

Pore-Scale Mechanisms for Spectral Induced Polarization of Calcite Precipitation Inferred from Geo-Electrical Millifluidics

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1	Pore-scale mechanisms for spectral induced polarization of calcite precipitation inferred
2	from geo-electrical millifluidics
3	Satoshi Izumoto ^{1,2*} , Johan Alexander Huisman ¹ , Egon Zimmermann ³ , Joris Heyman ² ,
4	Francesco Gomez ² , Herve Tabuteau ⁴ , Romain Laniel ⁴ , Harry Vereecken ¹ , Yves
5	Méheust ² , and Tanguy Le Borgne ²
6 7	¹ Agrosphere (IBG-3), Institute of Bio- and Geosciences, Forschungszentrum Jülich, Jülich, 52425, Germany
8	² Univ. Rennes, CNRS, Géosciences Rennes, UMR 6118, Rennes, 35042, France
9 10	³ Electronic Systems (ZEA-2), Central Institute for Engineering, Electronics and Analytics, Forschungszentrum Jülich, Jülich, 52425, Germany
11	⁴ Institute de Physique de Rennes, Université de Rennes 1, CNRS, Rennes, 35042, France
12	
13	Corresponding author: Satoshi Izumoto (satoshi.izumoto@hotmail.co.jp)
14	*Address: Géosciences Rennes, UMR 6118, CNRS, Université de Rennes 1, Rennes Cedex
15	35042, France
16	
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18 Abstract

Spectral induced polarization (SIP) has potential for monitoring reactive processes in the 19 subsurface. While strong SIP responses have been measured in response to calcite precipitation, 20 their origin and mechanism remains debated. Here we present a novel geo-electrical millifluidic 21 22 setup designed to observe microscale reactive transport processes while performing SIP 23 measurements. We induced calcite precipitation by injecting two reactive solutions into a porous medium, which led to highly localized precipitates at the mixing interface. Strikingly, 24 25 the amplitude of the SIP response increased by 340% during the last 7% increase in precipitate volume. Furthermore, while the peak frequency in SIP response varied spatially over one order 26 of magnitude, the crystal size range was similar along the front, contradicting assumptions in 27 the classical grain polarization model. We argue that the SIP response of calcite precipitation 28 29 in such mixing fronts is governed by Maxwell-Wagner polarization due to the establishment of a precipitate wall. Numerical simulations of the electric field suggested that spatial variation 30 31 in peak frequency was related to the macroscopic shape of the front. These findings provide new insights into the SIP response of calcite precipitation and highlight the potential of 32 geoelectrical millifluidics for understanding and modelling electrical signatures of reactive 33 34 transport processes.

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Keywords : Complex conductivity, Calcium carbonate, Mixing, Reactive transport, Porous
media, Chargeability, Maxwell-Wagner polarization, Heterogeneity

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Synopsis: Using a new technology called geo-electrical millifluidics, we uncovered the
microscale reactive transport mechanisms driving SIP, a promising geophysical technique for
monitoring soil biogeochemical processes.

43 Graphical abstract



46 **1** Introduction

Calcite (CaCO₃) is one of the most common minerals in the subsurface¹. It can be formed from 47 the calcium ion and dissolved carbon dioxide, which are major components in groundwater¹. 48 Calcite precipitation can cause undesirable effects, such as well clogging due to the reduction 49 of hydraulic conductivity^{2,3}. It has also been successfully used in geotechnical applications of 50 microbially-induced calcite precipitation (MICP) such as bioremediation^{4,5}, stabilization of 51 soil^{6,7} and the reduction of fracture permeability^{8,9}. The dynamics of calcite precipitation are 52 usually assessed by measuring hydraulic pressure, analysing sampled pore water, or performing 53 cone penetration tests^{2–9}. However, such methods only provide information on selected points 54 in space and time. Geophysical methods allow for non-invasive imaging of the subsurface with 55 higher spatial and temporal resolution. Spectral induced polarization (SIP) has shown potential 56 to detect biogeochemical processes 10-14, including calcite precipitation, in laboratory 15-18 and 57 field measurements^{19,20}. SIP measures the voltage between selected positions in the geological 58 material while injecting a sinusoidal current in the mHz to kHz frequency range^{21,22}. Due to an 59 external electric field, the charges in the material accumulate under geometric constraints 60 (induced polarization) ^{21,22}. The main purpose of an SIP measurement is to detect this process. 61 For this, the measured voltage is processed to obtain the phase shift between the applied current 62 and the measured voltage φ , the magnitude of the electrical conductivity $|\sigma|$, and finally the 63 complex conductivity σ^* : 64

$$\sigma^* = |\sigma|e^{-i\varphi} = \sigma' + i\sigma'' \,. \tag{1}$$

In the absence of a conductive solid phase, the real part of the conductivity (σ') results from the electrolytic conduction in the water-filled pore space and along solid surfaces whereas the imaginary part of the conductivity (σ'') corresponds to the induced polarization.

