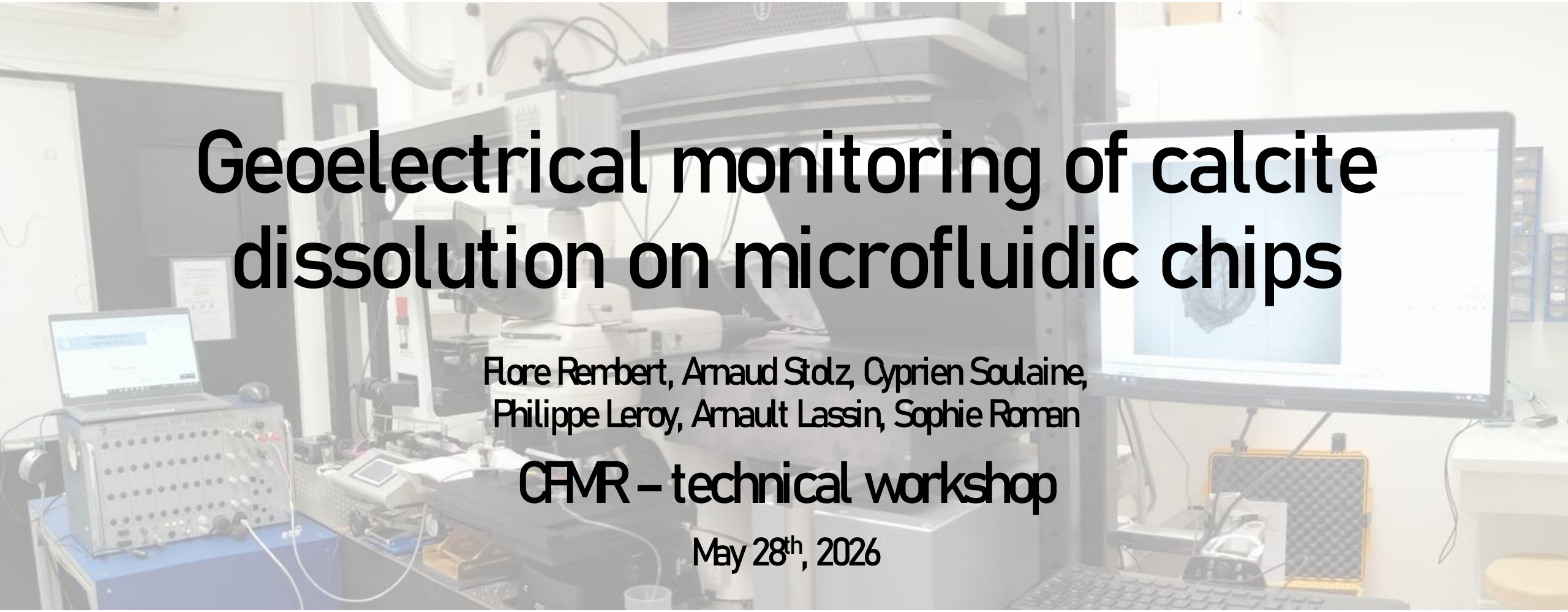


Geoelectrical monitoring of calcite dissolution on microfluidic chips

Flore Rembert, Arnaud Stolz, Cyprien Soulaine,
Philippe Leroy, Arnault Lassin, Sophie Roman

CFMR – technical workshop

May 28th, 2026

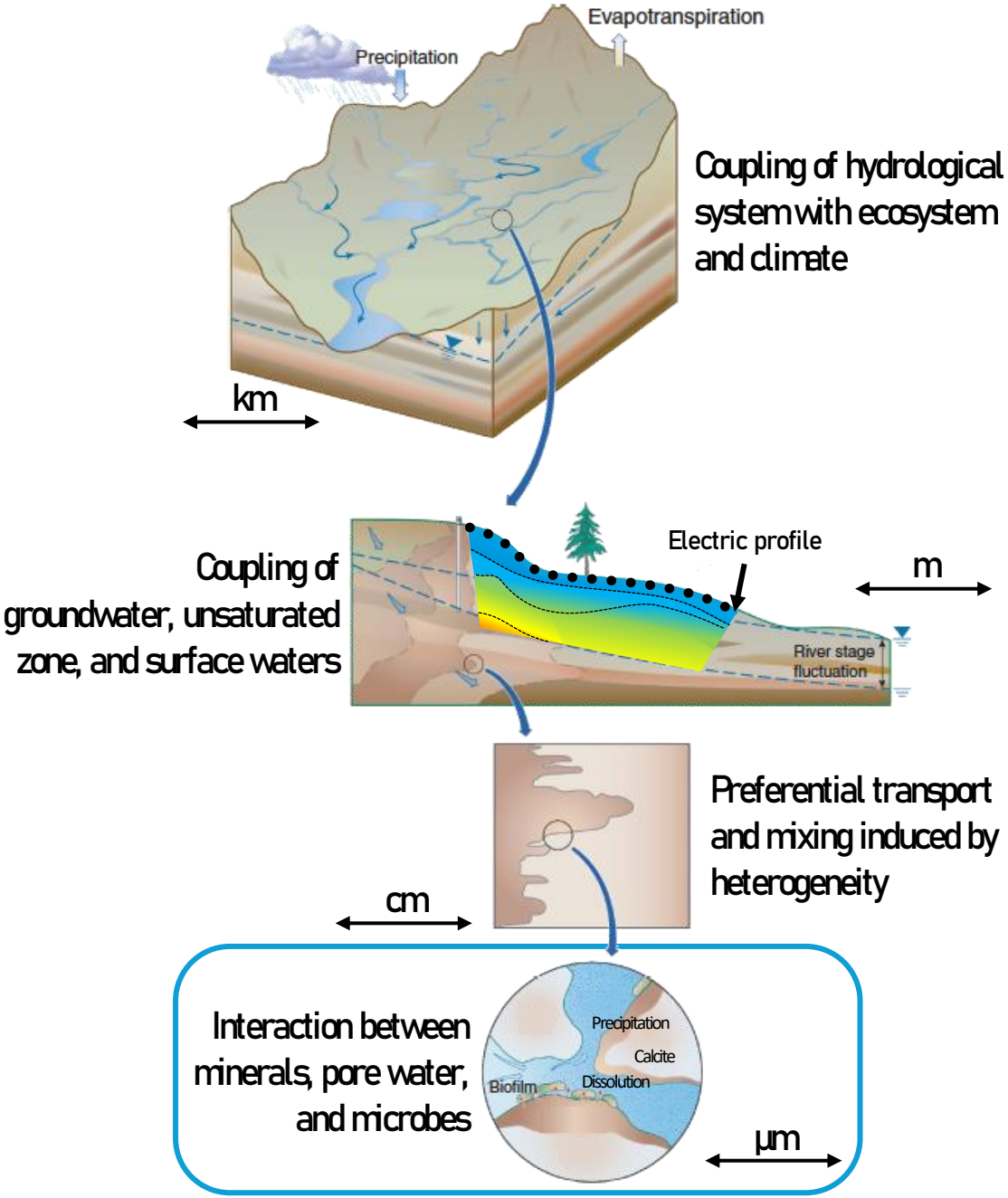
Using geophysical methods to characterize dynamic processes

1. Calcite dissolution is an important and ubiquitous process involved in many reservoir applications: CO_2 storage, karst hydrology, and hydrothermal fluids.

2. Calcite dissolution relies on microscopic couplings and has an impact on multiple scales

3. Geophysical methods in the field enable "seeing" into the subsurface environment.
   - → Geoelectrical methods are interesting for monitoring fluid dynamics and biogeochemical reactions.
   - → Petrophysical relationships enable a quantitative use of geophysical methods and signal prediction.

(Hubbard and Linde, 2011)

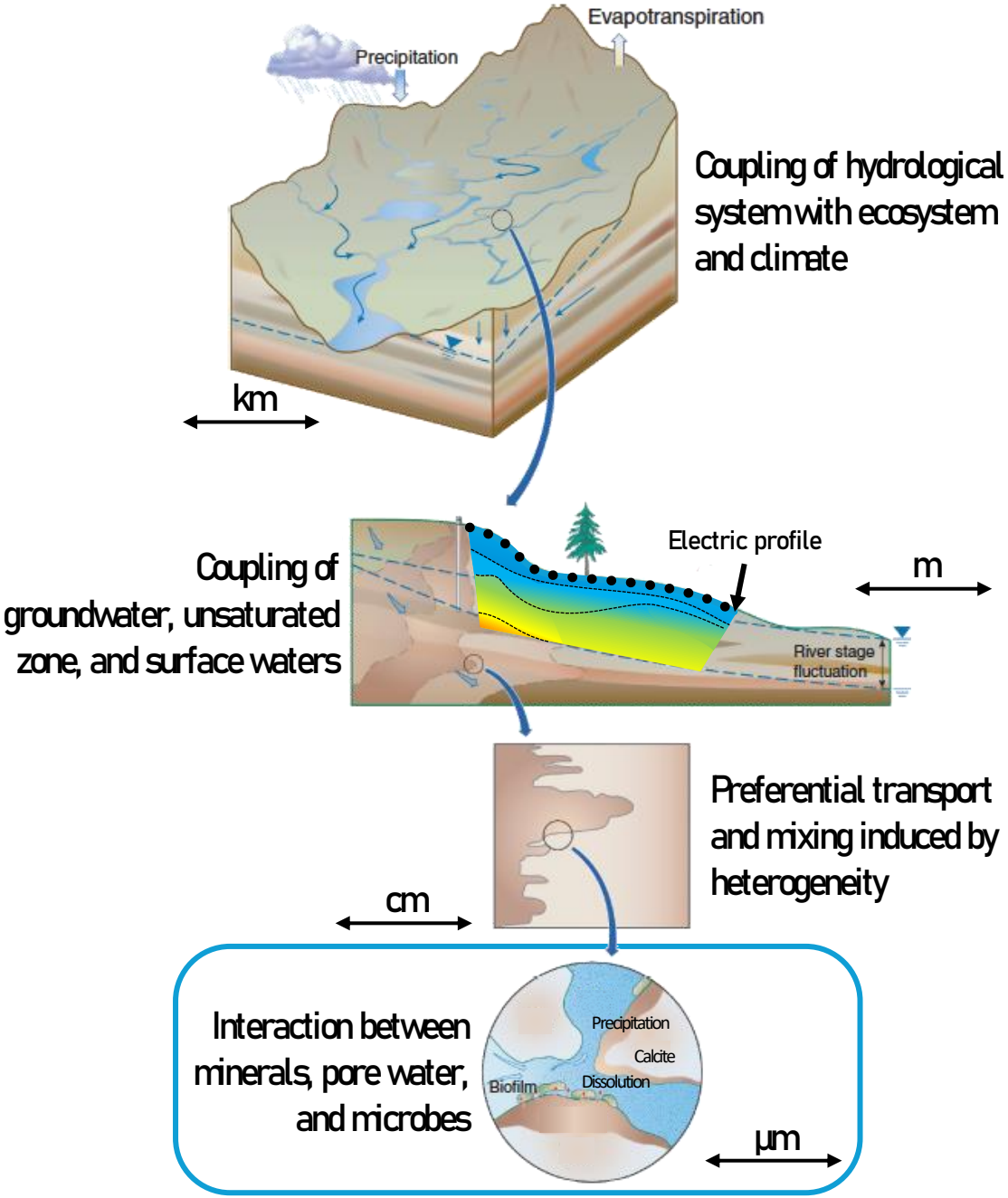


Using geophysical methods to characterize dynamic processes

Spectral induced polarization (SIP) response interpretation is a major challenge in the presence of superimposed signal sources and dynamic processes.

We aim at improving our petrophysical understanding of the SIP response through microscopic investigation.

