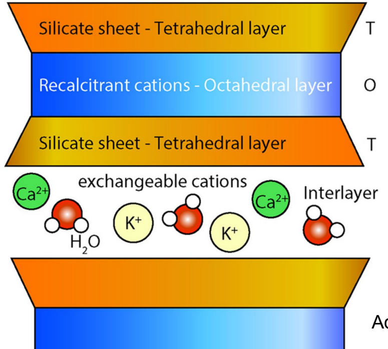
Combining X-ray absorption and Induced Polarization Spectroscopies for in situ monitoring of Cation Exchange in clay materials

A. Courtin[1], D. Jougnot[2], E. Paineau[3], D. Roy[4], D. Vantelon[4], A. Dallaporta[2] and E. Léger[1]

[1]Université Paris-Saclay, CNRS, GEOPS, Orsay, France; [2]Sorbonne Université, CNRS, EPHE, UMR 7619 METIS, Paris, France; [3]Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides,Orsay, France; [4]Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette, France.

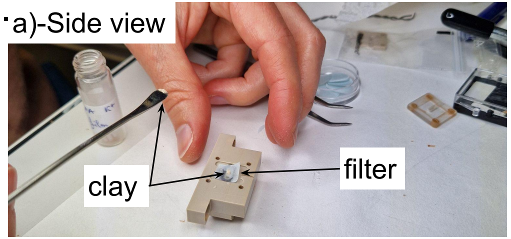


Adapted from Zeyen et al., 2022

Aims & Objectives

→Monitoring *in operando* cation-exchange $K^+ \leftrightarrow Ca^{2+}$ in a Ca-montmorillonite

- Three main objectives:
  - Purely technical : Monitor Cation exchange K^+ (and Ca^{2+}) within a Montmorillonite, using two in-situ techniques, in dynamic mode *in operando*;
  - Compare the reactivity of these two techniques and decipher what they actually sense ;
  - Link the signals with the chemical composition of the exchanged cations.
- Two non-destructive methods:
  - X-Ray Absorption Near Edge Structure (LUCIA beamine)
  - Spectral Induced Polarization

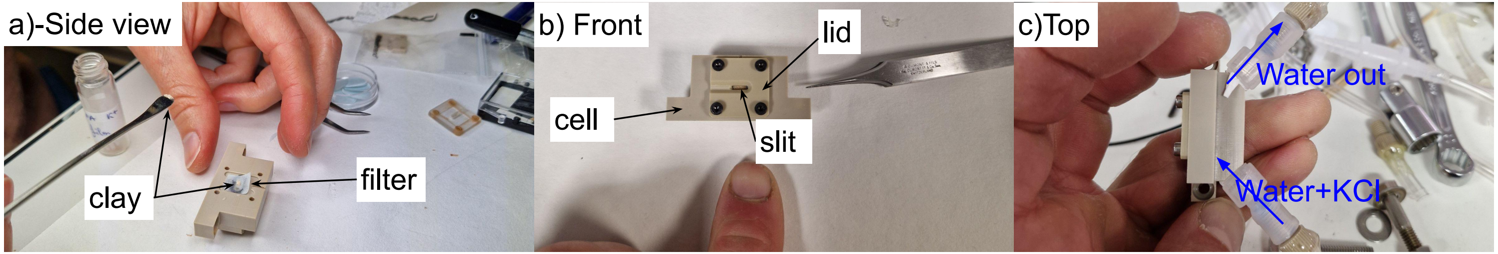


Material and Methods - Cell and material

- Material: Ca-Montmorillonite
- Protocol: cell filled with c.a. 0.1 g of Ca-Montmorillonite, 4 different KCl salinities (0.01, 0.05, 0.1, 1 M of KCl), continous solution flux of a 8 cc/min.

1. Method: **XANES** on LUCIA (SOLEIL synchrotron source, FR) with low energy K-edge for K (and Ca) to follow the interlayer evolution & microbeam size (2.5 x 2.5 μm^2).

2. Method: The **Spectral Induced polarization** (SIP) method allow the determination of the complex conductivity and its spatial distribution of the near surface Frequency range: 10 kHz - 0.02 Hz (58 steps)



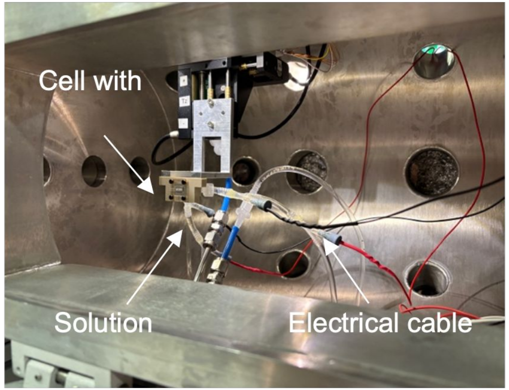
~0.1 g/1.7 mm^3

Material and Methods - Dual approaches

- Material: Montmorillonite saturated with Ca
- Protocol: cell filled with c.a. 0.1 g of Ca-Montmorillonite (Ca-MMT), different KCl salinities (0.01, 0.1 KCl), continous solution flux of a few cc per minute .

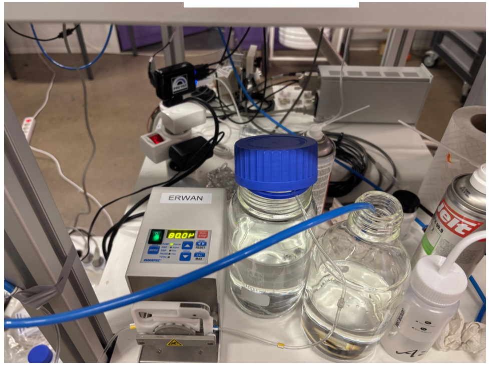
1. Method: **XANES** on LUCIA (SOLEIL synchrotron source, FR) with low energy K-edge for K (and Ca) to follow the interlayer evolution & microbeam size (2.5 x 2.5 μm^2).

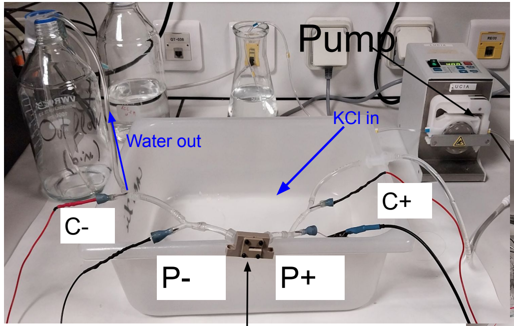
2. Method: **Spectral Induced polarization** (SIP), characterizes the electrical conduction of charge carriers (liquid) and polarization phenomenon (surface-fluid interface).