A range of studies have used SIP measurements to detect precipitation of a conductive mineral 68 phase²³⁻²⁶, but relatively few studies have investigated the SIP response of calcite 69 precipitation $^{15-17,27,28}$. These previous studies share the common limitation that the temporal 70 development and spatial distribution of calcite precipitation was inaccessible due to the opaque 71 72 nature of the porous media used in the column experiments. However, precipitation is a 73 dynamic process which only occurs when the pore solution is oversaturated. Thus, it is important to investigate what characteristics of the calcite precipitation process control the SIP 74 response in the presence of spatially heterogeneous calcite precipitation. 75

Here we present a geo-electrical millifluidic experiment coupling SIP monitoring with pore 76 scale imaging to investigate how spatially-variable and temporally-dynamic calcite 77 precipitation processes affect the SIP response. To this aim, we have combined a millimetre 78 scale 2D porous medium^{29–31} and electrodes for SIP measurements to visually observe calcite 79 precipitation at the pore scale while monitoring SIP (i.e. a millifluidic setup). Based on the 80 81 experimental results, we simulated the electric field distribution in the 2D millifluidic setup to support the interpretation of the measured SIP response. Finally, we present a simple electric 82 circuit model to provide a qualitative mechanistic explanation for the observed SIP response 83 84 of calcite precipitation.

85 2 Materials and methods

The experimental setup consists of (1) a millifluidic setup consisting of a sample holder, 2D porous medium and electrodes connected to the SIP measurement system and (2) equipment for visualization of pore-scale processes (Figure 1a), as described in the following.

89 2.1 Sample holder

The sample holder was made of transparent poly(methyl methacrylate) (PMMA) with a large 90 rectangular cavity (length: 300 mm, width: 50 mm, height 11 mm) (Figure 1b,c. See technical 91 92 drawings in Supplementary Figure S1). It has two fluid injection ports on one side and in the middle of the cavity, and a fluid outlet port on the other side. Two current electrodes made of 93 94 porous brass (length: 49.1 mm, width: 6.3 mm, depth: 3.7 mm) (Figure 1b) were positioned on both sides of the large rectangular cavity and completely retracted in the top plate to avoid 95 96 disturbance of the water flow. Four potential electrodes made of brass (diameter of 6.5 mm) were held by water-tight cable glands in the top plate (Figure 1b). They were positioned on one 97 side of the porous medium with equal spacing (33 mm). The measurement system of 98 Zimmermann et al.³² was used for SIP measurements. The measurement frequency range was 99 100 from 1 Hz to 45 kHz, and the injected voltage was 5V. We do not expect nonlinear effect by this voltage (see Supplementary section 1.1). In the frequency range above 100 Hz, the parasitic 101 capacitance of the measurement system can have significant impact on the measurement³³. To 102 evaluate this effect, we considered the parasitic capacitance of our measurement system during 103 data processing^{32,34}. The SIP response can be measured in different zones by choosing different 104 pairs of potential electrodes. Further information on the sample holder is provided in 105 Supplementary section 1.1. 106

108 2.2 2D porous medium

A fabrication method akin to soft lithography, a method commonly used to make microfluidic
flow cells³⁵, was used to produce a 2D porous medium whose solid grains are cylindrical pillars
made of Polydimethylsiloxane (PDMS) (Figure 1d, length: 12.5 mm, width: 50 mm, height:
11.6 mm, pillar height: 1 mm). The resulting porosity was 0.59. The grain size ranged between
0.34 and 0.82 mm, with a median grain size of 0.53 mm (see further details in Supplementary
section 1.2 and Figure S2).

115 **2.3** Visualization of pore-scale processes

To monitor calcite precipitation at different spatial scales, two different cameras were used 116 117 (Figure 1a) in combination with a homogeneous backlight (LFL-180BL2, CCS inc., Kyoto, Japan). The first camera was a mirrorless digital camera (14-bit, SONY alpha7s, SONY, Tokyo, 118 Japan) equipped with a macro lens (MACRO GOSS F2.8/90, SONY, Tokyo, Japan), which 119 resulted in a field of view of $16.6 \times 11.0 \text{ cm}^2$ and an image resolution of $0.03 \times 0.03 \text{ mm}^2$. 120 This "overview" camera was connected to a PC through a voltage output module (National 121 Instruments, Austin, TX) to enable automatic image acquisition. The second camera (denoted 122 "close-view" camera) was a high-sensitivity scientific CMOS camera (16-bit, Hamamatsu 123 124 ORCA flash 4.0, Hamamatsu Photonics K.K., Shizuoka, Japan) equipped with a set of lenses (6.5X zoom lens with 2X extension tube and 1.5X lens attachment, Thorlab, Inc., Newton, MA, 125 126 USA) to obtain close-up images. The field of view was 750×750 µm and the image resolution was $0.37 \times 0.37 \,\mu\text{m}^2$. This camera was fixed on a 3-axis table (Edmund Optics Ltd., Barrington, 127 128 USA), which was mounted on a 2-axis motorized table constructed from two 1-axis motorized tables (Edmund Optics Ltd., Barrington, USA and Thorlab, Inc., Newton, MA, USA) 129 controlled by a custom-made Matlab program (Mathworks, Natick, MA, USA). This allowed 130 automatic positioning of the close-view camera to monitor selected positions with regular space 131 intervals. Composite images were created using the open-source image processing program 132 ImageJ with the plugin TrackEM2 (https://imagej.net/TrackEM2). 133