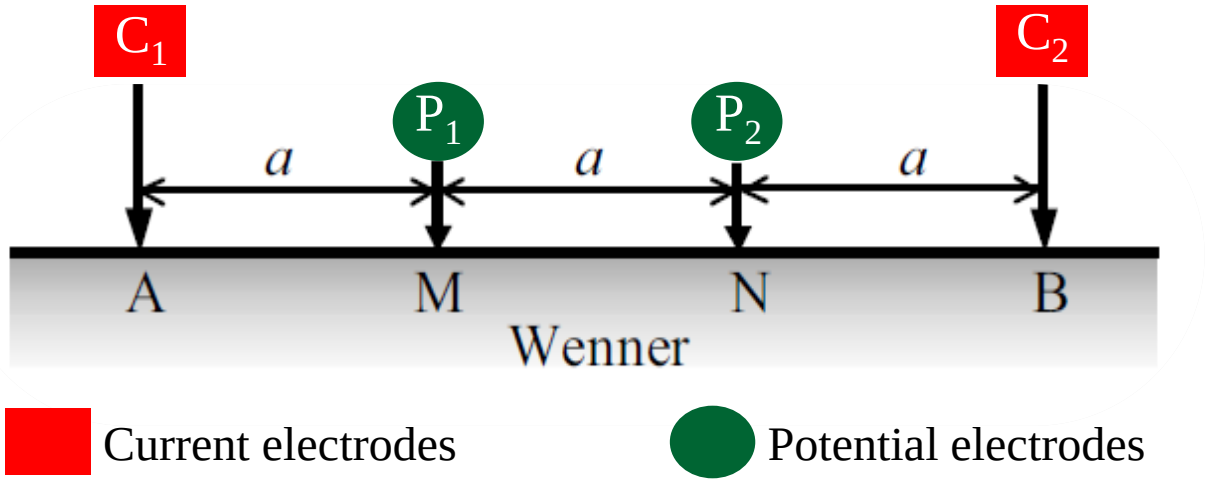
(Hubbard and Linde, 2011)



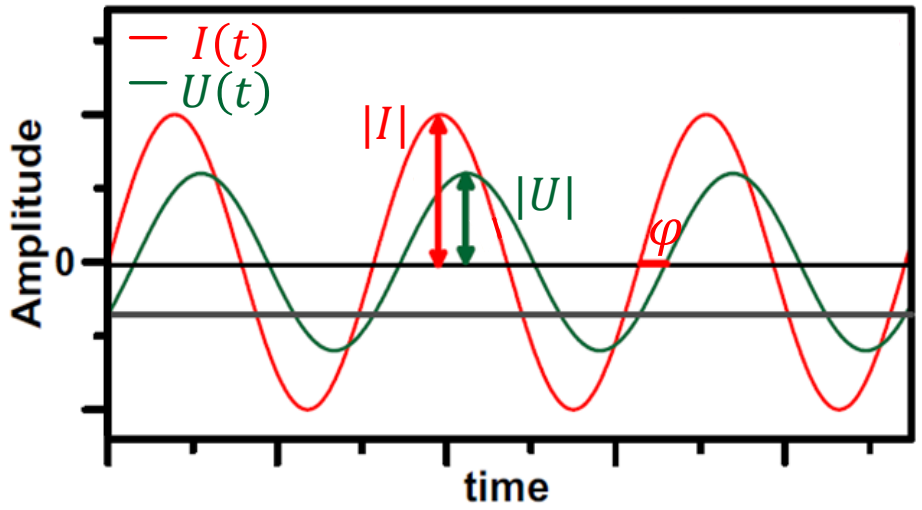
The spectral induced polarization (SIP) method

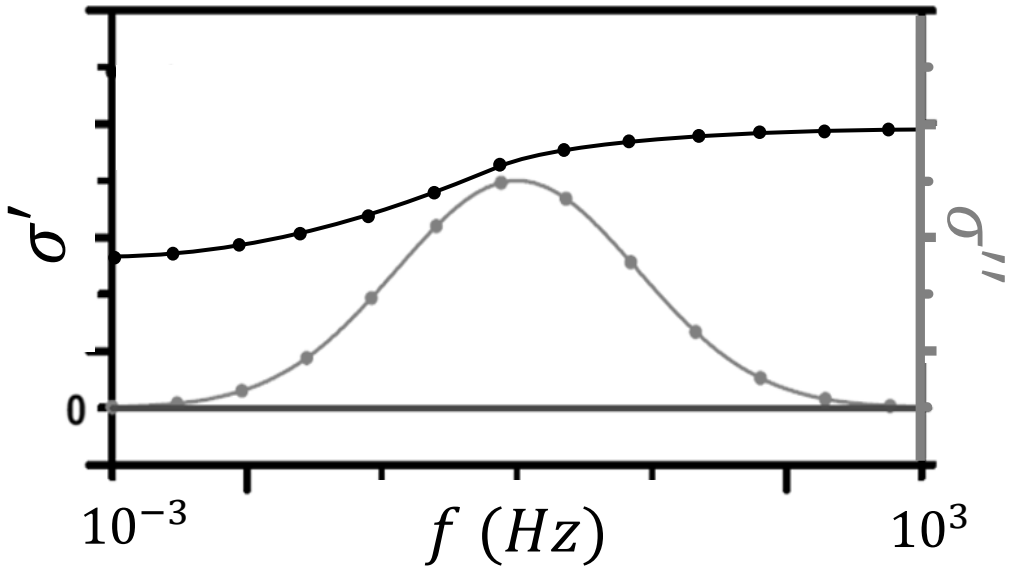
$$\sigma^*(\omega) = \frac{I^*(\omega)}{k_G\, U^*(\omega)} = |\sigma^*(\omega)|e^{-i\varphi(\omega)} = \sigma'(\omega) + i\sigma''(\omega)$$

Conduction Polarization



(Binley and Kemna, 2005)





(Ghorbani, 2007)

Electric conduction in porous media

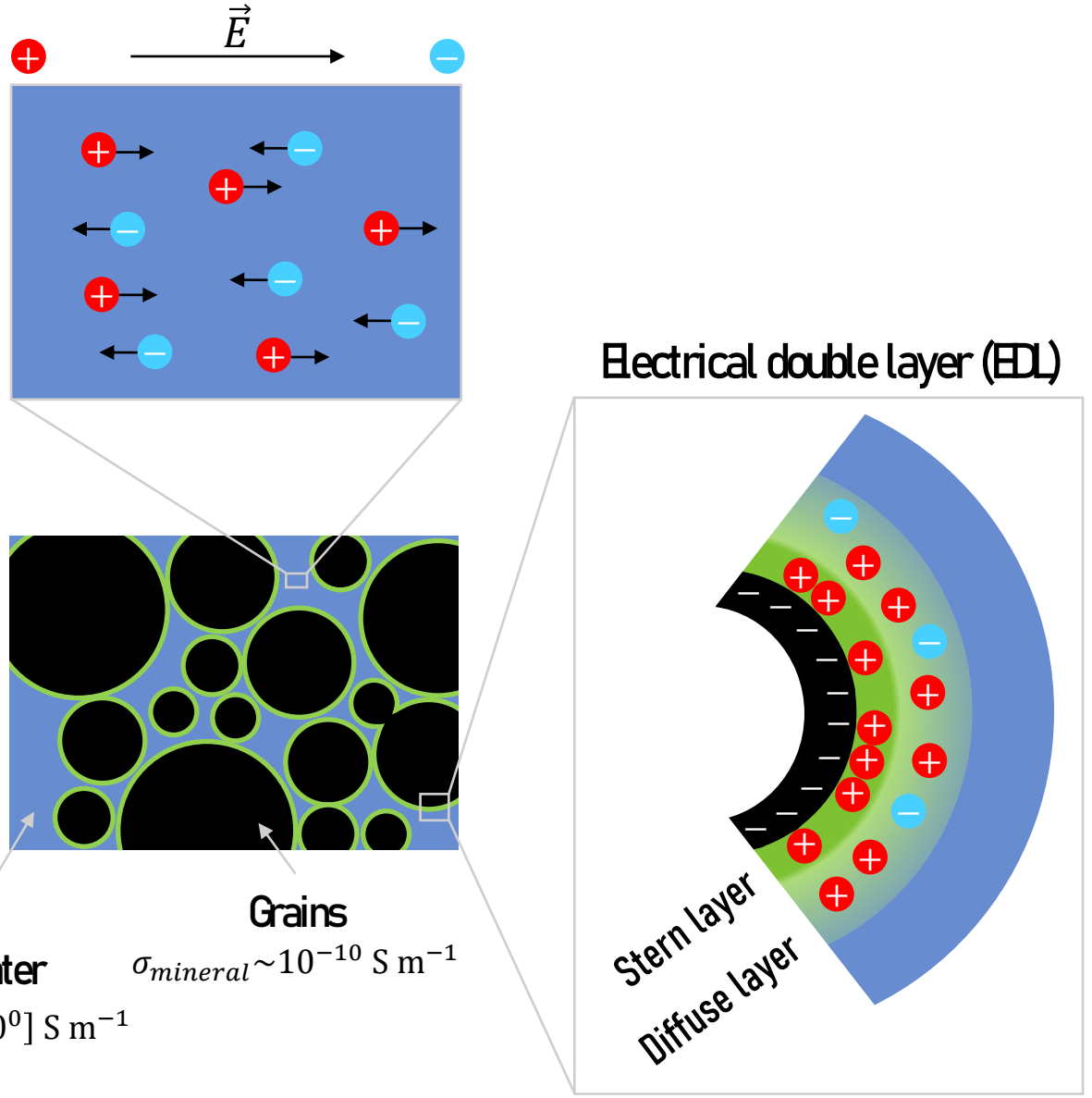
The electric current flows through the pores filled with water and dissolved ions.

$$\sigma_{bulk} = \frac{\sigma_w}{F}$$

← The formation factor

The surface of the grains is electrically charged and also contributes to the electric conduction of the porous medium

$$\sigma = \sigma_{bulk} + \sigma_s$$

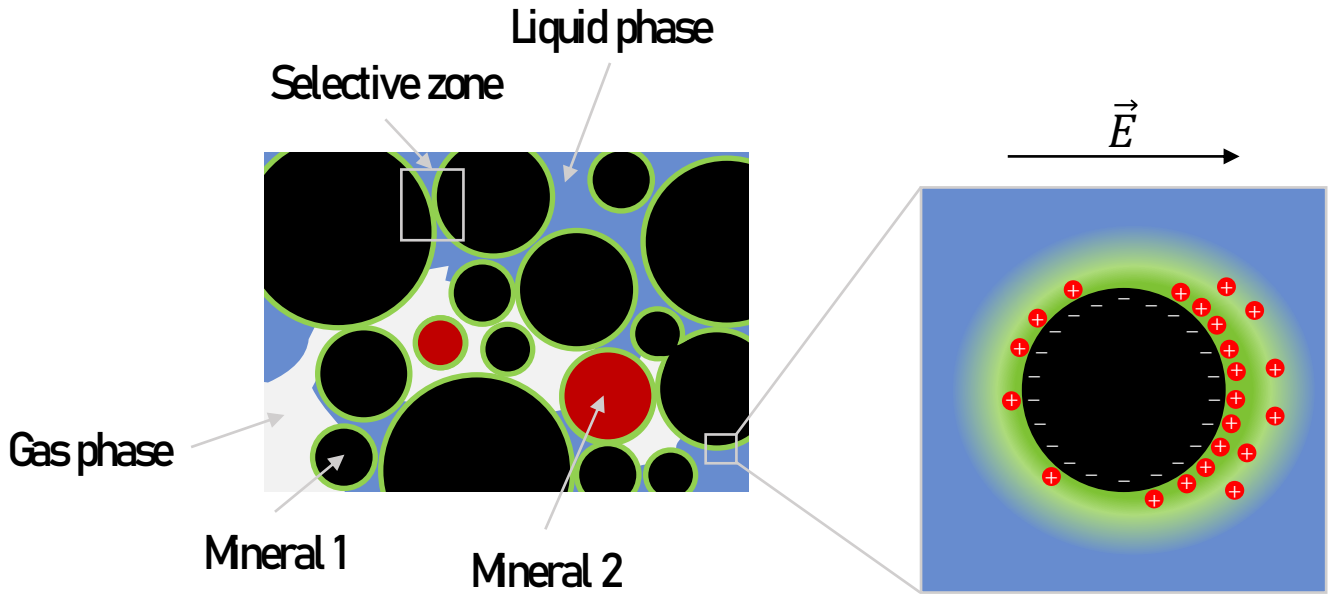


The complex electrical conductivity and surface polarization mechanisms

When a sinusoidal current is injected, ions in the confined pore space exhibit limited motion, creating charge accumulation, also called polarization.

