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Saturation dependence of the streaming potential coefficient

L. Jouniaux¹, V. Allègre^{2*}, R. Toussaint^{1†}, F. Zyserman^{3,4‡}

¹Université de Strasbourg, CNRS, Institut de Physique du Globe de Strasbourg UMR7516, 5 rue René Descartes, 67084, Strasbourg, France.

²Université de Bordeaux, Institut de Mécanique et d'Ingénierie, Département Génie Civil et Environnemental, CNRS UMR 5295, 33615

Pessac cedex, France.

³Facultad de Ciencias Astronómicas y Geofísicas, Universidad Nacional de La Plata, Paseo del Bosque s/n, B1900FWA La Plata, Argentina

⁴CONICET

*vincent.allegre@u-bordeaux.fr

†toussaint@unistra.fr

‡zyserman@fcaglp.unlp.edu.ar

Corresponding author: L. Jouniaux, l.jouniaux@unistra.fr

8 Abstract

9 Observations of streaming potential for unsaturated conditions do not always show the same trend de-
10 pending on the hydrodynamic conditions and because of a lack of coherency between the data processing
11 procedures. We combine the data from three studies published in the literature, acquired during non-steady
12 state drainage experiments, and apply the same processing steps. We model the hydrodynamic behaviour of
13 these experiments to confirm that they experienced different flow dynamics. We argue that the raw SP data
14 should not be corrected unless a clear drift of the electrodes stability is observed. The combined hydrody-
15 namic behaviour and the streaming potential response show that (a) the observations of one of the exper-
16 iment (exp #1) are associated to a limited range of water saturation (0.85-1). The corresponding signals could
17 therefore be fairly modelled assuming no saturation dependence of the SPC whatsoever; (b) the observations
18 of exp #3 led to a SPC that can be larger than its value at saturation; (c) the observations of the exp #2 show
19 a non-monotonous behaviour of the SPC as saturation decreases. The underlying physics of a non-monotonous
20 SPC is related to water/air interfaces as shown by the results of the lattice Boltzmann numerical simulations.
21 The main contribution to the SPC behaviour comes from the charged water/air interfaces and depends on
22 the dynamic state of moving or entrapped bubbles. We finally describe the consequences of such a behaviour
23 on the seismoelectric conversions for unsaturated conditions.

24 1 Introduction

25 Electrokinetics are at the origin of geophysical methods used to investigate the near-surface earth sys-
26 tem in terms of fluid transfers. Both seismoelectrics and most of self-potentials observations are interpreted
27 to be induced by a relative motion between the rock matrix and the saturating fluid, converted into an elec-
28 tric field and a magnetic field through electrokinetic coupling.

29 Seismoelectrics and electroseismics were developed to investigate hydrogeological reservoirs [*Dupuis*
30 *et al.*, 2007; *Dupuis et al.*, 2009; *Schakel et al.*, 2012; *Warden et al.*, 2013], specially in arid environments
31 [*Valuri et al.*, 2012], and hydrocarbon reservoirs [*Thompson et al.*, 2005; *Hornbostel and Thompson*, 2007;
32 *Hu et al.*, 2007; *Thompson et al.*, 2007; *Zyserman et al.*, 2012; *Guan et al.*, 2013; *Zyserman et al.*, 2015]. **More-**

33 **over numerical, experimental and field studies have also investigated borehole geometries [***Hunt and Wor-*
34 *thington, 2000; Hu and Liu, 2002; Dupuis et al., 2009; Wang et al., 2015a]* **and possible applications for**
35 **the vadose zone [***Zyserman et al., 2017a,b; Monachesi et al., 2017]*. **The reader can find more details with**
36 **many references in the large review from** *Jouniaux and Zyserman [2016]*. **Some other works studied the**
37 **seismo-electromagnetic signals that could be induced by earthquakes [***Matsushima et al., 2002; Gaffet et al.,*
38 *2003; Guglielmi et al., 2006; Ren et al., 2010; Gao et al., 2013, 2016]*.

39 Most of the works were developed considering a single saturating fluid at full saturation. It was only
40 in the few last years that attempts to introduce partial saturation in seismoelectrics/electroseismics have been
41 undertaken [*Warden et al., 2013; Zyserman et al., 2015]*. Besides of using different known effective media
42 models for the different physical parameters of the seismoelectrics/electroseismic equations, the key model
43 parameter, i.e., the electrokinetic coupling, has been modified to cope with partial saturations following the
44 ideas previously used to extend the streaming potential coefficient (SPC) to handle this situations.