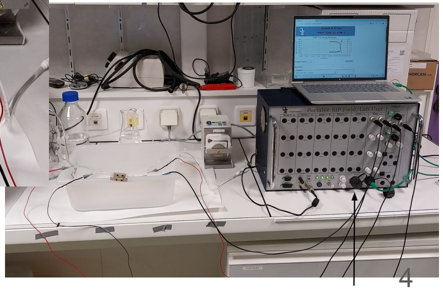
Beam Chamber

LUCIA





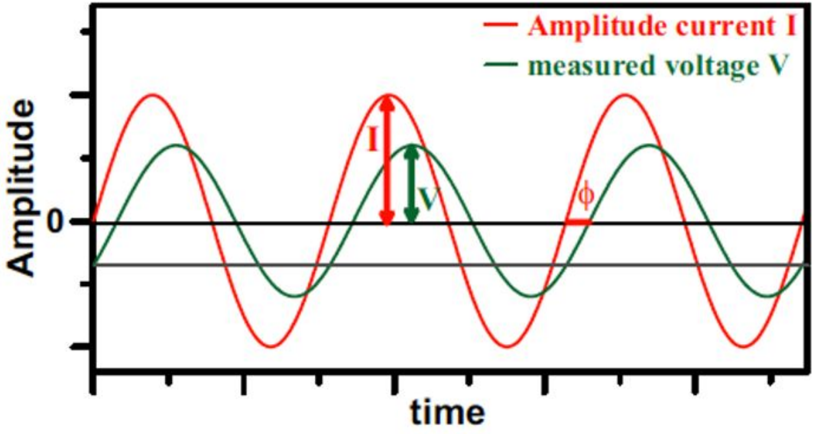
Cell (1.7 mm^3)

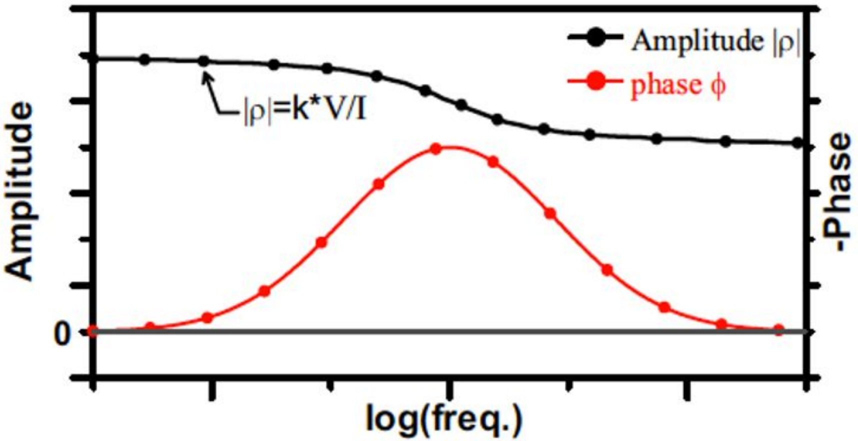


PSIP

M&Ms : Spectral Induced Polarization

The **Spectral Induced polarization** (SIP) method allow the determination of the complex conductivity and its spatial distribution of the near surface:





At a given frequency ω

I: injected sinusoidal current [A]

U: measured electrical potential difference [V]

$$\sigma^* = |\sigma| e^{i\varphi}$$

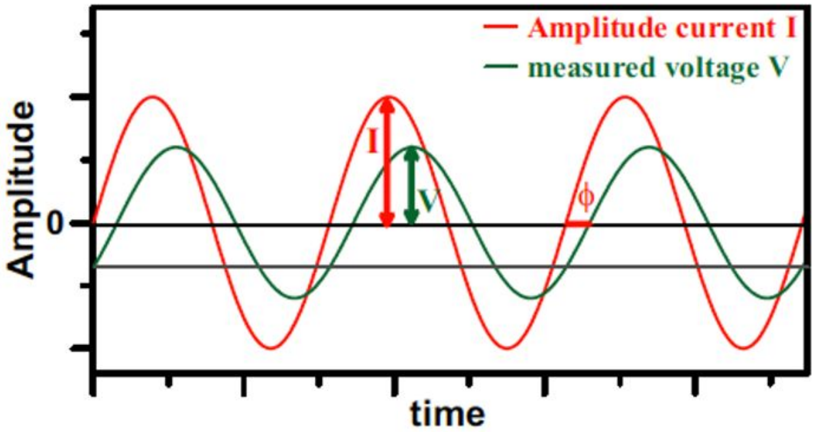
Complex conductivity

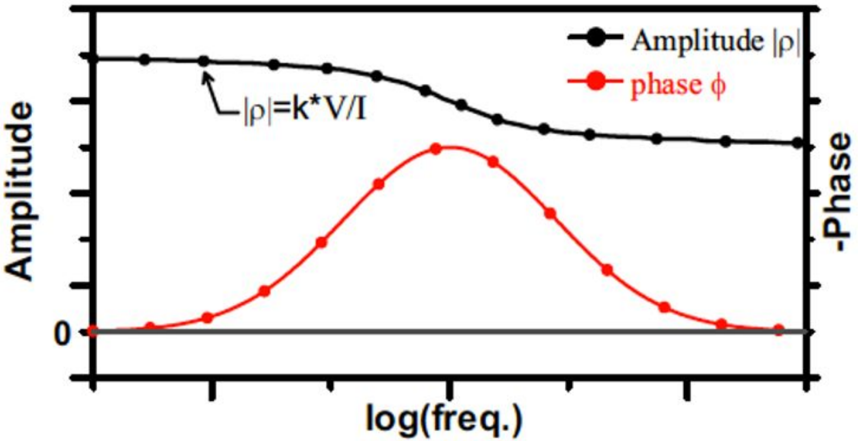
σ: electrical conductivity [S/m]

φ: phase shift [rad] between I and U (polarization of the medium)

M&Ms : Spectral Induced Polarization

The **Spectral Induced polarization** (SIP) method allow the determination of the complex conductivity and its spatial distribution of the near surface:





Measuring for a low-frequency range (mHz to kHz) and its spectral behaviour

$$\sigma^* = |\sigma| e^{i\varphi}$$

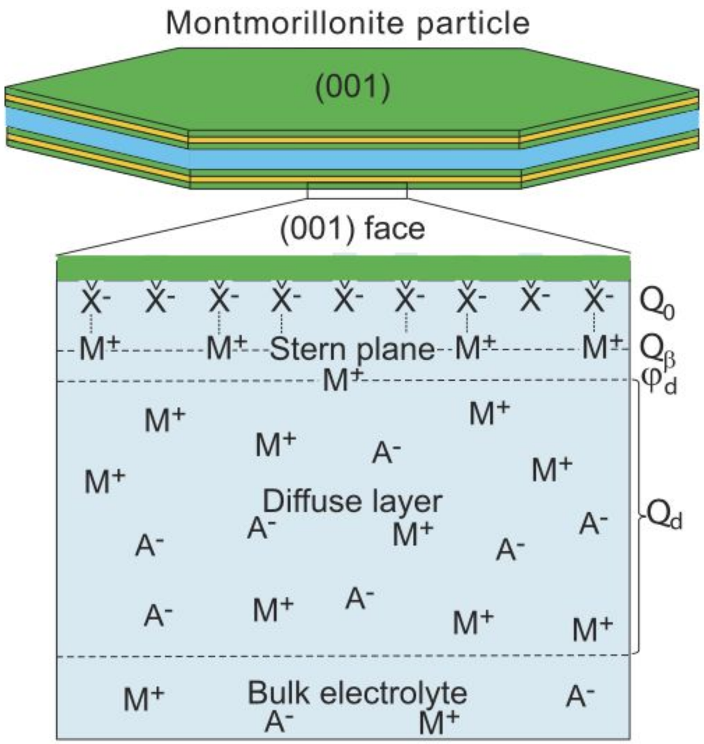
$$\sigma^* = \sigma' + i\sigma''$$

$\sigma'(\omega)$ real conductivity [S/m]: information on conduction currents (affected by pore geometry, fluid chemistry…)