Polarization mechanisms:

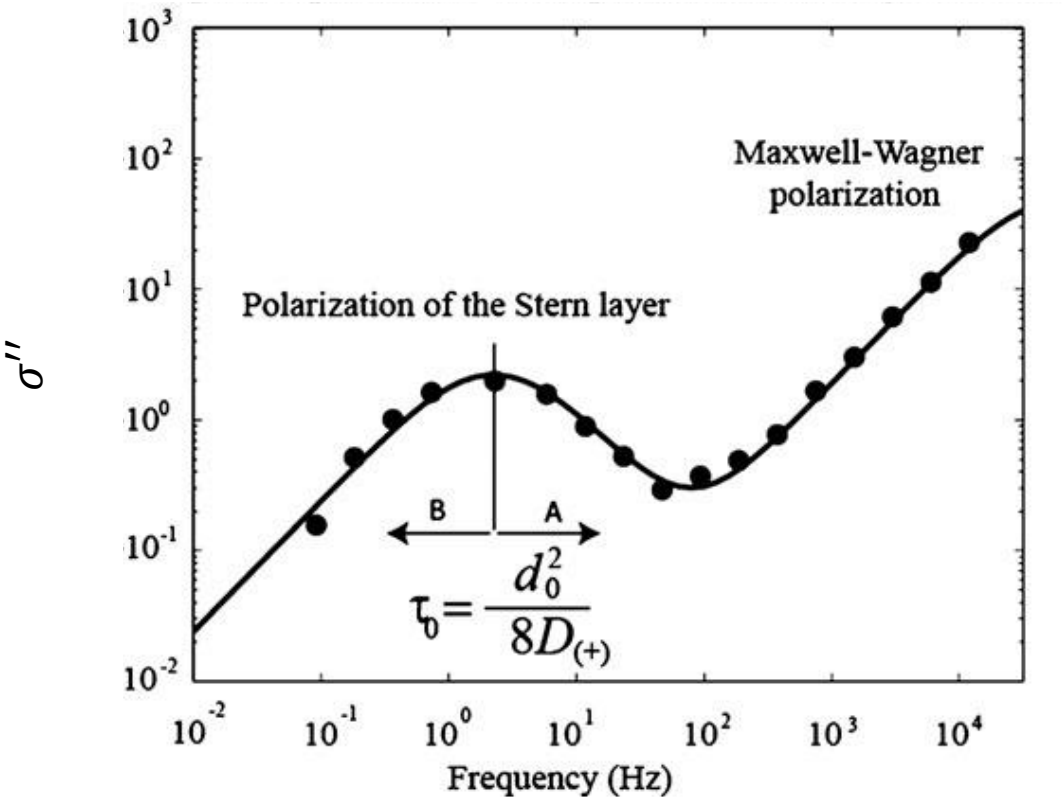
- The electrical double layer (EDL)
  - ➞ Transitory reorganization of the charges at the mineral surface ($10^{-2} - 10^{2}\,\mathrm{Hz}$)
- Membrane polarization
  - ➞ Ionic exclusion in pore throats ($10^{-3} - 10^{-2}\,\mathrm{Hz}$)
- Maxwell-Wagner polarization
  - ➞ Interfaces create discontinuities ($> 10^{3}\,\mathrm{Hz}$)



Interpretation of σ'' spectrum

The frequencies of phase local maxima correspond to specific relaxation times that can be related to characteristic polarization length scales:

- Grain size distribution
- Pore size distribution
- Surface roughness



The superposition of polarization lengths complexifies the interpretation.

→ Need for direct visualization at the microscale

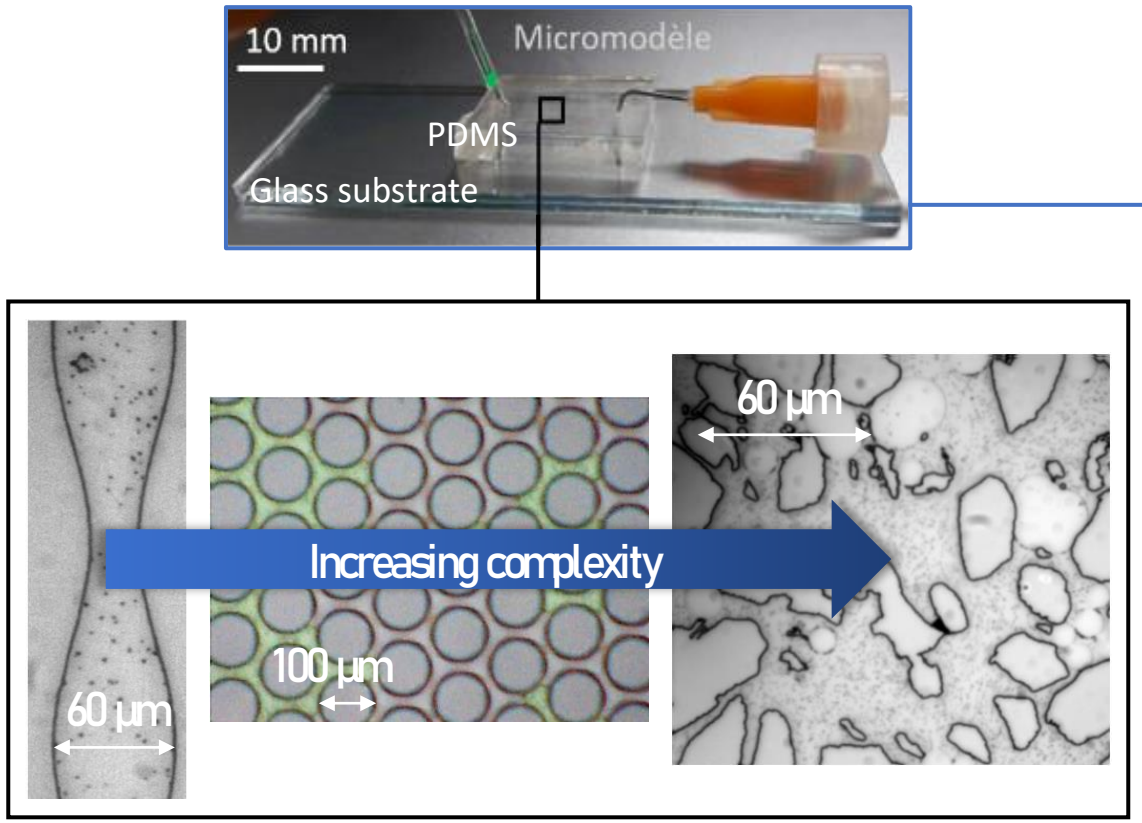
τ_0 Characteristic time

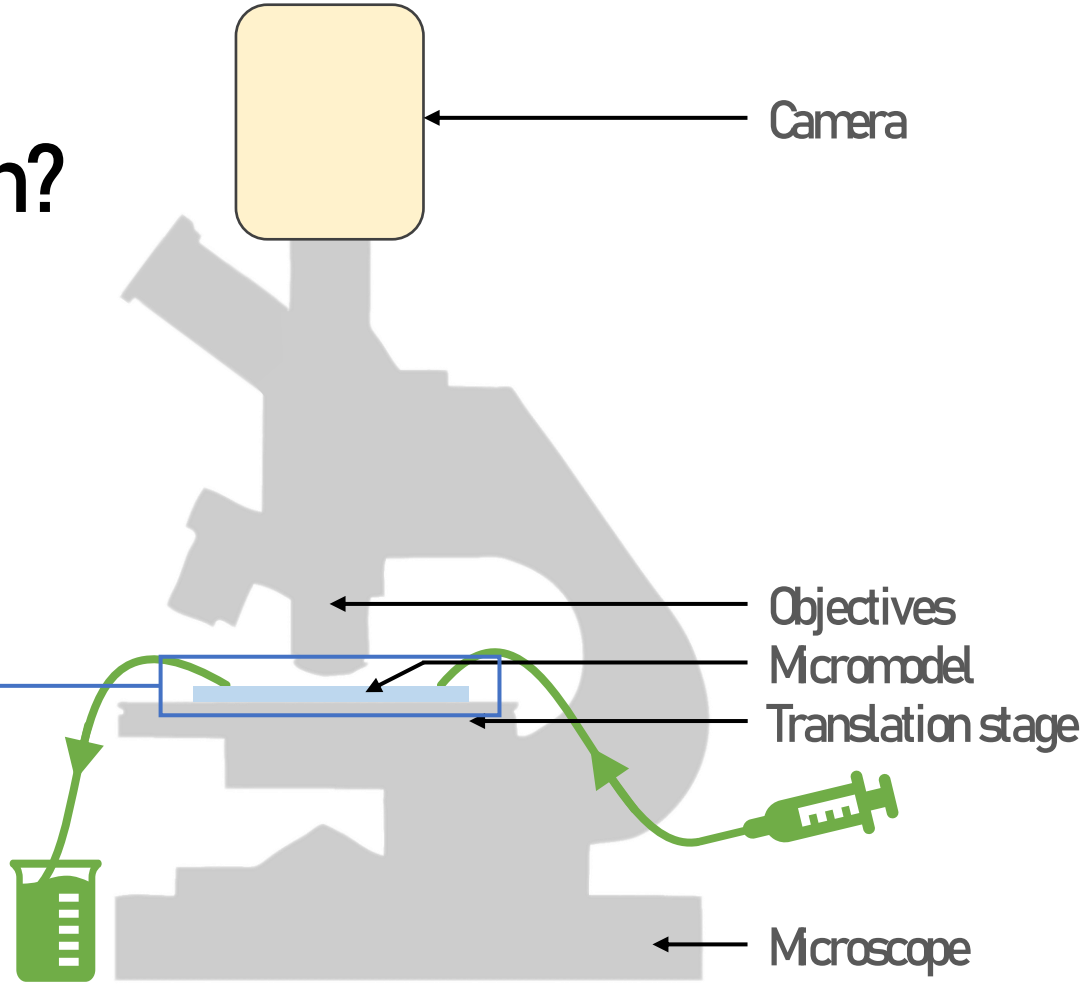
d_0 Characteristic length

$D_{(+)}$ Diffusion coefficient of the cations in the Stern layer

A way to conduct SIP at the microscale with direct visualization?

➥ Microfluidic experiments

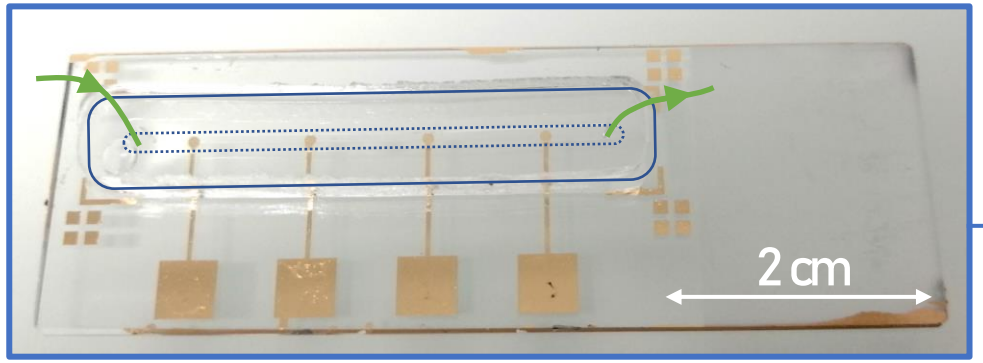




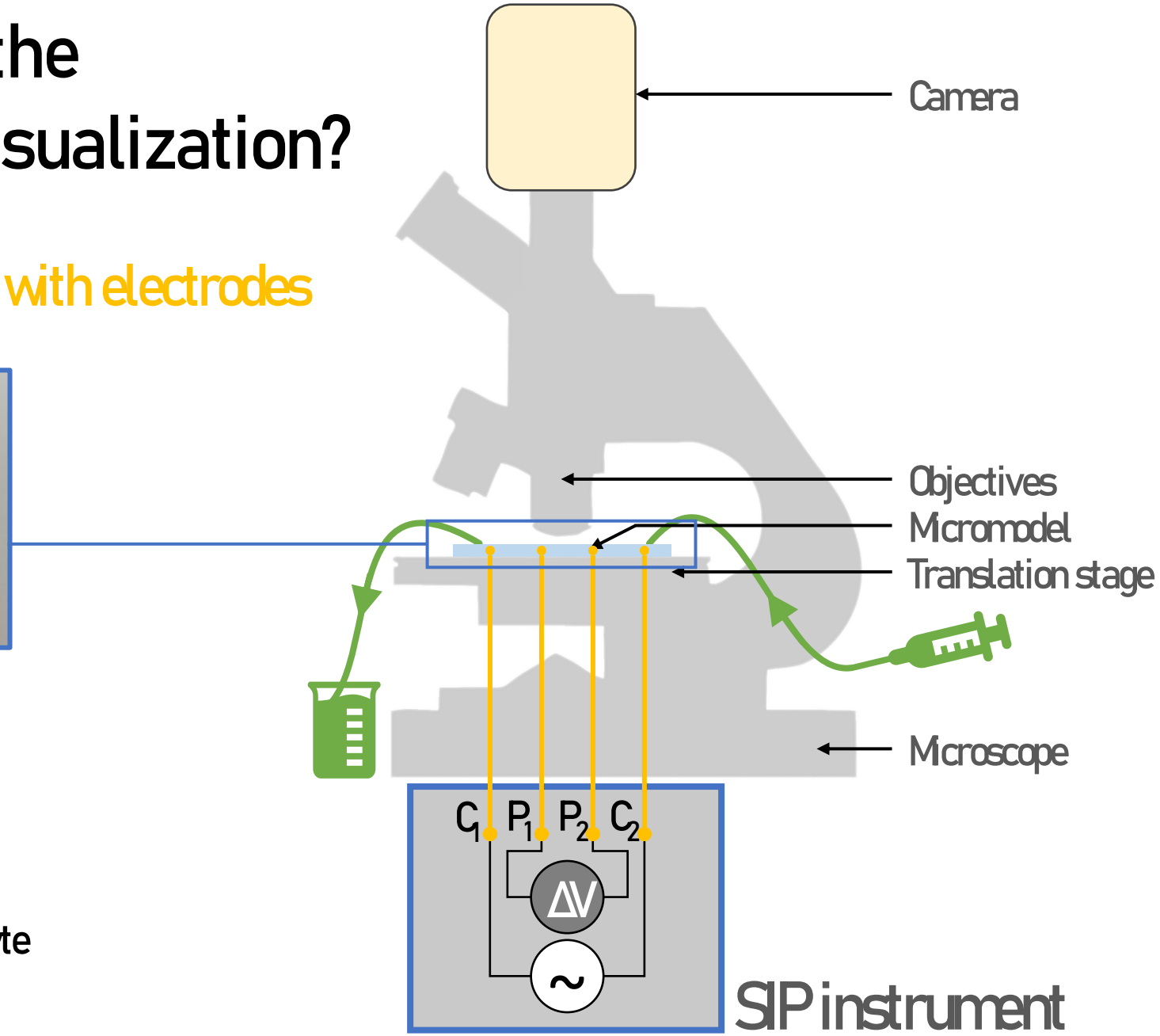
The transparency of the micromodel materials allows for direct observation with high-resolution imaging

A way to conduct SIP at the microscale with direct visualization?

