calcite/water interface

Parameters	Values
Na ⁺ concentration in bulk water (mM)	29.00
Ca ²⁺ concentration in bulk water (mM)	1.20
Cl ⁻ concentration in bulk water (mM)	29.00
CO ₃ ²⁻ concentration in bulk water (mM)	0.09
HCO ₃ ⁻ concentration in bulk water (mM)	1.20
pH	9.00
Surface charge density of the Stern layer Q_b (C m ⁻²)	0.56
Surface site density of adsorbed Na ⁺ in the Stern layer (10 ¹⁷ sites m ⁻²)	17.30
Surface site density of adsorbed Ca ²⁺ in the Stern layer (10 ¹⁷ sites m ⁻²)	8.91
Surface charge density of the diffuse layer Q_d (C m ⁻²)	0.012
Surface site density of adsorbed Na ⁺ in the diffuse layer (10 ¹⁷ sites m ⁻²)	0.383
Surface site density of adsorbed Ca ²⁺ in the diffuse layer (10 ¹⁷ sites m ⁻²)	0.032
Surface site density of adsorbed Cl ⁻ in the diffuse layer (10 ¹⁷ sites m ⁻²)	0.189
Surface site density of adsorbed CO ₃ ²⁻ in the diffuse layer (10 ¹⁷ sites m ⁻²)	0.0005
Surface site density of adsorbed HCO ₃ ⁻ in the diffuse layer (10 ¹⁷ sites m ⁻²)	0.033
Electrical potential at the beginning of the diffuse layer φ_d (mV)	-29.00
Differential capacitance of the diffuse layer C_d (C m ⁻² V ⁻¹)	0.69
Diffuse layer polarization effects on Stern layer polarization M	30.70

> Complex conductivity model parameters

Parameters	Values
Ions mobility in the Stern layer β_b (m ² s ⁻¹ V ⁻¹)	5.7×10 ⁻⁹
Initial cementation exponent of the particles m	1.35
Initial glass beads porosity ϕ	0.30
Bulk pore water conductivity σ_w (S m ⁻¹)	0.356

Conclusions and perspectives

- > Complex conductivity model of the electrochemical polarization of the Stern layer surrounding calcite particles
- > Monovalent and multivalent counter-ions in the Stern layer
- > Effects of the diffuse layer on Stern layer polarization
- > Grain conductivity model combined with a triple layer model of the electrochemical properties of the calcite/water interface
- > Measured complex conductivity spectra of calcite precipitation on glass beads successfully reproduced by our surface complexation and conductivity models
- > Particle size distribution and particle shape deduced from our models
- > Application of our models to estimate transport properties of sandstones containing saline solutions favoring calcite precipitation according to SIP measurements

A photograph of a snowy mountain landscape. In the center-right, a large, light-colored, layered rock formation rises, partially covered in snow. To the left, a tree with bare branches and snow-laden evergreen trees are visible. The ground in the foreground is covered in snow and some bare branches.

Thank you for your attention!