134

Figure 1. Overview of the experimental setup: (a) Entire setup including 1) overview camera,
2) close-view camera, 3,4) 3-axis stage, 5) 2-axis moving table, 6) lenses, 7) millifluidic setup,
8) backlight, (b) sample holder with porous medium and electrodes (see Supplementary Figure
S1 for actual position of porous medium in the experiment), (c) plan view of the middle plate
of the sample holder, and (d) 2D porous medium made of PDMS.

140 2.4 Experimental procedure

A first millifluidic calcite precipitation experiment was performed with a total duration of 80 141 hours using the same solute concentrations as in previous column studies^{15,28}. The sample 142 holder was first filled with a 26.2 mM CaCl₂ solution. Next, the same solution was injected 143 through the injection port at the side of the 2D porous medium, and a 29 mM Na₂CO₃ solution 144 was injected through the injection port in the middle of the porous medium (Fig. 1b). Both 145 solutions were injected with the same flow rate (4 mL h⁻¹) using a syringe pump (model 22, 146 Harvard Apparatus, Inc., Holliston, MA, USA). The Péclet number, which characterizes the 147 ratio of the characteristic diffusion and advection times, is defined as Pe = vL/D, where v is 148 the average velocity downstream of the injection ports, L is the average pore throat size of the 149 porous medium and D is the molecular diffusion coefficient. The selected experimental 150 parameters ($v = 3.86 \times 10^{-5} \text{ m s}^{-1}$, $L = 3.63 \times 10^{-4} \text{ m}$, $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$) yield Pe = 14. 151 This corresponds well with the order of magnitude of many applications^{36,37}. 152

153 Mixing between the Na₂CO₃ and CaCl₂ solutions induced calcite precipitation according to:

$$Ca^{2+} + CO_3^{2-} \to CaCO_3(s) \tag{2}$$

This is the approximated equation of the two-step reaction in our highly oversaturated system: 154 formation of amorphous calcium carbonate (ACC) and subsequent crystallization³⁸. When the 155 two solutions mix, ACC quickly forms (within seconds³⁸), sinks because of its high density 156 $(2.18 \text{ g cm}^{-3})^{39}$ and crystalizes to calcite (timescale ~10⁴ s⁴⁰). The Damköhler number, which 157 characterizes the relative strength of reaction and advection, is defined as $Da = \tau_a/\tau_r$, where 158 τ_a and τ_r are the characteristic advection and reaction times, respectively. The advection time 159 is $\tau_a = L/v = 9.4$ s, with $L = 3.63 \times 10^{-4}$ m the average pore throat size and $v = 3.86 \times$ 160 10^{-5} m s⁻¹ the mean velocity downstream of the injection point. We approximated the 161 characteristic time for ACC formation as 5 s based on visual observations when mixing the 162 163 solutions. By taking this ACC formation time as a characteristic reaction rate, the Damköhler 164 number is about $Da \approx 2$, which indicates that reactions are fast compared to the advective transport. 165

SIP measurements were made in three measurement zones, which will be referred to as the 166 upstream, middle, and downstream measurement zone, using the electrode pairs P1 and P2, P2 167 and P3, and P3 and P4, respectively (Figure 1b). To capture the early formation of the 168 precipitation front, we measured more frequently in the upstream zone (every 18 minutes) than 169 in other zones (every 8 hours). Images were taken every 8 minutes with the overview camera 170 and with the close-view camera for four selected horizontal positions. Two of these positions 171 were located in the upstream zone and the two other positions were located in the middle and 172 173 downstream zones. At each position, the close-view camera took 10×10 images with a regular space interval using the motorized stage, which resulted in a composite image size of 7.5 mm 174 175 \times 7.5 mm. At the end of the experiment, the close-view camera took images of the entire zone with calcite precipitates. 176

After the flow experiment, the 2D porous medium was removed from the sample holder to measure the height of the precipitate using a profilometer (Altisurf 500, Altimet, France) with a vertical resolution of 5 μm and a horizontal resolution of 50 μm. A calibration function was established to relate the image grey levels and the height of the precipitate (further details are given in section 1.3 of the Supplementary Information and Figure S3). After the calibration, the calcite precipitates were observed using a microscope with 10X and 40X lenses (Inverted Laboratory Microscope, Leica microsystems, Cambridge, United Kingdom).