➥ Microfluidic experiments equipped with electrodes

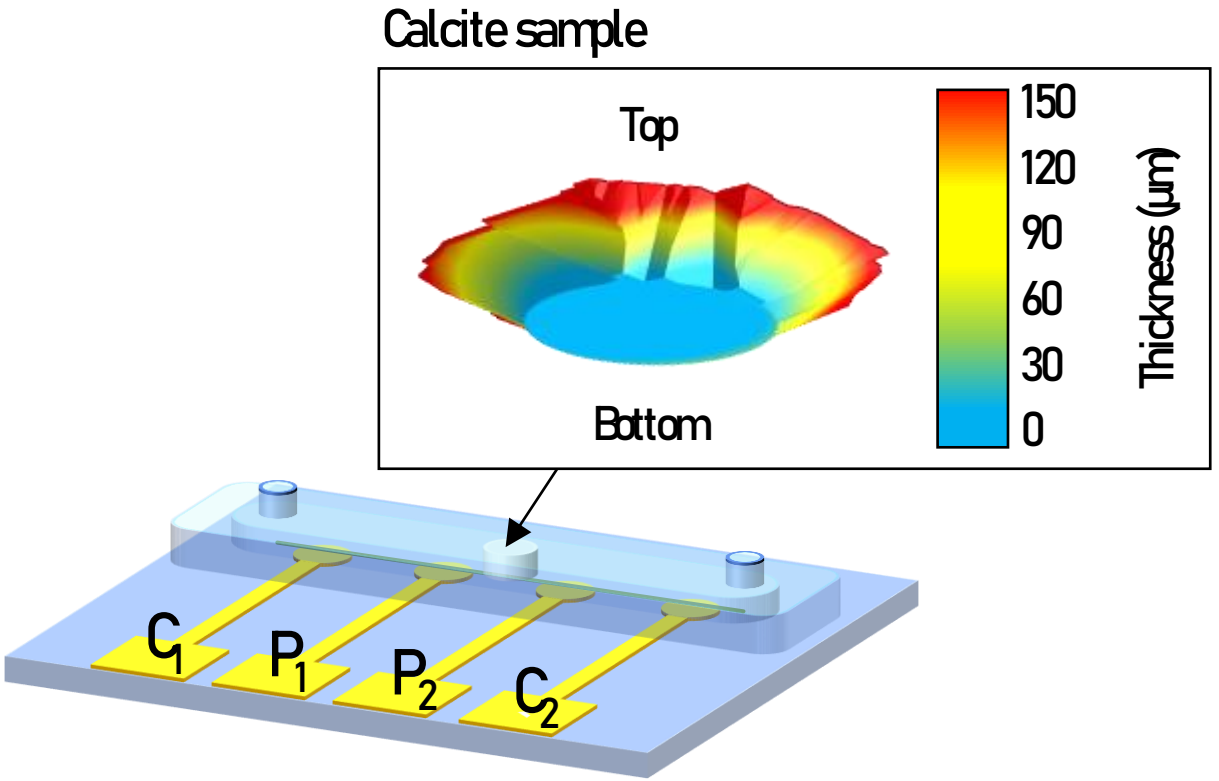


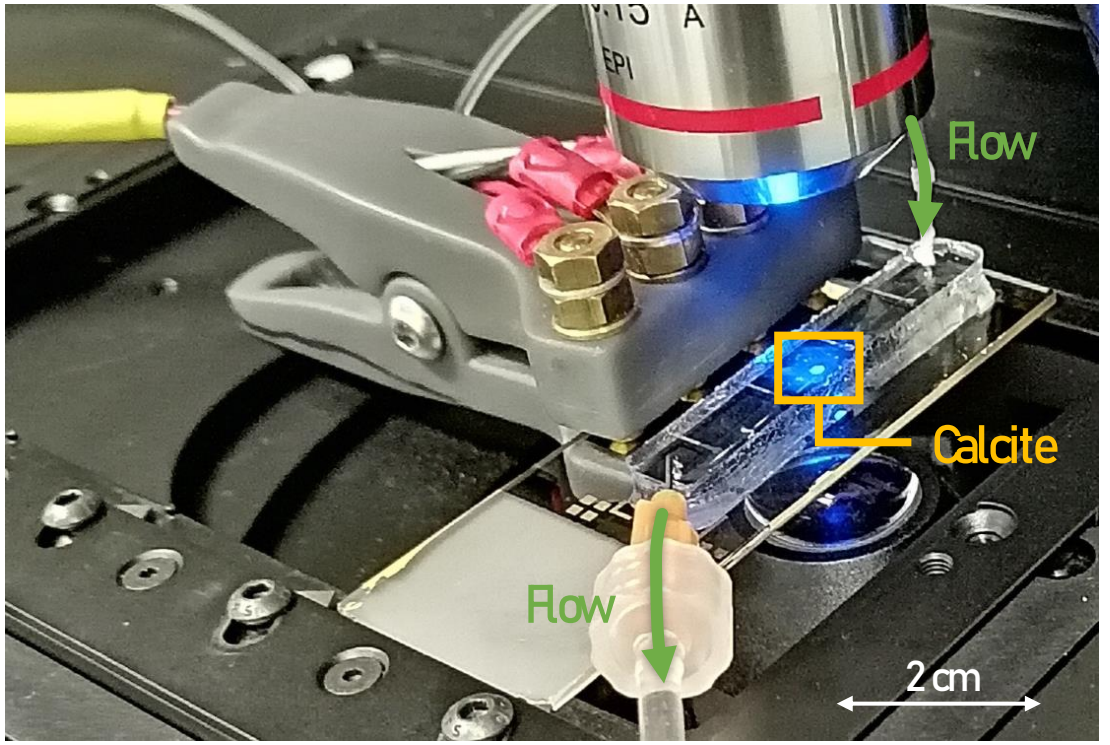
- PDMS channel (LxlxH = 4000x1500x150 µm)
- Glass substrate
- 4 gold electrodes per channel
  400 nm thickness
  The head (900 µm) is in contact with the electrolyte
  Square electric contacts next to the PDMS cap



Experimental protocol for the experiment of calcite dissolution

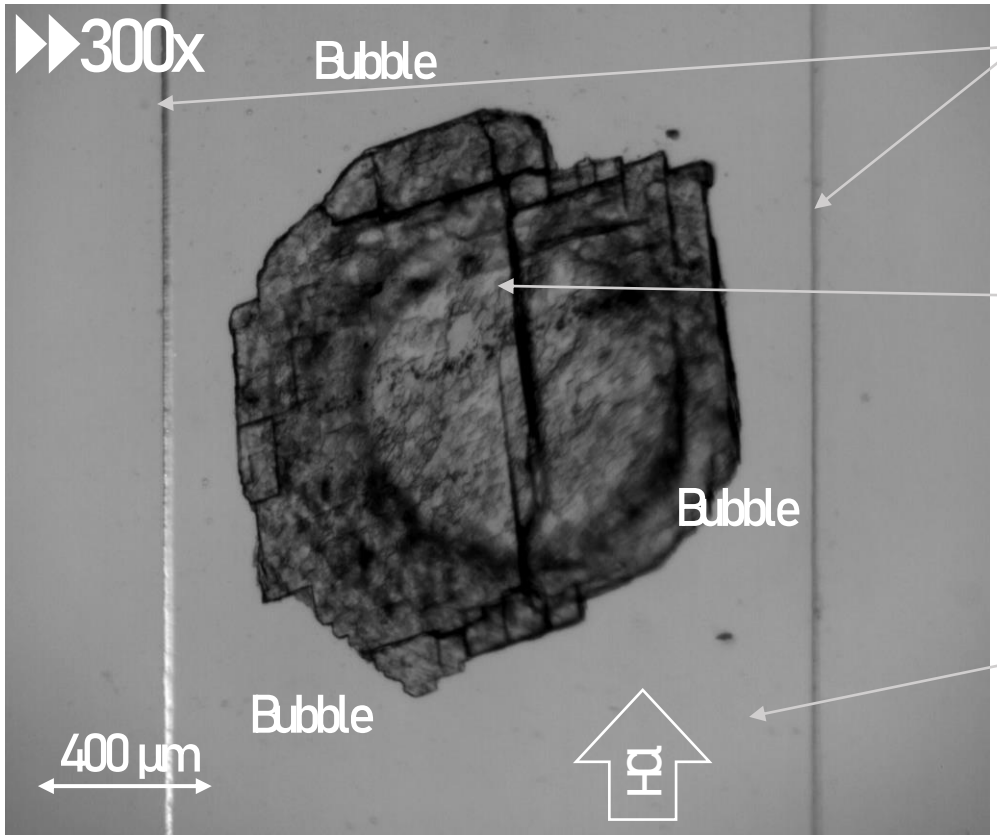
$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2$$





- Sample: carved calcite thin section of 150µm thickness
- Initial solution S_0:
  Deionized water saturated with calcite
- Acid solution: HCl at 0,05 $\%_{w/w}$ concentration
- Constant flow rate: 21 $\mu L.min^{-1}$

Monitoring the dissolution of calcite with high-resolution microscopy



Channel's walls

Calcite

An initial saturating solution saturated with calcite

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2O + CO_{2\,(g)}$$

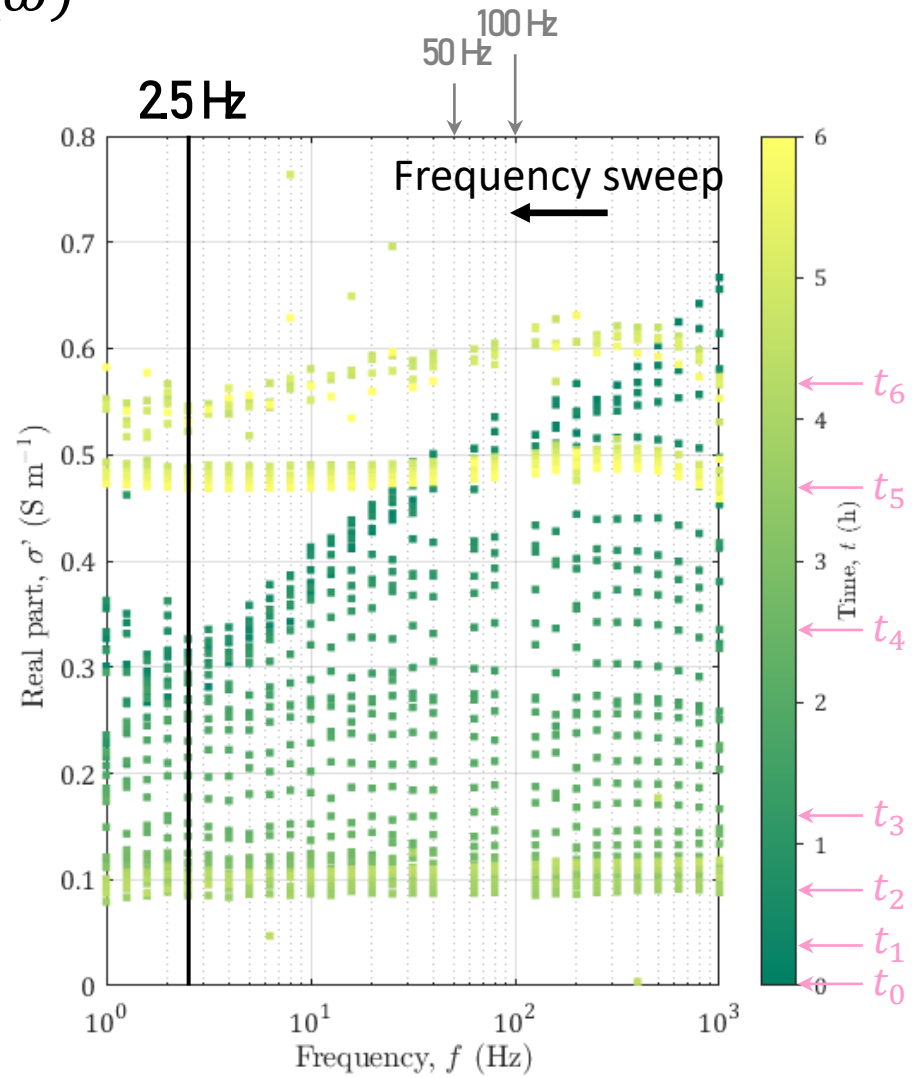
- Image sequence captured every 30 s.
- Video speed of 10 frames per second.