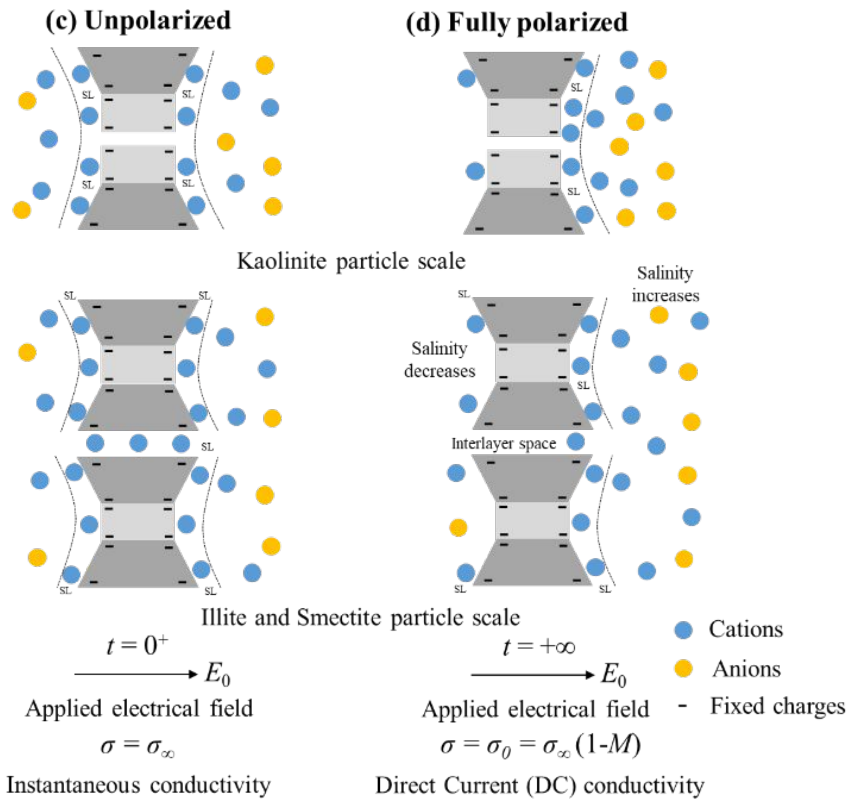
$\sigma''(\omega)$ imaginary conductivity [S/m]: information on polarization currents (affected by interface properties EDL)

M&Ms : Spectral Induced Polarization

Electrical Double Layer - Concept



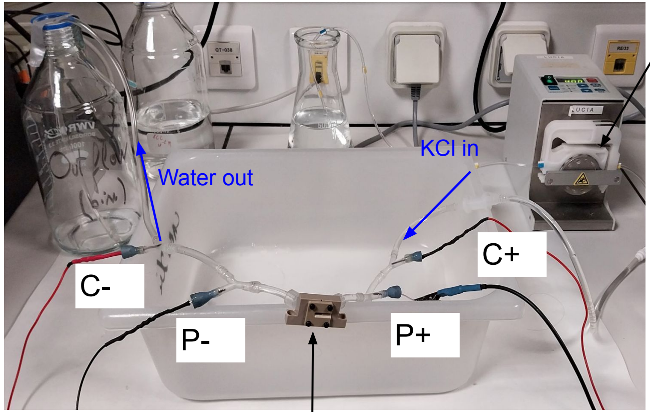
Maineult et al. 2025

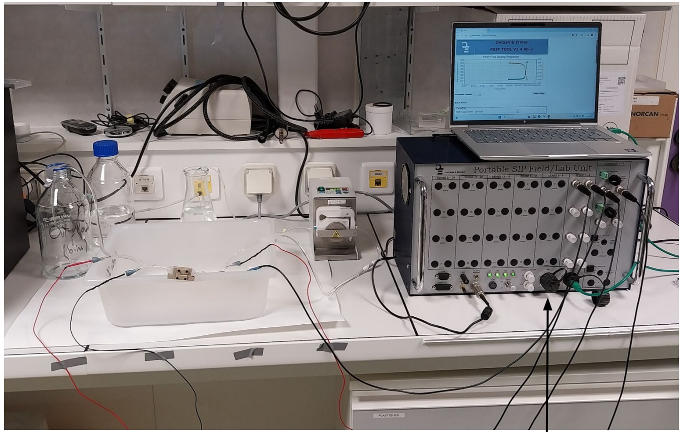


Luo et al. (under revision)

M&Ms : Spectral Induced Polarization

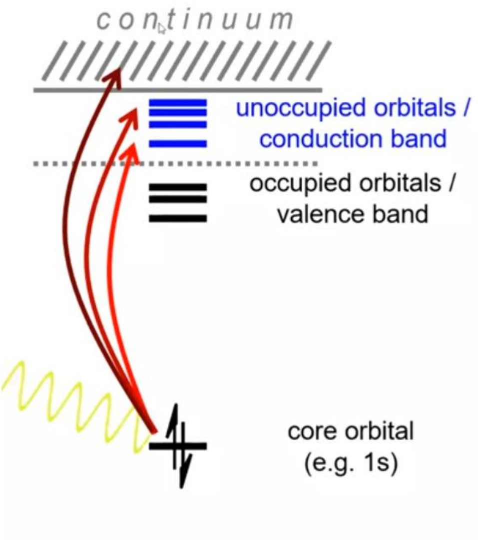
Frequency range: 0.02 Hz-10 kHz (58 steps). Ag-AgCl electrodes. KCl @8 cc/min @ [10^{-2},10^{-1}] mol/l

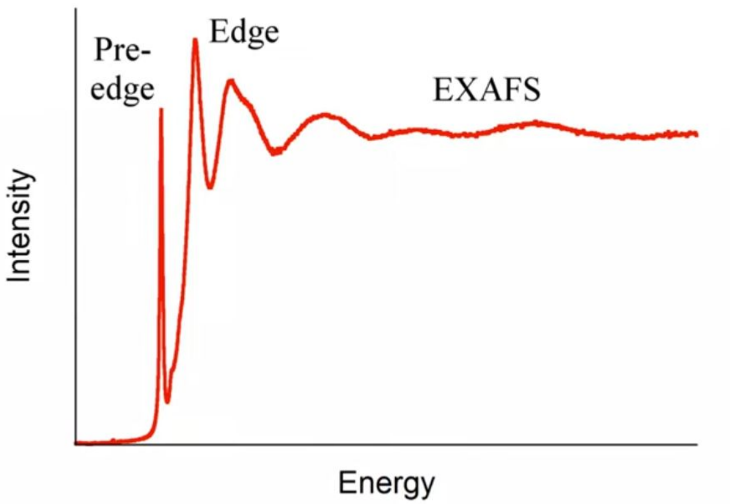




M&Ms : XANES

- XANES gives information on local site symmetry, is charge state sensitive, and reflects orbital occupancy.
- Used to elucidate the local electronic structure of an atom as it evolves throughout a reaction or electrochemical process





Cornell University, PREM XANES talk by Chris Pollock and Louise Debefve.