184 The SIP response obtained during injection of $CaCl_2$ and Na_2CO_3 solutions is potentially 185 affected by spatial and temporal variations in solute concentration²⁸ because of the ongoing

precipitation reactions. To investigate the effect of such variations, we performed a second 186 experiment in which the injected reactive solutions were replaced by a single, non-reactive 187 solution during two time periods. By this replacement, the solute concentration becomes 188 spatially homogeneous. To prepare the replacement solution, a 26.2 mM MgCl₂ solution and a 189 29.0 mM Na₂CO₃ solution were mixed and centrifuged to remove any MgCO₃ precipitates. 190 This mixed solution was expected to be non-reactive with calcite precipitates and to induce a 191 relatively large SIP response due to the presence of Mg^{2+} and CO_3^{2-} ions⁴¹ (see section 1.4 of 192 the Supplementary Information for more details). We call this mixed solution the MgCO₃ 193 194 solution. The experimental approach was the same as in the first experiment up to 47 h: calcite precipitation was first induced by injecting CaCl₂ solution and Na₂CO₃ solutions, and the 195 precipitation was visually monitored while making SIP measurements. After 47 h, the two 196 injected solutions were changed to the MgCO₃ solution. After the SIP response stabilized in 197 response to the injection of MgCO₃ solution (after ~16 pore volumes), the original Na₂CO₃ and 198 CaCl₂ solutions were injected again. About 27 pore volumes of Na₂CO₃ and CaCl₂ solution 199 were sufficient to obtain a SIP response similar to the response before the injection of MgCO₃ 200 201 solution. The same procedure was repeated after 87.5 h. This procedure provided the SIP response of calcite with a spatially homogeneous solute concentration at two different times 202 203 (47 h and 87.5 h).

204 **2.5 Simulation**

To investigate how the spatial distribution of the calcite precipitates affects the SIP measurements, electrical field simulations were performed with a custom-made finite-element modelling approach implemented in Matlab (Mathworks, Natick, MA, USA). The governing equation is:

$$\nabla \cdot \boldsymbol{J} = \nabla \cdot (\sigma^* \nabla \Phi^*), \qquad (3)$$

where J is current density (A m⁻²), Φ^* is the complex potential (V) and σ^* is the complex 209 conductivity (S m⁻¹). The modelling domain was the rectangular area between the current 210 electrodes $(30 \text{ cm} \times 5 \text{ cm})$, which was discretised in right-angled triangles with a base and side 211 length of 2 mm. Because it was not computationally feasible to use a mesh sufficiently fine to 212 resolve the pore scale, a Darcy-scale approach had to be used with effective properties assigned 213 to different areas⁴². Thus, the simulations were only used to analyse qualitative trends. The 214 effective electrical conductivity of the background was determined from the solute 215 concentration and the formation factor. The shape of the area with calcite precipitates was 216

obtained from images of the overview camera. A modified Cole-Cole model⁴² describes the
 effective complex conductivity of this area :

$$\sigma^* = (1 - m) R_{\sigma} \sigma_{\text{bulk}} \frac{1}{1 - m \left(1 - \frac{1}{1 + (2\pi f T i)^c}\right)}$$
(4)

where *m* is the chargeability, *f* is the frequency (Hz), *T* is the characteristic time (s), *c* is a shape exponent and R_{σ} defines the ratio between the high-frequency limit of the conductivity, σ_{∞} , and the bulk conductivity σ_{bulk} :

$$R_{\sigma} = \frac{\sigma_{\infty}}{\sigma_{\text{bulk}}} < 1 \tag{5}$$

Electric current without imaginary part was applied at the right boundary (see Eq.3) and the current ejected from the left boundary. The potentials were determined at the positions identical to those of the voltage measurements in the experiments. The parameters and simulation domains were based on the experimental results (section 3.3.1).

226

227 **3** Results and discussion

228 **3.1** Precipitation process

The large-scale images show that the front develops as a continuous region, which becomes 229 230 darker over time at the boundary between the two injected solutions (Figure 2a). The shape of this boundary corresponds with the streamlines of the Rankine half-body potential flow⁴³. The 231 composite images obtained from the close-view camera (Figure 2a, middle and right column) 232 successfully captured the development of individual crystals (also see section 2.1 of the 233 234 Supplementary Information, Figure S4, S5 and Movie S1). Calcite precipitation created a solid wall along the mixing interface without visible pores at $0.16 \times 0.16 \,\mu\text{m}^2$ resolution (Figure 2b). 235 This likely occurred because the amorphous calcium carbonate settled on the bottom plate due 236 to its higher density and could attach on calcite surfaces that were already present. Further 237 details are provided in section 2.2 of the Supplementary Information and Figure S6 therein. 238



240

Figure 2. (a) Digital images of the entire measurement area taken at different times (left 241 column), composite images of a selected area along the calcite precipitation front (center 242 column), and calcite crystals in close-up images (right column). The yellow dots indicate the 243 position of the electrodes. The black line connected to the fluid injection port is the tubing. (b) 244 Side view of the calcite wall. (c) Change in volume of precipitate over time in the entire 245 measurement zone as well as in the upper (near the potential electrodes) and lower half of the 246 sample holder in Figure 2a; the change in mean precipitate height for the entire domain is 247 248 superimposed on that of the volume. (d) Spatio-temporal diagram showing the time evolution of the V_f -normalized PDF of the precipitate heights (V_f being the final volume of precipitate). 249