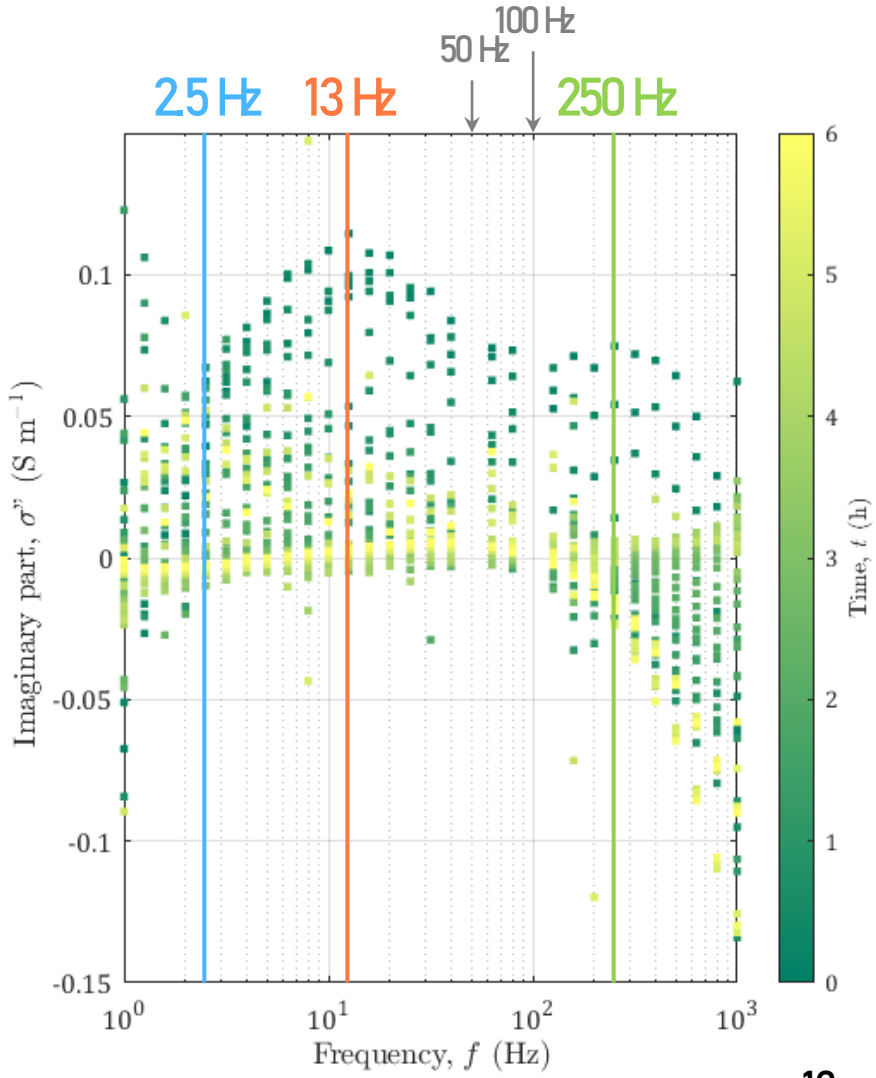
1. Dissolution in saturated conditions
2. Surface roughness vanishes
3. Nucleation of small bubbles
4. Growth of the bubbles
5. Merging of the bubbles with their neighbors
6. Small bubbles feed large bubbles
7. Uniform spacing between the bubbles
8. Big bubbles are size changing
9. Calcite sample has drastically reduced in size
10. Brutal detachment of the bubbles
11. End of dissolution

Monitoring the dissolution of calcite with SIP

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$$

- Spectra are recorded every 7 min.
- 50 Hz and 100 Hz data are removed due to power grid coupling.
- Time variations seem related to calcite dissolution and bubbles' growth.
- Polarization is distributed around peaks at 13 Hz and 250 Hz.





IP spectra and abrupt changes

0. No dissolution ◊

1. Acid arrival ● ●

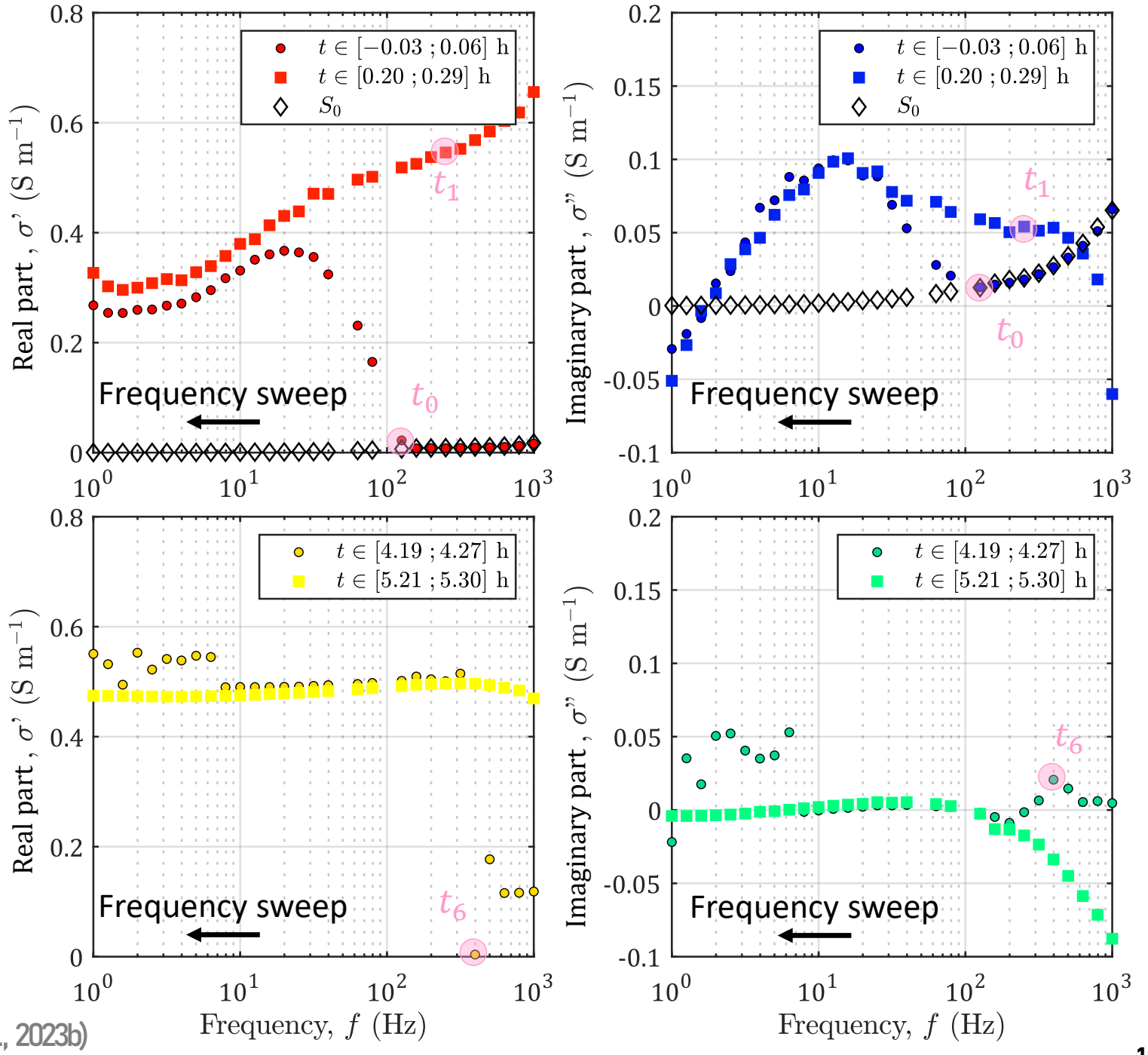
t_0 Acid arrival

t_1 Dissolution in saturated conditions

2. Dissolution ■ ■

3. Bubbles detachment ● ●

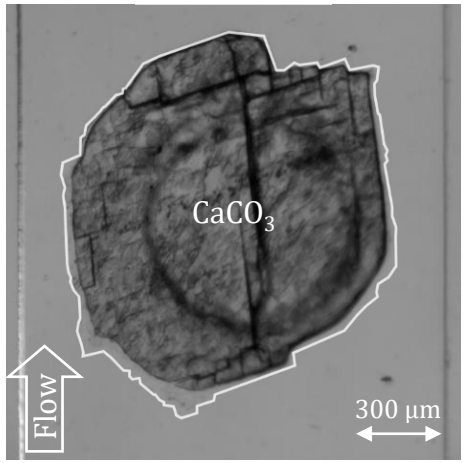
t_6 Bubbles detachment



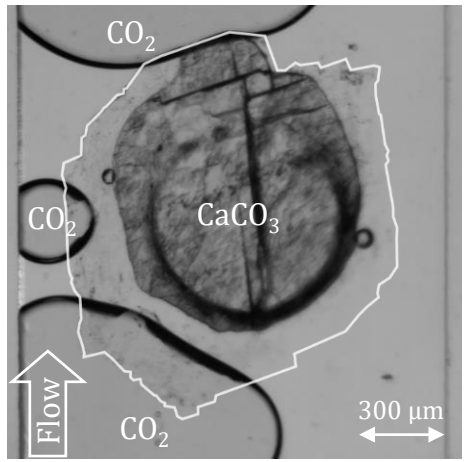
(Rembert et al., 2023b)

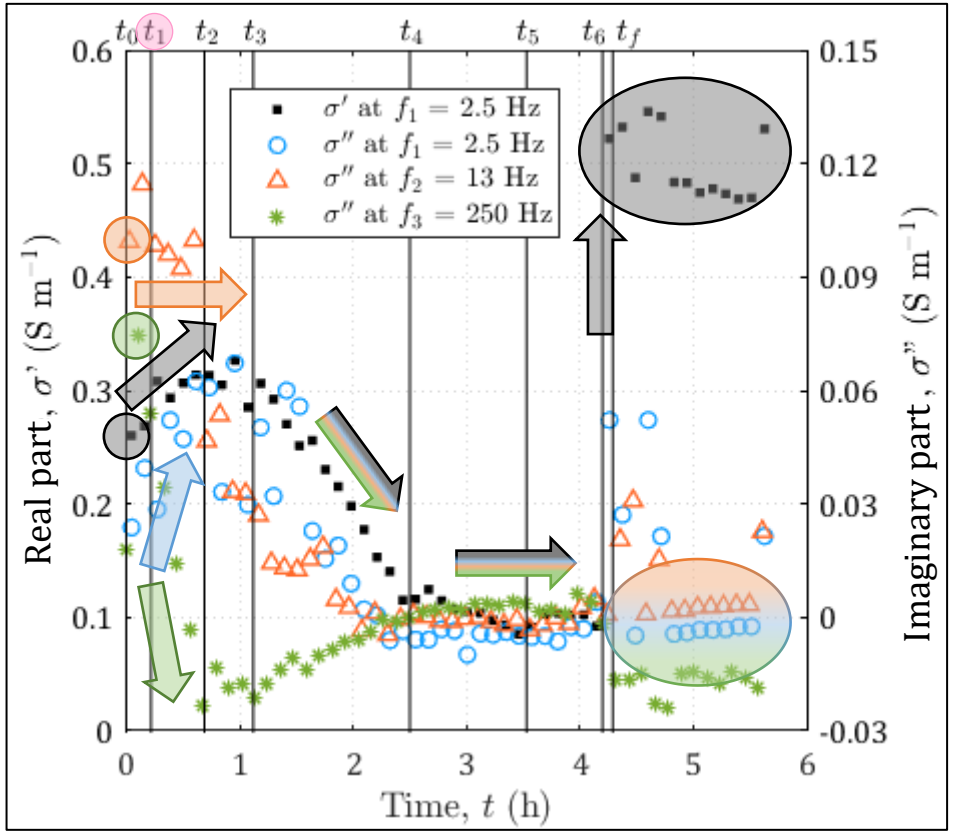
Qualitative interpretation from direct visualization