M&Ms : XANES

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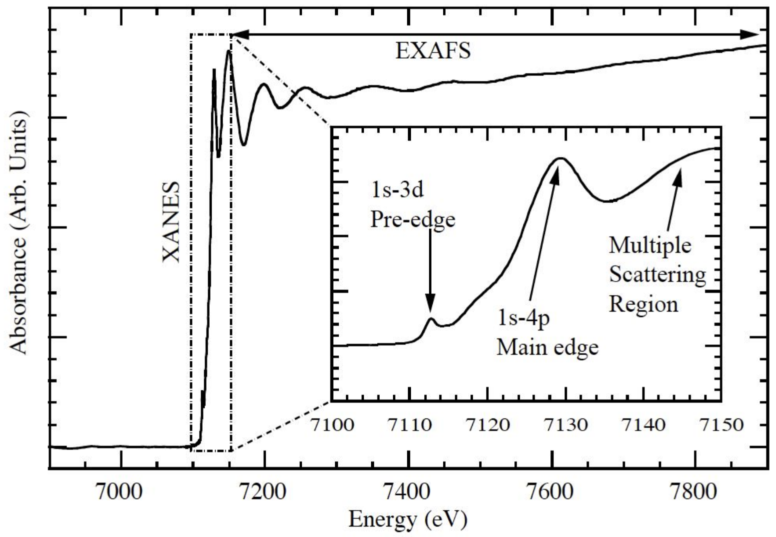

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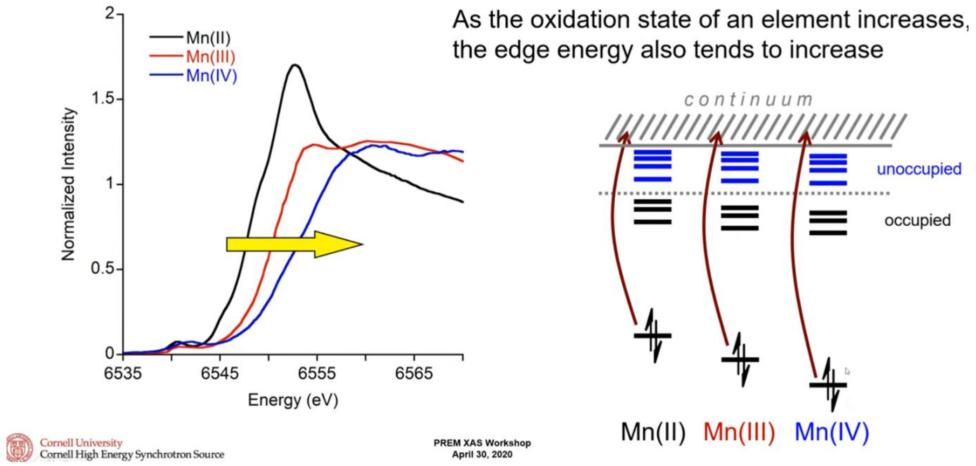
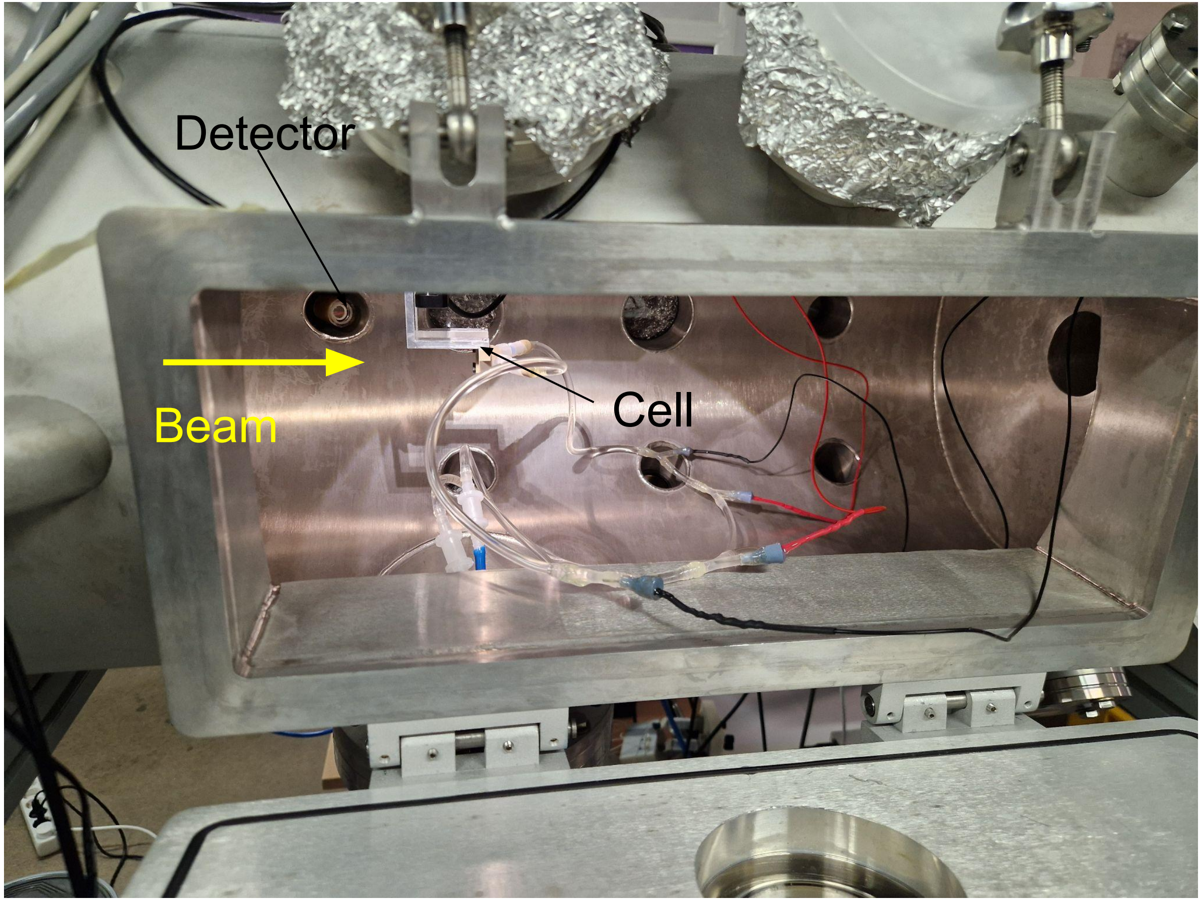
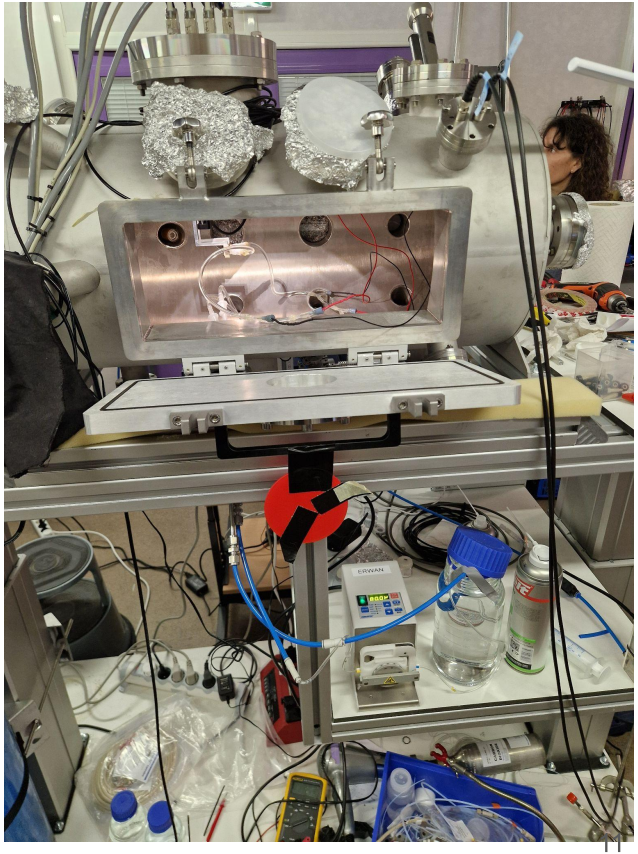