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In a next step, we quantified the relationship between the grey level of the image and the height of the precipitate from the profilometer. This correlation was found to be relatively good with a small spread of data. The tendency was well fitted by an arctangent function, which captured most data points within ± 0.1 mm (section 1.3 of the Supplementary Information and Figure

S3). Because calcite did not have pores (Figure 2b), this calibration curve can be used to obtain 255 the spatial distribution of the total volume of precipitate from the grey level in the overview 256 images. It was found that both the volume and the mean height increased up to 20 h, followed 257 by relatively constant value (Figure 2c). This suggests that the surface area of the reactive zone 258 is relatively constant and that the quick increase in volume in the first 20 hours can be attributed 259 260 to the rise of the calcite wall. Note that the peak of the volume change in early time was probably because the amorphous phase started to crystalize at this time. Figure 2d shows the 261 time evolution of the probability density function (PDF) of precipitate heights. Note that only 262 263 the final PDF is normalized to 1 as a standard PDF and that the entire data set has the same normalization factor as this final PDF. Figure 2d thus shows the relative evolution of the height 264 histogram with time, and we denote them "V_f-normalized PDFs". The PDF has a strong peak 265 around 0.9 mm after 20h. This peak corresponds to the height of the solid calcite precipitate 266 wall, whereas the lower height corresponds to the stacked calcite crystals surrounding the 267 268 calcite wall (Supplementary Figure S6). This analysis also shows that the height only increased further in areas where a high wall of precipitation was already present after 20 h (i.e. a 269 270 continued vertical development of the calcite wall). Because of the differences in the development of calcite precipitation before and after 20 h (Figure 2c,d), these two periods will 271 272 be considered separately in the following.

The observed reduced speed of calcite precipitation with time can be understood conceptually. 273 The calcite precipitation divided the two injected fluids and precipitation is expected to occur 274 in the mixing zone (Supplementary Figure S7). As the height of the calcite precipitation 275 increases, the size of this mixing zone is reduced⁴⁴. This leads to a decrease in the reaction rate 276 and a reduced growth of the height of the calcite precipitates. This feedback mechanism 277 between the reaction rate and the height of the calcite precipitates thus leads to a slow but 278 279 continuous growth of the volume of calcite precipitates even after 20 h. By considering the diffusive flux toward the calcite wall in combination with this feedback mechanism, we 280 developed an analytical model that predicts the change in volume with time (section 2.3 of the 281 Supplementary Information). This model was able to describe the observed volume (Figure 2c), 282 which supports the notion that the described feedback mechanism controls mixing and 283 precipitation. 284

285

287 **3.2** SIP response

Calcite precipitation generally resulted in an increase of the imaginary part of conductivity σ'' 288 (Figure 3a). The comparison between the σ'' with and without correction of parasitic 289 capacitance showed that the results were not much influenced by the parasitic capacitance 290 below 10 kHz (Supplementary section 2.4). The measurement at time 0 h without correction 291 (Figure 3a) also showed a low σ'' for frequencies below 10 kHz with sufficient accuracy, which 292 again indicates that the effect of parasitic capacitances was small enough in this frequency 293 range. Hence, uncorrected data were used for further analysis. In all three measurement zones, 294 a clear peak in σ'' appeared (Figure 3a). Also, relatively strong negative σ'' values were 295 measured in the low frequency range in the upstream measurement zone. Such negative σ'' 296 297 values are not physically possible for homogeneous samples but can occur in the case of heterogeneous samples (section 3.3). We further analyzed σ'' regarding the peak value σ''_p 298 (Figure 3b) and the peak frequency (Figure 3c). The increase in $\sigma_p^{\prime\prime}$ was much smaller up to 20 299 hours than afterwards even though the volume of precipitates increased strongly in this period 300 (Figure 3b). The value of $\sigma_p^{\prime\prime}$ strongly increased by 340% after 24 h, while the volume of the 301 precipitates changed only slightly by 7%. This suggests that the SIP response is not only 302 sensitive to the amount of precipitates. The peak frequency was relatively constant in time and 303 304 ranged from about 200 Hz to 2 kHz depending on the measurement zone. It was larger in the upstream zone close to the injection point than in other areas (Figure 3c). The duplicated 305 306 experiment showed qualitatively similar trends for all key features of the SIP response. In this 307 duplicate experiment, it was also verified that streaming potential did not have much influence by comparing the SIP response with and without flow (Supplementary Figure S12). 308

According to the grain polarization model^{45,46}, the radius of the crystal, *r*, can be predicted from the peak frequency as:

$$r = \sqrt{2D_s M/f} , \qquad (6)$$

where *f* is the peak frequency, D_s is the surface diffusion coefficient, which was assumed to be roughly 10 times smaller than the bulk diffusion coefficient in previous studies $(10^{-10} \text{ m}^2 \text{ s}^{-1})^{41}$, and *M* is a parameter accounting for the effect of the diffuse double layer, which was assumed to be 31 based on a previous study⁴¹. This model suggests that the mean crystal size in the downstream region (*f* = 200 Hz) should be twice as large as in the middle region (*f* = 900 Hz). However, our pore scale imaging results showed that the range of the crystal sizes was similar in all measurement zones on the same side of the Rankine half-body flow, except at the stagnation point (Supplementary Figure S5). In addition, the largest predicted crystal radius is 5.6 µm for f = 200 Hz. We observed that most of such small crystals disappeared after 10 hours (Supplementary Movie S1) because smaller crystals are thermodynamically less stable and experience Ostwald ripening^{48,49}. If such small crystals were responsible for the SIP response, σ'' should have been larger early in the experiment, which was not the case. Hence, we conclude that the grain polarization model is not able to describe this feature in our experiments.