$t_1 = 0.22$ h

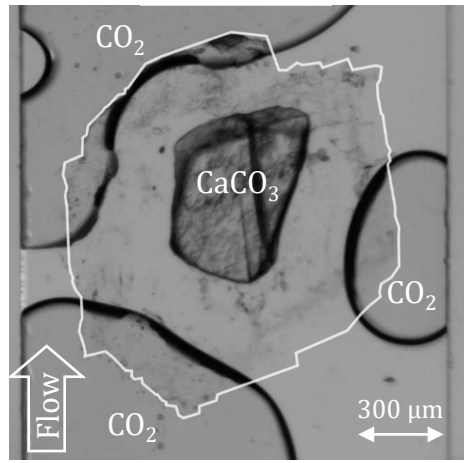


$t_3 = 1.12$ h

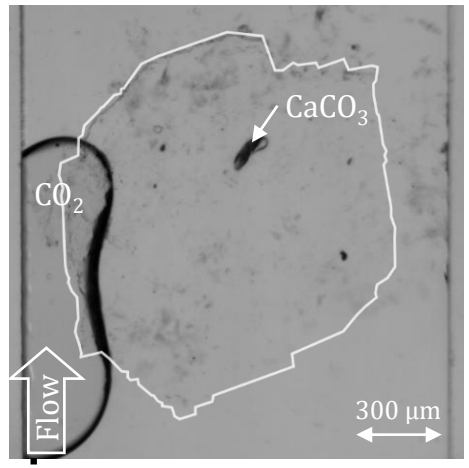




$t_4 = 2.50$ h



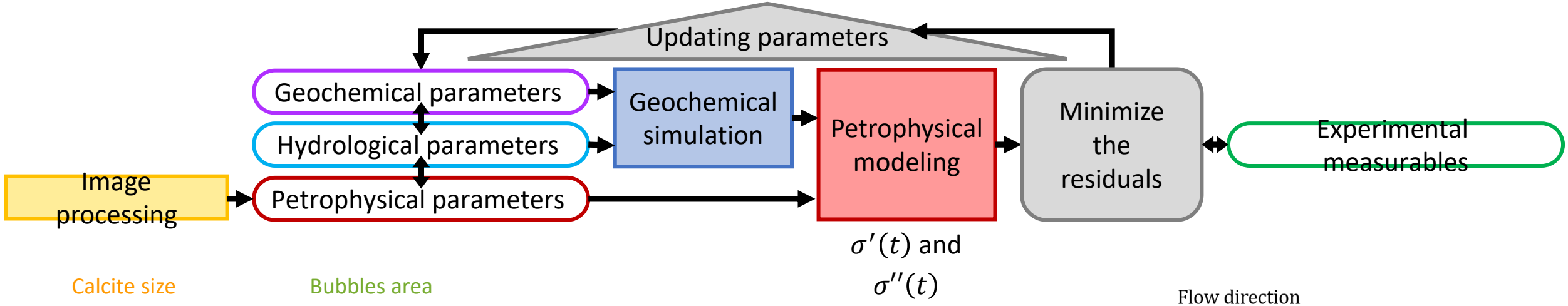
$t_6 = 4.20$ h



Increase of σ'

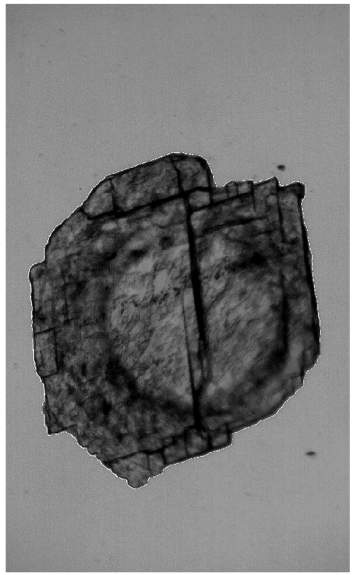
Initial polarization that shifts toward lower frequencies

Modeling workflow for quantitative simulation

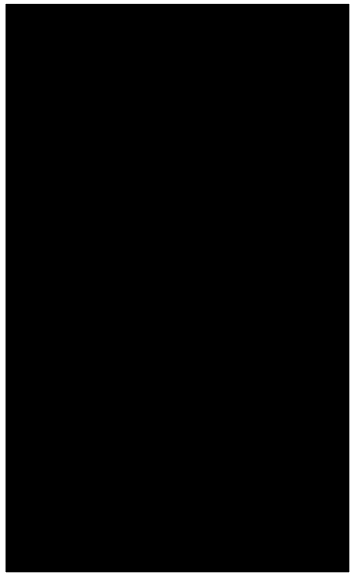


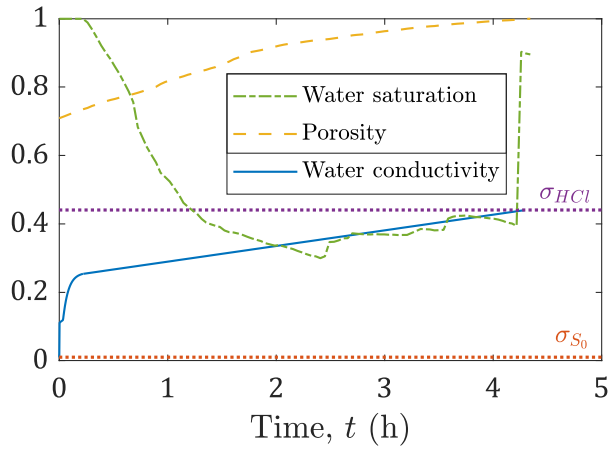
$\sigma'(t)$ and $\sigma''(t)$

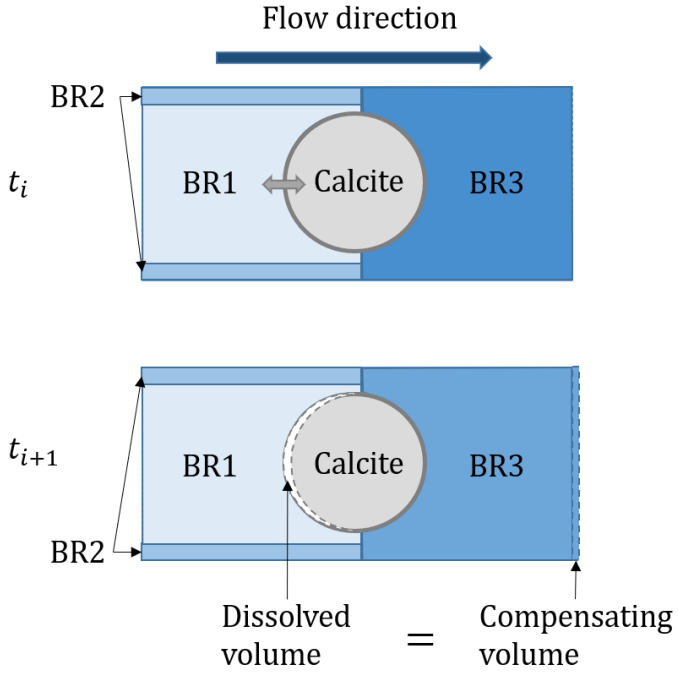
Calcite size ⇒ Porosity



Bubbles area ⇒ Water saturation



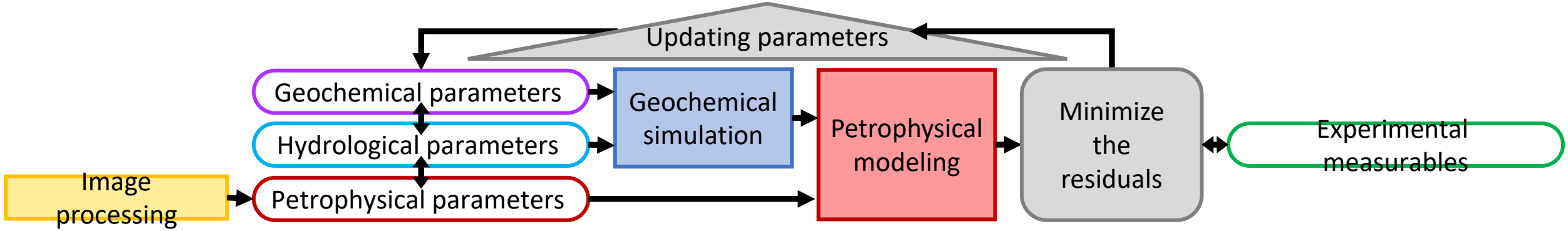


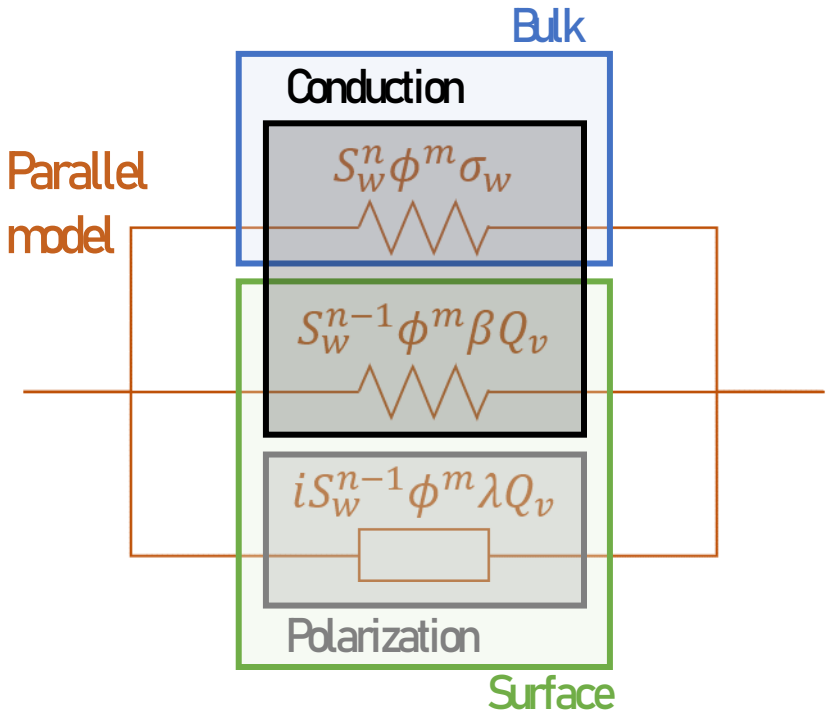


(Rembert et al., 2024)

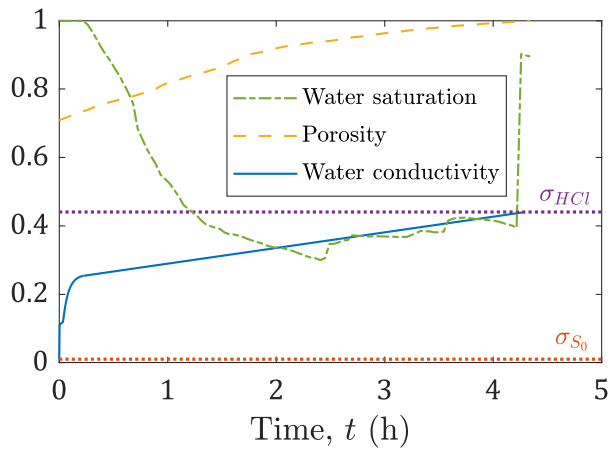
(Rembert et al., 2024)

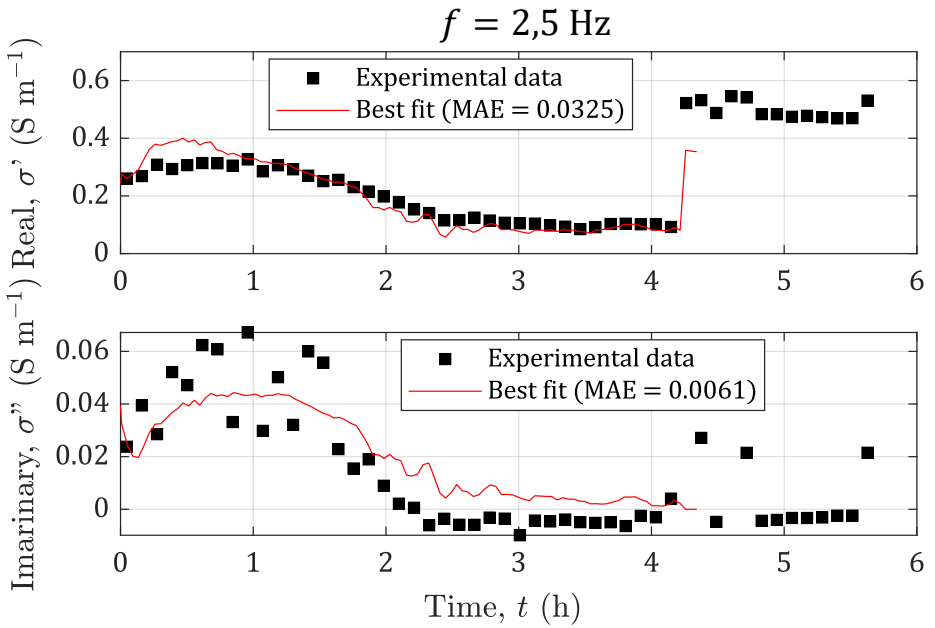
Modeling workflow for quantitative simulation