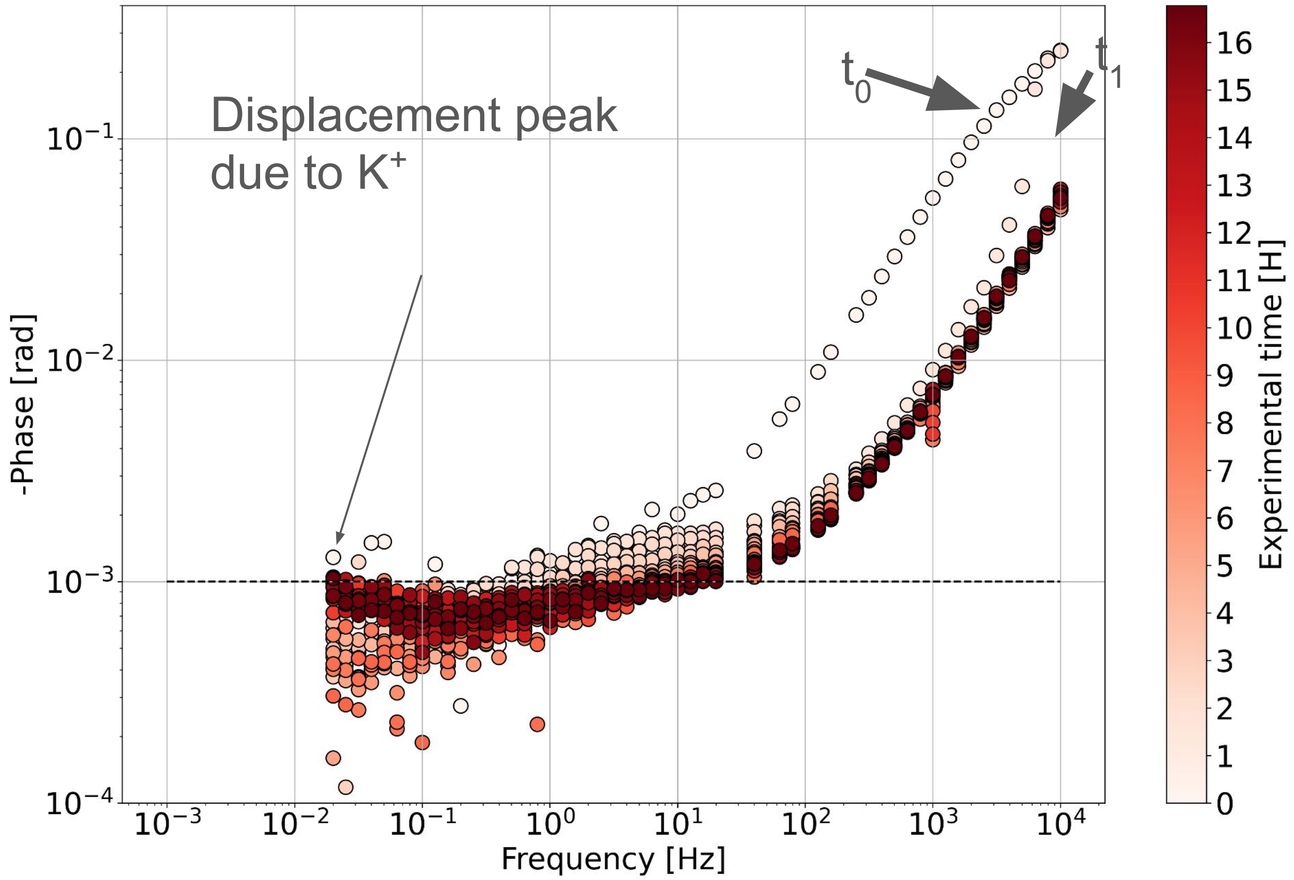
Cornell University, PREM XANES talk by Chris Pollock and Louise Debefve.