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Figure 3. (a) SIP response as a function of time for the three different measurement zones and key characteristics of the SIP response as a function of time for the three measurement zones: (b) peak frequency, (e) σ'' at peak frequency, (d) σ' at 1 Hz and (e) σ' at 10 kHz. The absence of early time results in (b) and (e) is due to the absence of a peak in σ'' .

329

The interpretation of the real part of conductivity σ' is challenging for the period before 20 h (Figure 3d,e) because the reactions strongly affect solute concentration as well as the fraction of precipitates in the solution, and therefore the conductivity (see further details in section 2.5 of the Supplementary Information and Figure S10). After 20 h, σ' at 10 kHz was almost constant and σ' at 1 Hz decreased over time. These different trends of σ' between 1 Hz and 10 kHz after 20 h are the key to understanding how the SIP response increased (more detail in section 3.3).

In the additional experiment where the sample holder was flushed twice with the $MgCO_3$ 337 solution, the injection of MgCO₃ solution decreased the imaginary part of conductivity as 338 expected from previous studies²⁸ and increased the peak frequencies (Figure S13 and S14). 339 However, the SIP response after injection of MgCO₃ solution still showed a higher peak 340 frequency in the upstream region, similar peak frequencies in both injection periods for each 341 measurement zone, and a slightly larger σ'' later in the experiment. In the period between the 342 injections of MgCO₃ solution, a slight increase in σ'' was observed as in the main experiment 343 with CaCl₂ and Na₂CO₃ solutions only. Since the solute concentration was homogeneous due 344 to the injection of MgCO₃ solution, these characteristics of the SIP response are thus not 345 governed by a heterogeneous distribution of solute concentration. 346

347 **3.3** Microscopic and macroscopic controls on SIP response

Our experiments revealed some unexpected effects of pore scale transport and reaction on the SIP response: i) a temporal lag between the peak σ'' value and the precipitation and ii) spatial variation in peak frequency. In the following, we argue that the former is related to pore scale dynamics, while the latter is governed by the macroscopic precipitate distribution.

352 **3.3.1 Pore scale processes**

353 The most unexpected result is that the peak σ'' value mostly increased after 20 hours (Figure 2b) while the volume of precipitates only slowly increased (Figure 3c). At the same time, σ' at 354 1 Hz decreased (Figure 3d) while σ' at 10 kHz was almost constant (Figure 3e). This indicates 355 an increase in chargeability with time^{42,50}. It is again difficult to explain these results with the 356 grain polarization model for two reasons. First, the calcite wall cannot adequately be modelled 357 by the grain polarization model because it is not a porous medium with identifiable grains but 358 a solid precipitate (Figure 2b). Second, the grain polarization model suggests that the 359 chargeability may increase due to an increase in surface area, changes in crystal size or an 360 increase in the solute concentration⁴¹. It seems unlikely that the observed increase in 361 chargeability can be explained by an increase in surface area or crystal size because changes in 362 the volume of calcite precipitation were quite small after 20 h (Figure 2c) and the crystal size 363

did not change after 20 h (section 2.1 of the Supplementary Information). It is also unlikely
that variations in solute concentration over space are responsible for the characteristics of the
SIP response because the experimental results obtained with homogeneous concentration fields
(section 2.7 of the Supplementary Information) showed the same key characteristics of the SIP
response as those obtained with heterogeneous concentration fields, such as different peak
frequencies depending on the measurement zone.

An alternative explanation for the strong increase in SIP response is that it may be associated 370 371 with Maxwell-Wagner polarization associated with the thin calcite precipitation wall. Maxwell-Wagner polarization considers the entire material body as a dielectric material with 372 a certain capacitance²². To test the potential importance of this source of polarization, we 373 considered a simple conceptual model (Figure 4a) consisting of a calcite wall (length 10⁻³ mm, 374 width 1 mm), a mixing zone above the calcite wall (length 10⁻³ mm, width 1 mm), and the 375 surrounding water (length 5 mm, width 1 mm, height 1 mm). In the experiments, we observed 376 377 a slow but continuous growth of the calcite precipitation after 20 hours and a calcite wall that almost filled the pore space in vertical direction. Thus, we specified a thin mixing zone above 378 the calcite wall (0.01-0.0001 mm) and a high calcite wall (0.99 - 0.9999 mm). The width of 379 the calcite wall is based on the actual dimensions of the calcite precipitation front obtained 380 from images acquired after the experiment. The water in the mixing zone is assumed to be in 381 equilibrium with the calcite (0.375 S m^{-1}) , whereas the pore water conductivity was taken as 382 the average of the injected solutions (0.50 S m⁻¹). The relative permittivity of calcite was 383 assumed to be 12⁵¹. For simplicity, pure calcite without an electric double layer is considered 384 here (i.e. only Maxwell-Wagner polarization). 385