$\sigma'(t)$ and $\sigma''(t)$





We quantify the microscopic couplings in terms of parameters of interest obtained from this mechanistic appr

Conclusions and perspectives

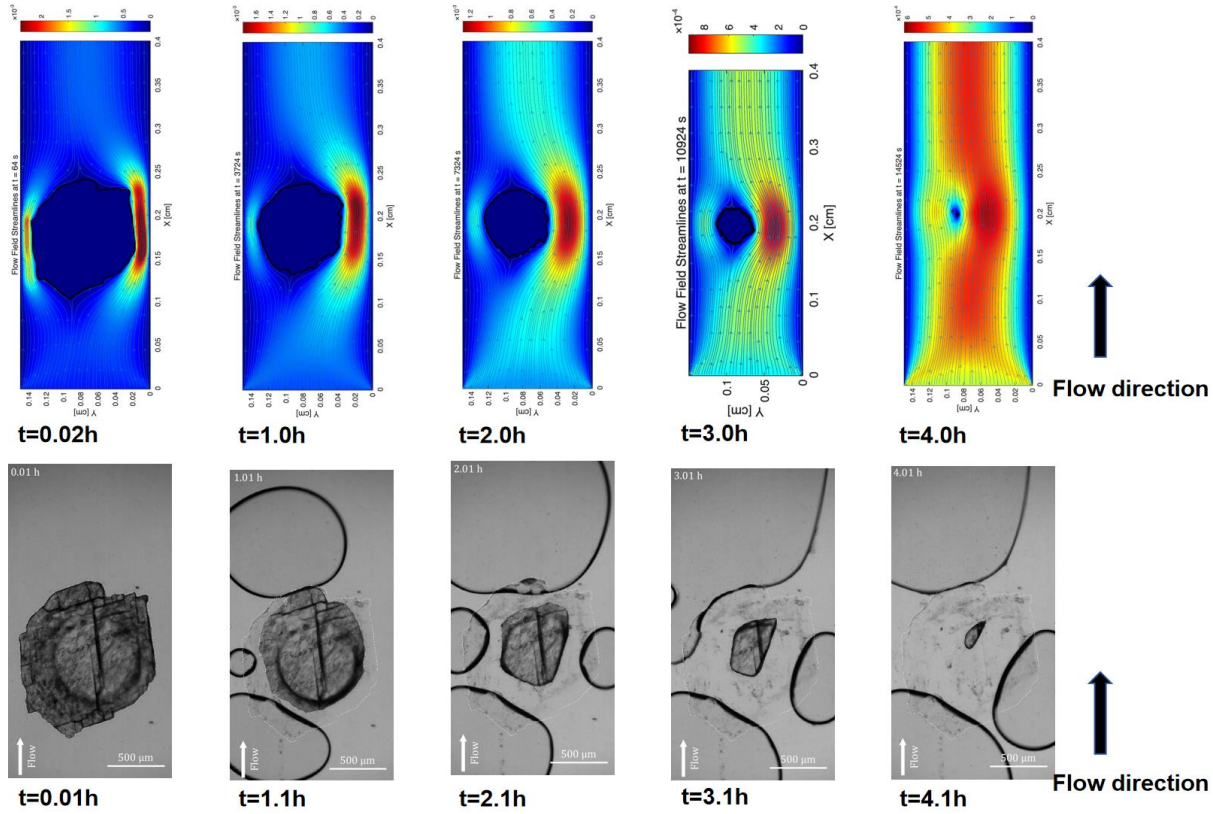
Conclusions

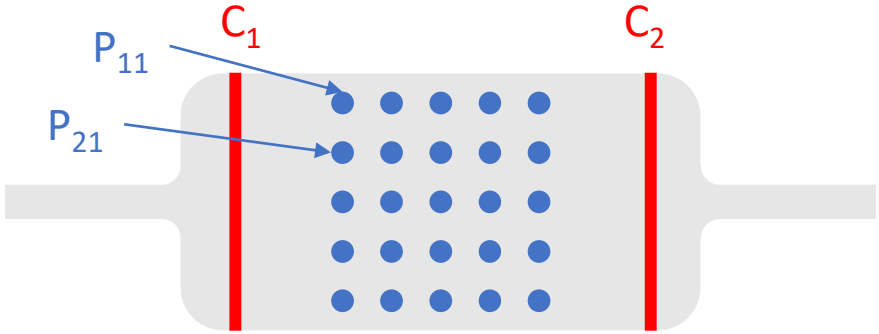
- Pioneer study that miniaturizes SIP on microfluidic chips,
- Direct visualization helps the SIP interpretation,
- Strong polarization is measured during calcite dissolution,
- The developed workflow enables quantifying petrophysical and geophysical parameters.

Perspectives

- ➥ Enhance the model toward a fully mechanistic approach based on CFD,
- ➥ Complexify the geometry towards a matrix of electrodes for 2D acquisition to mimic the geological porous matrix,
- ➥ Explore SIP for other coupled processes, including diphasic flow, colloidal transport, and biological activity.

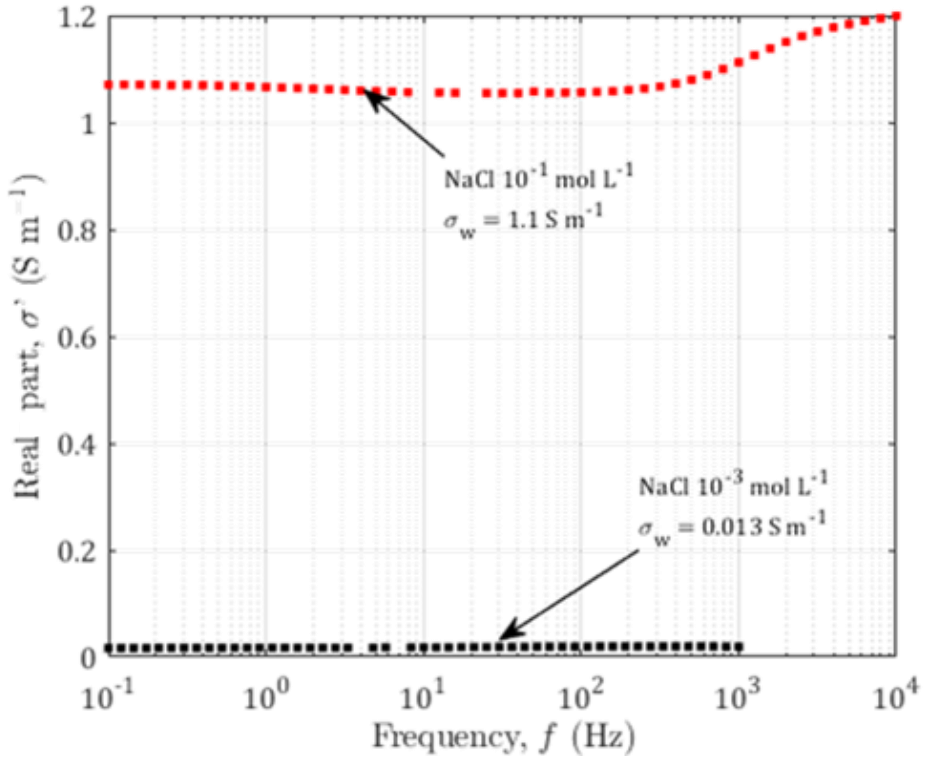
(Wang et al., in prep)

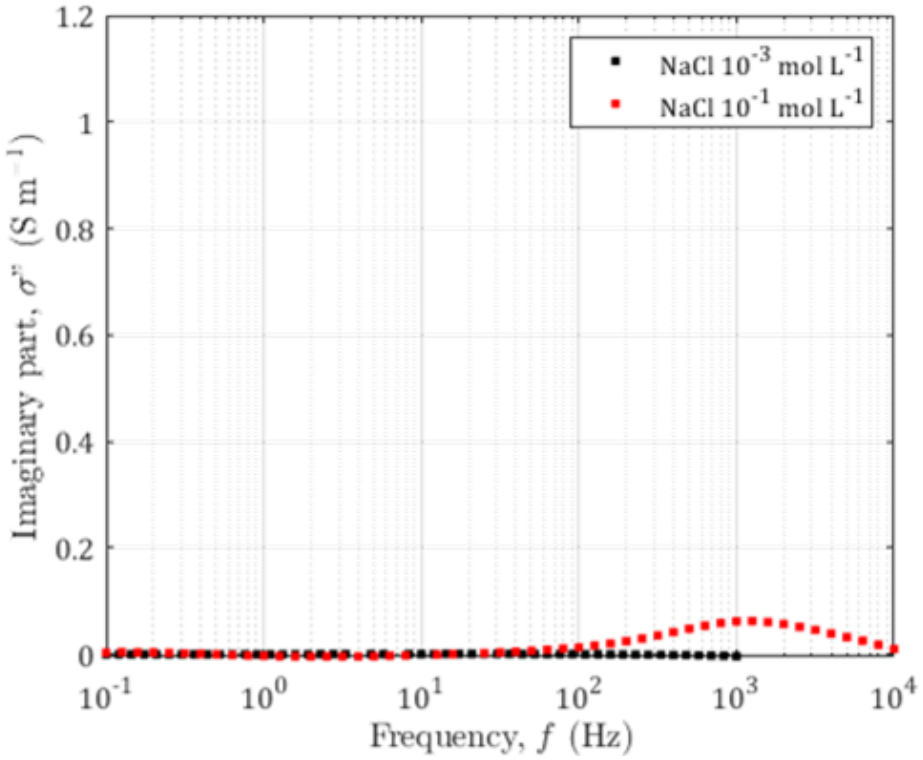




Testing the feasibility of the measurement at this scale

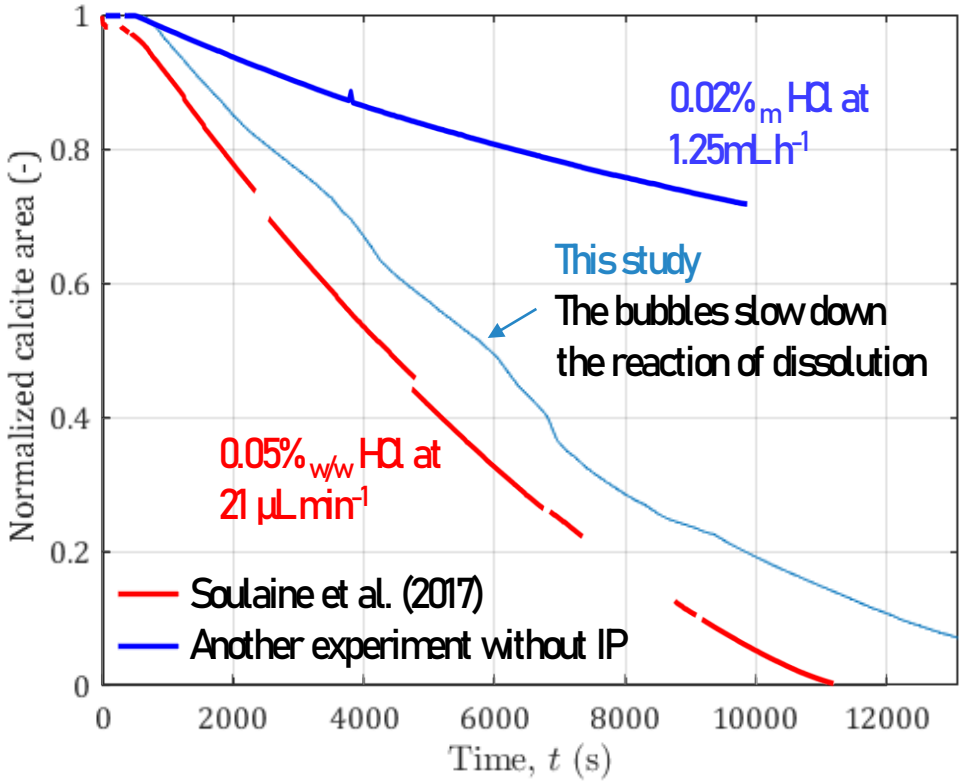
Saturating the micromodel with brine at two different concentrations