M&Ms : Lucia Beamline



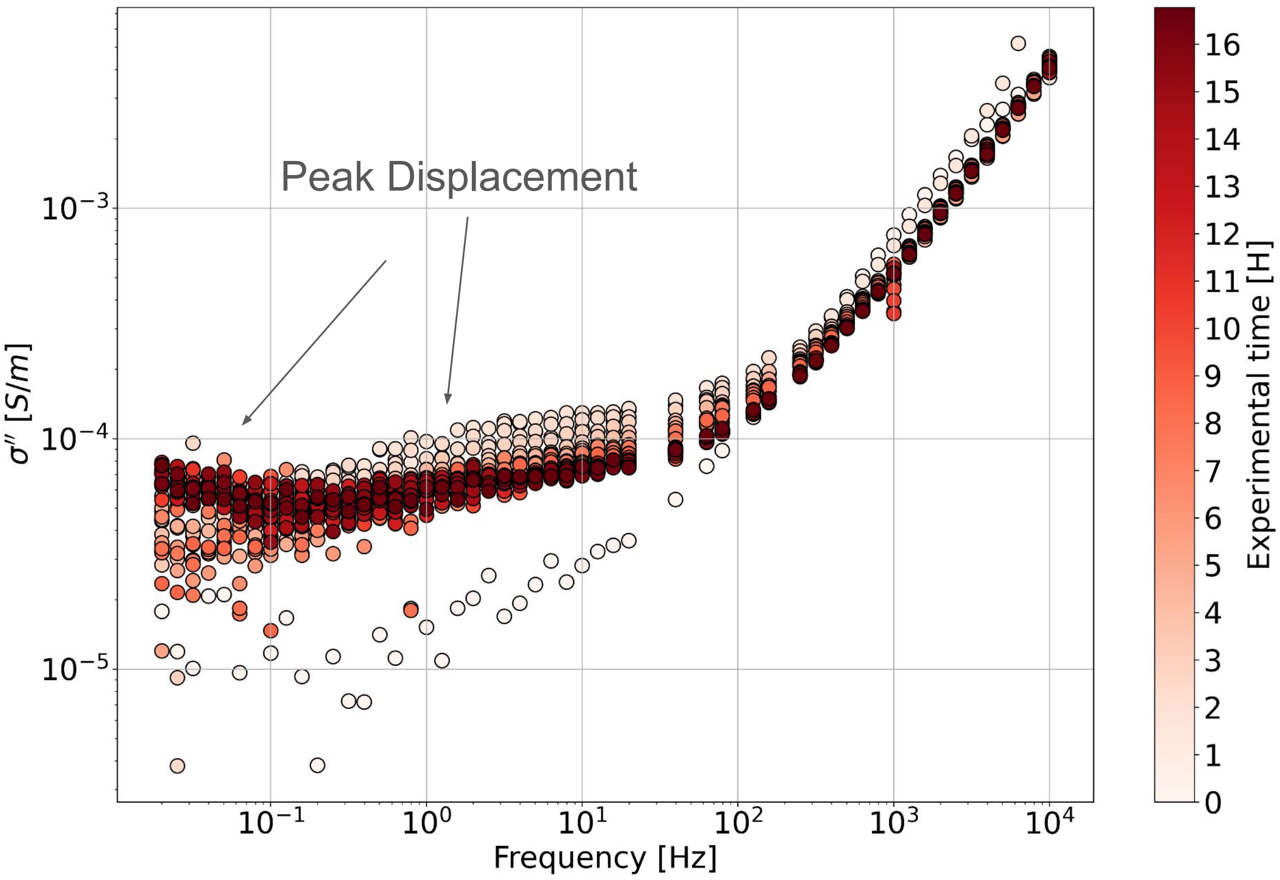


Results : SIP



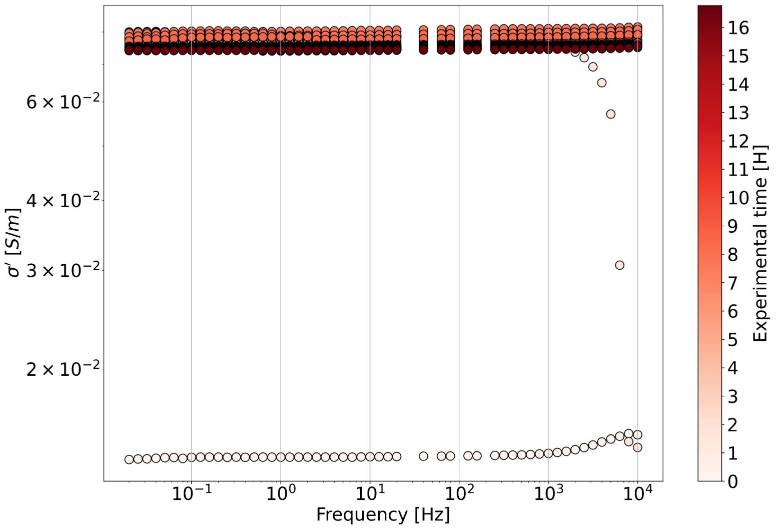
Displacement peak
due to K+
t0
t1
-Phase [rad]
Frequency [Hz]
Experimental time [H]

Results : SIP

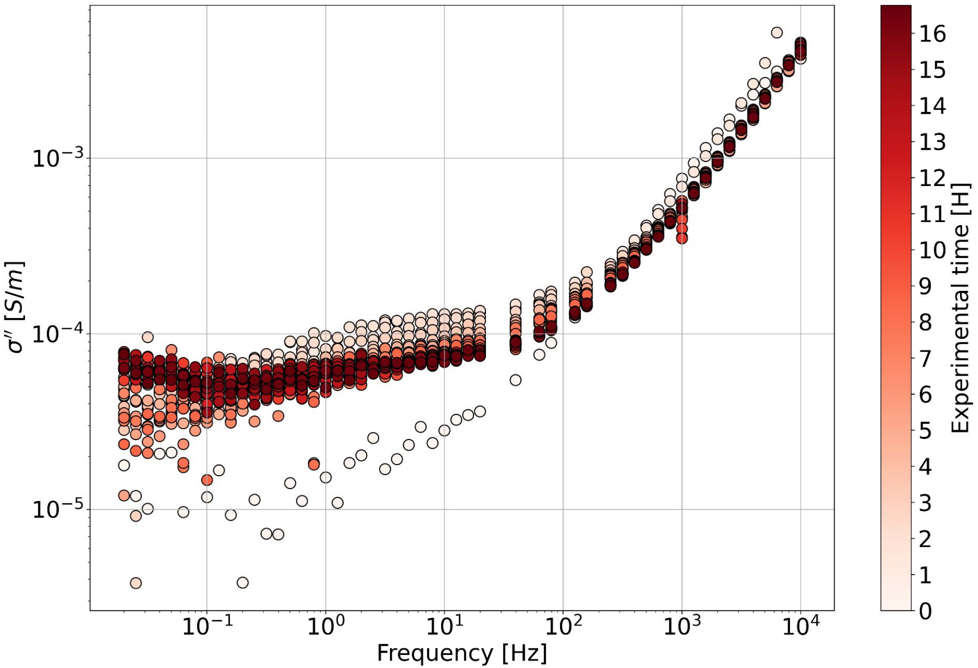


Peak Displacement
10^{-3}
10^{-4}
10^{-5}
σ'' [S/m]
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
Frequency [Hz]
Experimental time [H]
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Results : SIP



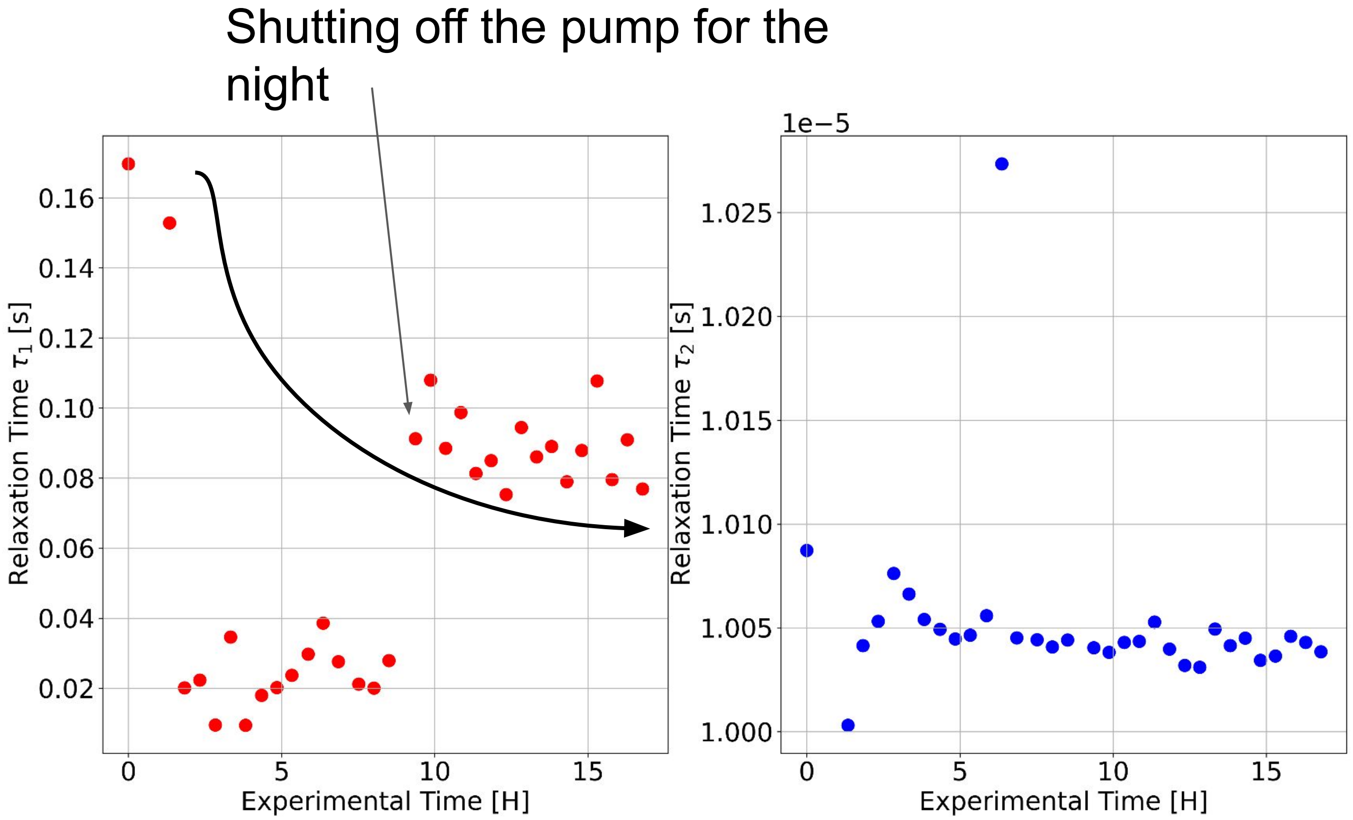
σ' [S/m]
6×10^{-2}
4×10^{-2}
3×10^{-2}
2×10^{-2}
10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}
Frequency [Hz]
Experimental time [H]
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16