386 This conceptual model can be simplified to an electric circuit model as shown in Figure 4a, in which the electrical properties (R1, R2, C) can be calculated based on the dimensions and 387 388 parameters provided above (see section 3.1 of Supplementary Information for more details). The model suggests that an increase in calcite wall height will lead to a lower peak frequency, 389 an increase in the peak σ'' , a plateau at constant σ' at high frequencies, and a decrease in σ' at 390 low frequencies (Figure 4b). Thus, this conceptual model is highly sensitive to the size of the 391 392 gap between the top of the calcite wall and the top plate, especially when the gap is nearly closed (high R₂). This may explain why small increases in the height of the calcite precipitation 393 394 resulted in large increases in chargeability after 20 h in the experiment. Also, the small σ'' before 20 h can be partly attributed to the large gap between the top plate and the calcite wall. 395

396 This simple model thus qualitatively captures some of the key characteristics of the 397 experimental results.

The reason why the Maxwell-Wagner polarization model can describe our experiments can be 398 further elucidated by contrasting it with the grain polarization model. If the calcite wall is 399 modelled by the grain polarization model, the surface of the calcite (electrical double layer) is 400 associated with a complex conductivity, but the body of the calcite crystal is purely resistive 401 because no pores were observed. Thus, an increase in height of the calcite precipitation 402 (increase in the volume of calcite) would decrease σ' in the entire frequency range because the 403 non-conductive calcite crystal replaces conductive water. It is unlikely that this decrease is 404 405 fully compensated by an increase in the volume of the electrical double layer because the size of the electrical double layer (a few Angström⁴¹) would be much smaller than that of calcite 406 407 crystals if the grain polarization model is applied (µm scale, see section 3.2). In contrast, Maxwell-Wagner polarization simply considers the entire calcite crystal as a capacitance, 408 409 which has zero resistance in the high frequency limit. This thus provides a straightforward explanation of why σ' decreases at low frequencies and remains constant σ' for high 410 411 frequencies (Figure 3e, Figure S10).



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Figure 4. (a) Conceptual model to explain the Maxwell-Wagner polarization associated with the calcite precipitation front and equivalent electrical circuit of the conceptual model, (b) simulated σ'' as a function of the height of the calcite precipitation front. (c) SIP response simulated for the different measurement zones under continuous calcite precipitation front, (d) discontinuous calcite precipitation front, and (e) spatially variable complex electrical conductivity of calcite.

419 **3.3.2 Effect of macroscopic precipitate distribution on peak frequency**

A second striking result is that the peak frequency varied significantly in space while the range
of crystal size did not change substantially along the mixing front except at the stagnation point
(Figure S5). We hypothesized that this was due to the macroscopic spatial arrangement of the
calcite precipitation. To test this, we performed electrical field simulations in three scenarios.

The first scenario corresponds to t = 20 h, where a clear and continuous precipitate wall was observed (Supplementary Figure S16a). The background electrical conductivity was 0.162 S m⁻¹ based on the measured formation factor and the solute conductivity. The complex electrical

427 conductivity of the area with calcite was defined using the modified Cole-Cole model (eq. 4).

To determine suitable parameters to reproduce the observed SIP response, simulations were 428 run with a varying m (0.5 to 0.999) and R_{σ} (0.005 to 0.99). The relaxation time was fixed to 429 10^{-3} s. It was found that a *m* of 0.995 and an R_{σ} equal to 0.9 times the background conductivity 430 provided a qualitatively similar SIP response as in the experiments (Supplementary Figure S17). 431 These parameters resulted in a peak frequency at 100 kHz, which corresponds to the peak 432 frequency near the calcite precipitation front modelled by Maxwell-Wagner polarization in 433 section 3.3.1 (Figure 4b and Figure S19). The chosen *m* was two orders of magnitude higher 434 than in a previous study¹⁵. This is because this previous study used a parameterization for an 435 entire column occupied by glass beads and a small fraction of calcite, whereas we used a 436 parameterization for a small domain mostly filled by calcite wall without pores, which is non-437 conductive at low frequencies. The high m also reflects the concept of Maxwell-Wagner 438 439 polarization, which suggests that the calcite wall becomes fully conductive at high frequencies.