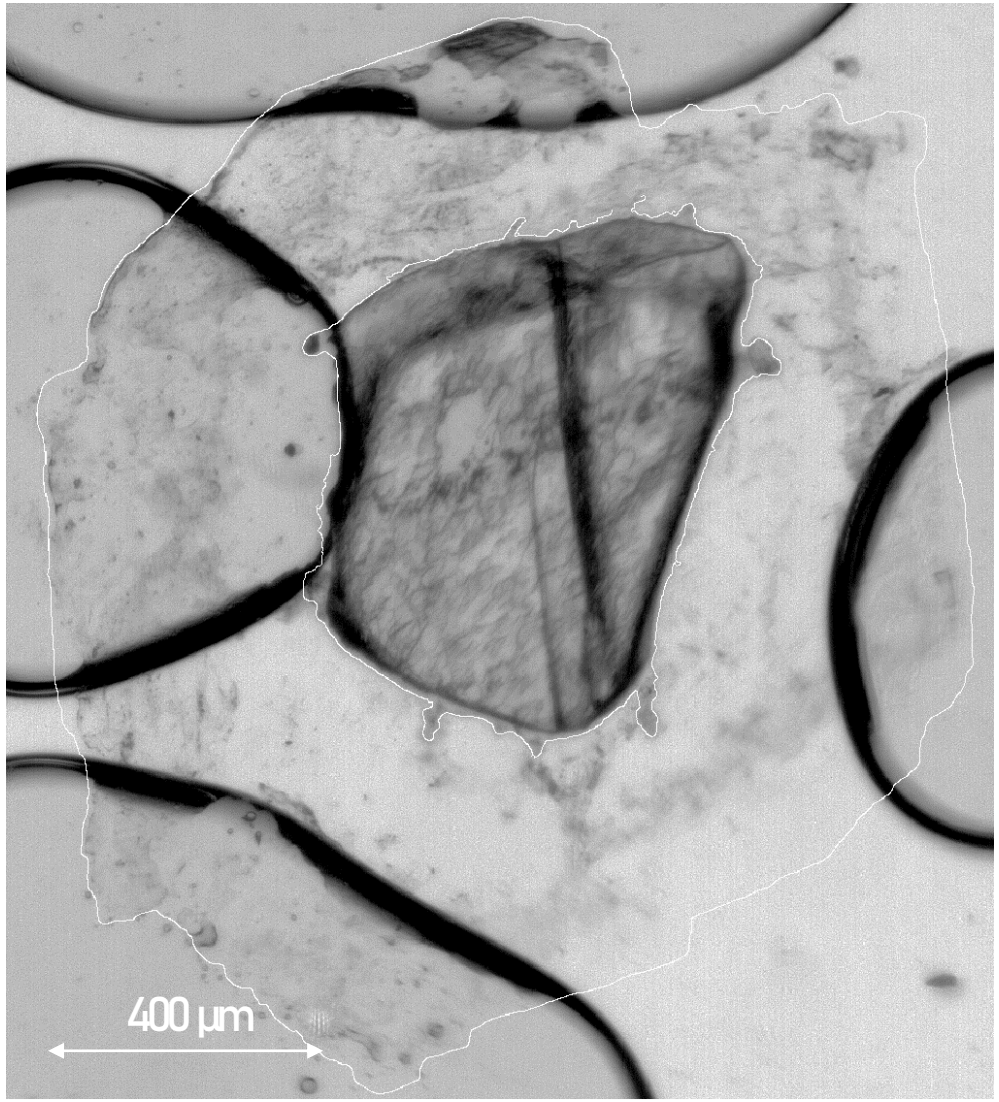
- We obtain consistent amplitudes on the in-phase conductivity
- There are low non-zero quadrature conductivities towards high frequencies for high salinity.

Monitoring the dissolution rate



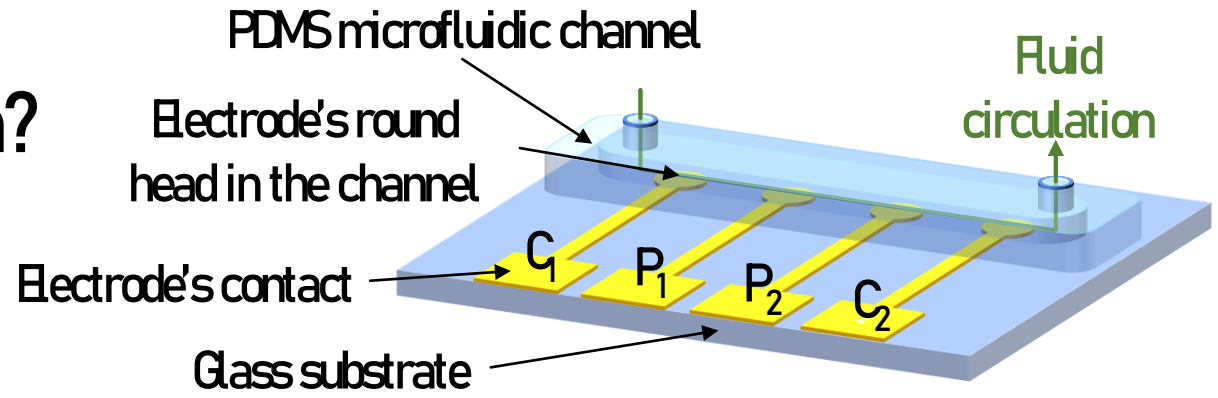
Entire image sequence

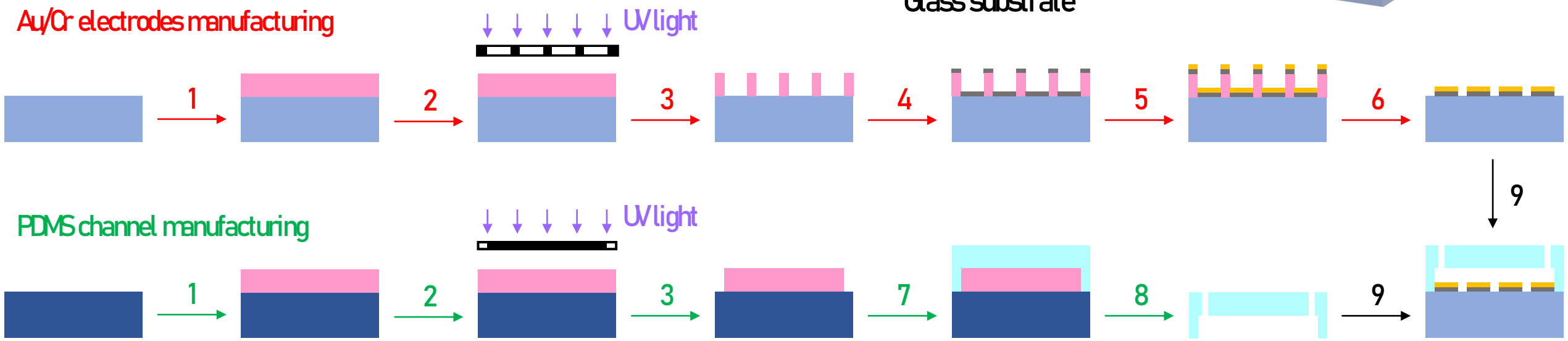
Contour detection with image processing



A way to conduct SIP at the microscale with direct visualization?

→ Microfluidic experiments equipped with electrodes





Resin
Glass
Au
Cr
PDMS
Silicon wafer

1. Resin deposit
2. Insolation
3. Development
4. Cr deposit
5. Au deposit
6. Lift-off
7. PDMS molding
8. Demolding and piercing
9. O_2 plasma bonding

Key equations of the workflow

Image processing

Porosity: $\phi = \frac{V - V_{CaCO_3}}{V}$

Water content: $\theta = \frac{V_w}{V} = \frac{V - V_{CO_2} - V_{CaCO_3}}{V}$

Water saturation: $S_w = \frac{\theta}{\phi} = \frac{V_w}{V - V_{CaCO_3}}$

Specific surface area: $S_s = \frac{h\, P_{CaCO_3}}{V_{CaCO_3} \rho}$

V: volume of the window

V_{CaCO_3}: calcite volume

V_w: pore water volume

V_{CO_2}: CO_2 volume

h: height of the channel

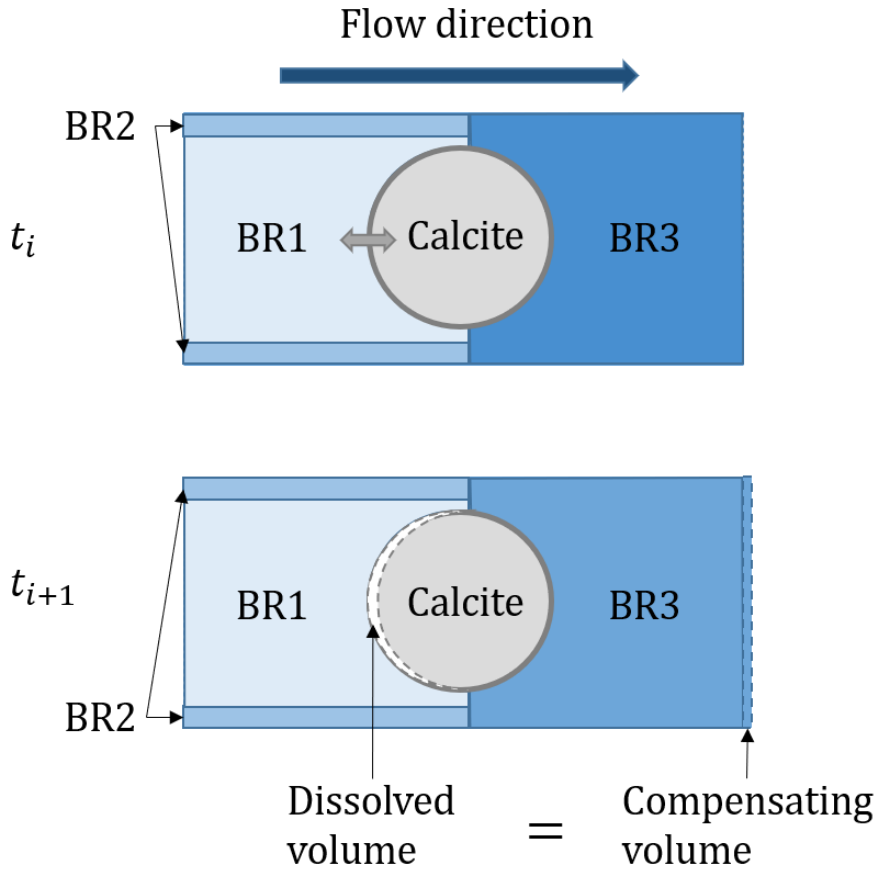
P_{CaCO_3}: calcite perimeter

ρ (= 2710 kg m^{-3}): calcite density

Key equations of the workflow

Geochemical modeling: PhreeqC model

- Batch reactors:
  - BR1: pre-reaction
  - BR2: non-reactive
  - BR3: post-reaction
- 10 s time step for partial replacement (55% of initial PV).
- The volume of BR2 was estimated to retrieve the porosity.
- BR3 volume is adapted to compensate calcite dissolution.



Key equations of the workflow

Petrophysical modeling

Vinegar and Waxman (1984) model for partially saturated conditions:

$$\sigma' = \phi^m S_w^n \left(\sigma_w + \frac{\beta Q_v}{S_w}\right)$$

$$\sigma'' = \phi^m S_w^{n-1} \lambda Q_v$$

$$Q_v = \frac{\phi - 1}{\phi} \rho \mathrm{CEC}$$

$$\beta = \frac{1}{2}\left(\gamma_{H^+}\beta^0_{H^+} + \gamma_{Ca^+}\beta^0_{Ca^{2+}}\right)$$

m: cementation exponent ($m = 1$)

n: saturation exponent ($n = 2$)

β ($m^2 s^{-1} V^{-1}$): mobility of counterions contributing to conduction (hydrogen and calcium)

$\lambda = \beta/6$ ($m^2 s^{-1} V^{-1}$): mobility of counterions contributing to polarization ($m^2 s^{-1} V^{-1}$)

Q_v ($C m^{-3}$): charge compensating the surface charge of the solid phase per unit of pore volume

ρ ($= 2710\ kg\ m^{-3}$): calcite density

CEC ($mEq\ g^{-1}$): cationic exchange capacity

γ: activity coefficient obtained from PhreeqC model

Key equations of the workflow

Petrophysical modeling result

Vinegar and Waxman (1984) model for partially saturated conditions:

$$\mathrm{CEC} = -Q_0 S_S$$

The proportionality means that Q_0 remains stable.

Q_0 ($\mathrm{Cm^{-3}}$): surface charge density of calcite