σ'' [S/m]
10^{-3}
10^{-4}
10^{-5}
10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}
Frequency [Hz]
Experimental time [H]
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Results : SIP

Double Cole-Cole model fitting (Pelton et al., 1978)- Low and High frequency Relaxation time



Results : SIP

- Low frequency relaxation time τ decreases:
  - According to Schwarz (1962), could be due to change in the TOT geometry (interlayer spacing is different because of Ca^{2+} to K^{+} substitution)
  - Ionic diffusivity increases, $D(K^{+}) > D(Ca^{2+})$

$$\tau = \frac{L_c^2}{2D}$$

- $D \nearrow\nearrow$ thus $f \nearrow\nearrow$

$$f = \frac{2D}{L_c^2}$$

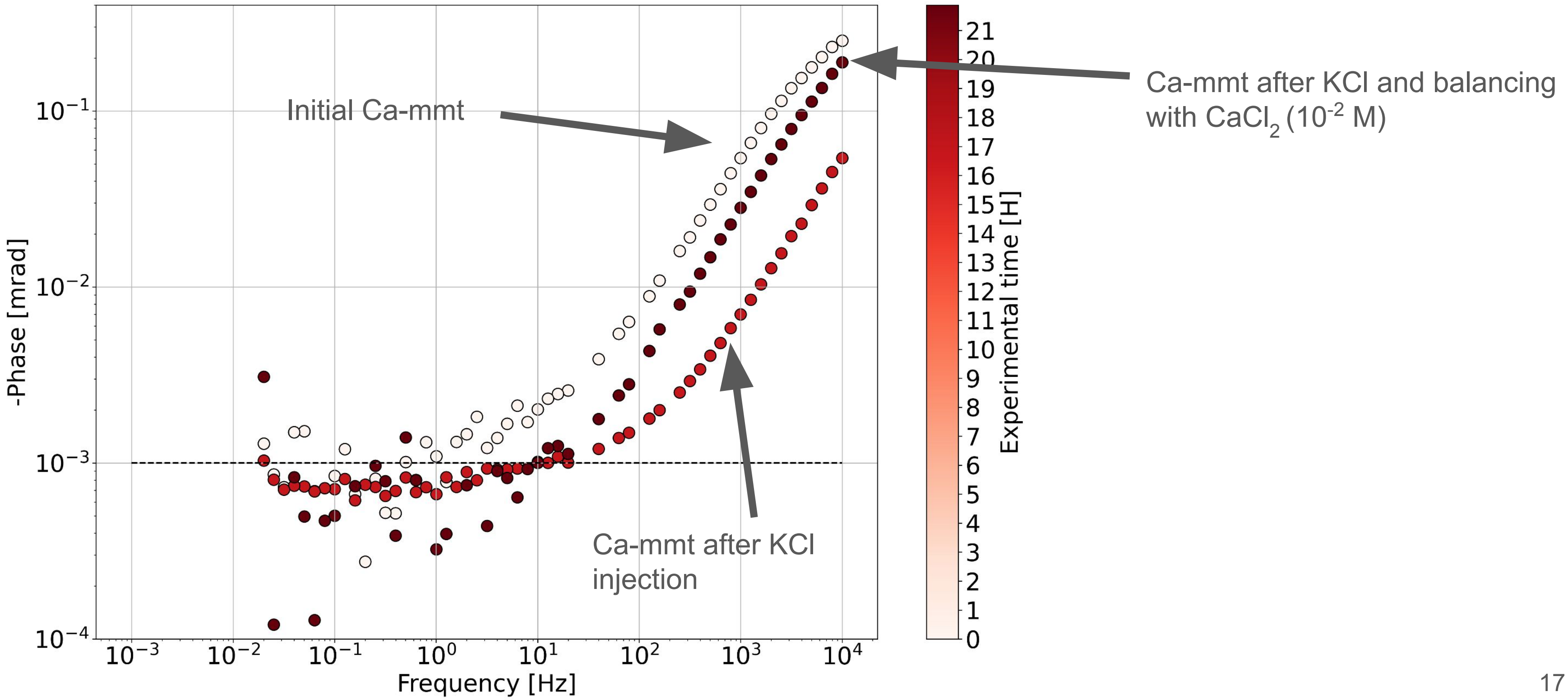
This time constant corresponds to the relaxation time of the diffusion process of the counterions in the Stern layer with a characteristic distance L_c

$$\rho^*(\omega) = \rho^0\left[1 - m_{c1}\left(1 - \frac{1}{1+(i\omega\tau)^{c_1}}\right)\right]\left[1 - m_{c2}\left(1 - \frac{1}{1+(i\omega\tau)^{c_2}}\right)\right].$$

Double Cole-Cole

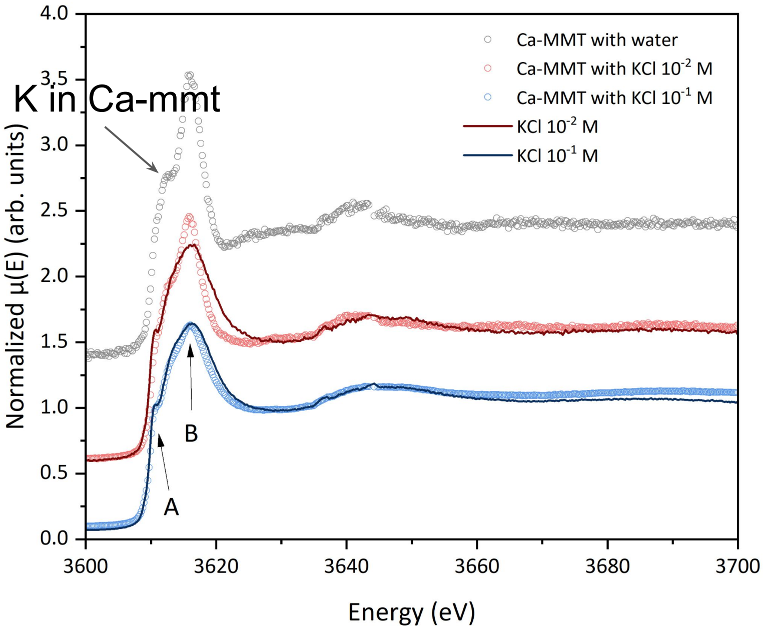
Results : SIP

Hysteresis on the phase. Perenniale chang in the Ca-mmt.