The simulation results showed that the peak frequency for the three measurement zones can be 440 different even if the complex electrical conductivity of the calcite precipitates is the same 441 everywhere (Figure 4c left). In particular, this occurred when both m and R_{σ} values were high. 442 This likely explains why differences in peak frequency were observed between the three 443 444 measurement zones, although the crystal size range was similar. Furthermore, multiple peaks in the dependence of σ'' on the frequency can occur in the middle and downstream zones with 445 high m and R_{σ} values even though the specified frequency-dependent complex electrical 446 conductivity for calcite only exhibited a single peak. Only the lower peak frequencies were in 447 the frequency range in the experiments. Also, σ'' in the middle zone was larger than that of the 448 two other zones (Figure 4c left), which is consistent with the experimental results. 449

A second simulation scenario represents a relatively early stage of the experiment where the calcite precipitate wall was not yet completely continuous (Supplementary Figure S16b). In this case, a fraction (33%) of the calcite precipitate was replaced by solution. With this discontinuous precipitation front, the simulated σ'' decreased substantially (Figure 4b middle), which suggests that σ'' is sensitive to the continuity of the precipitation front. The small σ'' before 20 h in the experiments can thus be partly attributed to the discontinuity of the calcite wall at these early times.

In a third simulation scenario, we explored how a heterogeneous distribution of the complex
electrical conductivity of the calcite precipitate influences the SIP response (Supplementary
Figure S16c). The experimental results suggested that calcite precipitation was slightly faster

and more abundant in the vicinity of the electrodes than elsewhere (Figure 2c), likely due to 460 the local pore arrangement or a slight tilt of the injection tube with respect to the cell's 461 longitudinal direction. To test the effect of this heterogeneous distribution, the chargeability 462 was set higher for the half part of calcite that was closer to the electrodes (m=0.995) than for 463 the calcite further away from the electrodes (m=0.4) corresponding to upper and lower part in 464 Figure 2a (also Supplementary Figure S16c). This setting is based on the faster calcite 465 precipitation in upper part (Figure 2c). Here, the experimental conditions after 20 h are 466 considered again. In this case, the simulated σ'' partly showed negative values for the upstream 467 measurement zone (Figure 4c right). Thus, heterogeneous calcite properties likely explain the 468 469 observed negative σ'' values obtained in the upstream measurement zone. Further explanations about σ' and the origin of different peak frequencies can be found in section 3.2, 3.3, and 3.4 470 of the Supplementary Information and Figure S19, S20 and S21. 471

Finally, the discussed macroscopic and microscopic mechanisms also explain the reproducibility of the experiments. It was possible to precisely reproduce the observed peak frequency because it is controlled by the macroscopic shape of the reaction front, which is strongly controlled in our experimental approach. The magnitude of σ'' was less precisely reproduced because it is controlled by pore scale processes that are sensitive to local flow conditions (see section 3.5 of the Supplementary Information for more details).

478 **4. Implications**

We have developed a novel geoelectrical millifluidic system to understand the role of pore 479 scale reactive mixing processes in the SIP response to calcite precipitation. We observed the 480 481 development of a calcite precipitation front at the interface between two reactive solutions, both micro- and macroscopically, while measuring the SIP response. The calcite precipitation 482 483 was highly localized at the mixing interface, which resulted in wall like calcite precipitates. The SIP response was relatively low during the early stage of the experiments, even though 484 485 most of the precipitation occurred in this stage. Surprisingly, the amplitude of the SIP response 486 increased strongly in the later stage when the calcite front was evolving much slower. 487 Furthermore, the peak frequency of SIP response varied over one order of magnitude depending on the measurement zones without significant difference in the range of crystal size. 488

We proposed a pore scale electric circuit model to explain the apparent contradiction between the volume of precipitates and SIP response. By including Maxwell-Wagner polarization, the model reproduced the experimental results: the continuous filling of the gap between the top

plate of the millifluidic cell and the top of the calcite wall can increase the SIP response with 492 only small increase in the volume of precipitates. We further simulated the electrical field in 493 the entire measurement zone to explain the spatial variation of the peak frequencies. The 494 simulation results showed that this variation in peak frequency is likely due to the macroscopic 495 shape of the highly localized calcite precipitation front. In addition, these simulations showed 496 that negative σ " values observed in the experiments may be explained by the heterogeneous 497 development of the electrical properties of the calcite precipitates and the macroscopic 498 discontinuity of the calcite wall largely decreases SIP response. 499

500 These findings will be useful to interpret SIP measurements in field conditions. Although our flow field (Rankine half-body) was 2D, similar 3D shapes of the reaction front are common in 501 field conditions where a point solute source exists in a uniform groundwater flow field⁵². Even 502 though calcite precipitation is typically induced biochemically in geotechnical applications^{4,5} 503 instead of chemically as in our experiments, the process of closing pore space also happens in 504 such systems²⁰. Therefore, our findings open new insights into the mechanisms driving the SIP 505 response of calcite precipitation. Coupling SIP monitoring with pore scale imaging allows 506 unravelling the contribution of different microscale processes driving the SIP response. Results 507 highlight the importance of key pore scale and Darcy scale processes that need to be integrated 508 in models for relating quantitatively the SIP response to reactive transport dynamics. The 509 developed geoelectrical millifluidic system may be used in the future to investigate the role of 510 micro-scale processes in the geoelectrical signature of a range of reactive transport dynamics. 511

512

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