Results : XANES

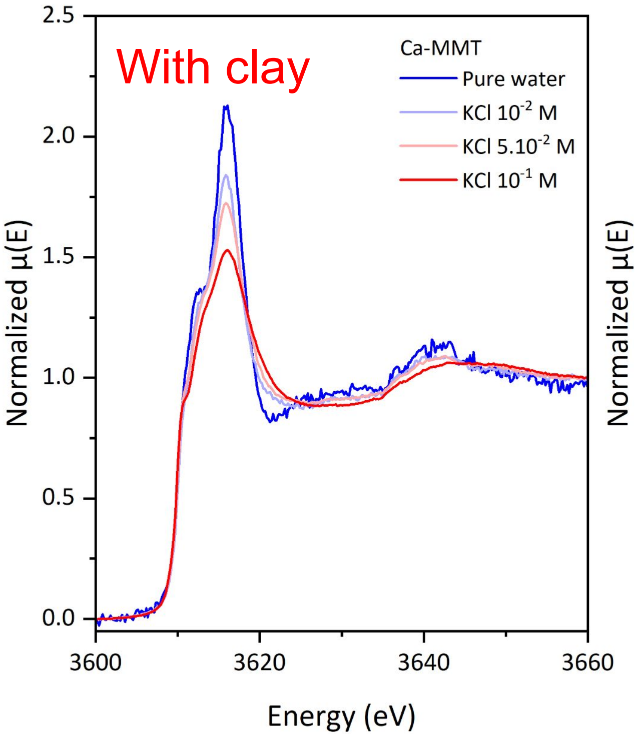
- Discrete but clear evolution of the XANES spectra from K K-edge signal of the solution to the K K-edge signal within the interlayer of Montmorillonite

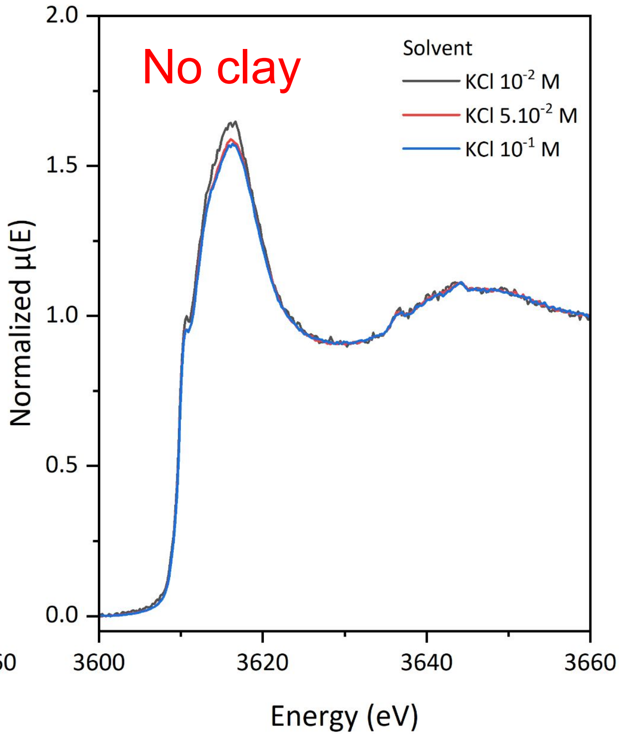


- Peak widening because of different K state and positions
- Losing shoulder indicating a local structural arrangement of atoms around the K
- K in the interlayer, in the solution and in the Ca-mmt

Results : XANES

- Discrete but clear evolution of the XANES spectra from K K-edge signal of the solution to the K K-edge signal within the interlayer of Montmorillonite

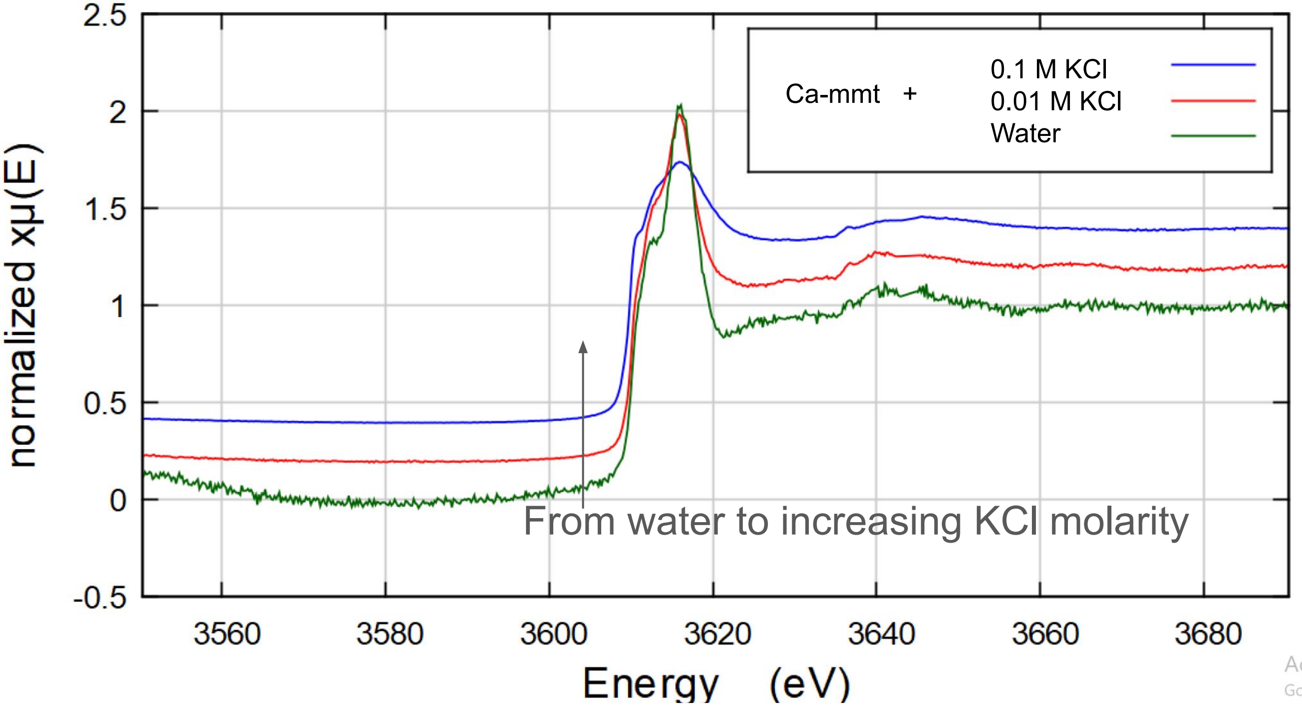




- Molarity effect

Results : XANES

- XANES gives information on local site symmetry, is charge state sensitive, and reflects orbital occupancy
- Highlighting K in the interlayer -> structural evolution



Ac
Go

Conclusions and Outlooks

- Both methods see something happening
  - SIP is certain that it is K^+ <-> Ca^{2+} in the EDL
  - XANES sees K in the different phases, solution and interlayer.
  - XANES+SIP monitor K getting into the interlayer !

❖ TODO :

➢ Need to compare with Ca, K Edge for computing Cation exchange rate

➢ EXAFS need to be processed for environment characterization

➢ Performed SIP under electron beam (shielding issues)

➢ Performed XRF first on the sample to constrain mineralogy