45 Self-potentials rely on electrokinetic coupling and proved to be efficient for characterizing groundwa-
46 ter resources and mapping contamination plumes, since those signals are directly sensitive to hydrological
47 fluxes [*Fournier, 1989; Titov et al., 2002; Pinettes et al., 2002; Mainault et al., 2004; Jouniaux et al., 2009;*
48 *Desroches and Butler, 2016]* and solute transport [*Mainault et al., 2005; Kabir et al., 2015; Giampaolo et al.,*
49 *2016]*. Self-potentials appeared especially useful to estimate fluid flow [*Jouniaux et al., 1999; Sailhac et al.,*
50 *2004; Rangarajan et al., 2014]*, to detect propagating vapor-front during oil-extraction processes [e.g., *Saun-*
51 *ders et al., 2008]*, to detect hydrothermal flows [*Mauri et al., 2010; Brothelande et al., 2014; Gonzales et al.,*
52 *2014]*, to map advected reacting redox fronts [*Mainault et al., 2006a,b]*, and to provide a tool to evaluate the
53 evolution of the corrosion of metallic casings [*Mainault, 2016]*. Self-potentials are also often associated with
54 natural hydrothermal circulation [*Ishido and Pritchett, 1999; Matsushima et al., 2000; Jouniaux and Ishido,*
55 *2012; Monetti et al., 2014]*. The knowledge of the electrokinetic coupling is therefore significant to the in-
56 terpretation of a broad range of geophysical methods.

57 Many experimental studies on streaming potential measurements in porous samples have been pub-
58 lished in the past three decades [*Wang et al., 2015b; Walker et al., 2014; Luong and Sprik, 2014; Glover et al.,*

59 2012; *Glover and Déry*, 2010; *Vinogradov et al.*, 2010; *Jaafar et al.*, 2009; *Aizawa et al.*, 2008; *Guichet et al.*,
60 2006; *Perrier and Froidefond*, 2003; *Hase et al.*, 2003; *Guichet et al.*, 2003; *Jouniaux et al.*, 2000; *Lorne et al.*,
61 1999; *Pozzi and Jouniaux*, 1994; *Jouniaux et al.*, 1994; *Ishido and Mizutani*, 1981].

62 A few experimental studies addressed the SP (self-potential) behaviour associated with unsaturated flow.
63 Early observations performed during unsaturated water flow experiments on sand showed that SP amplitudes
64 decrease at smaller water content [*Guichet et al.*, 2003], which was supported by some theoretical models
65 [e.g., *Perrier and Morat*, 2000; *Revil et al.*, 2007]. *Linde et al.* [2007] proposed similar SP measurements that
66 were also coherent with the existing model by *Revil et al.* [2007].

67 The first SPC measurements performed as a function of continuously decreasing water saturation were
68 reported by *Allègre et al.* [2010]. The raw SPC curves unexpectedly showed a non-monotonic shape as wa-
69 ter content decreases, which could not be described by any existing models at the time. *Revil and Linde* [2011]
70 argued that inconsistent signal processing as well as experimental issues regarding electrode stability were
71 responsible for *Allègre et al.* [2010] conclusions, which was demonstrated to be very unlikely [*Allègre et al.*,
72 2011]. *Allègre et al.* [2012] then supported *Allègre et al.* [2010] observations with a combined modelling of
73 the hydrodynamic conditions and the electrical potential simulating the same drainage experiments.

74 The influence of electrode stability on unsaturated SP measurements has to be treated carefully and
75 was investigated by *Jougnot et al.* [2012] who proposed that a drifting correction should be applied to raw
76 SP measurements, especially at low water saturation. Another kind of experimental correction was used by
77 *Mboh et al.* [2012] to address electrode drifting. *Allègre et al.* [2014] proposed continuous self-potential mea-
78 surements performed during drainage and imbibition cycles. After demonstrating that electrodes were ex-
79 tremely stable over time, especially at very low water saturation, they concluded that none of the existing
80 SPC models could correctly describe their observations. A semi-empirical expression addressing the drainage/imbibition
81 cycles dynamics was used to model the SP measurements. The flow dynamics and the behaviour of water/air
82 interfaces were argued to be of significant influence on the response of unsaturated SP [*Allègre et al.*, 2015].

83 Few theoretical and numerical studies showed that large values of the SPC can be observed under spe-
84 cific conditions regarding the chemistry of the electrolyte and structural properties of the porous medium [e.g.,

85 *Jackson, 2008, 2010*]. Numerical simulations performed by *Zhang et al.* [2014] suggested that the SPC ex-
 86 hibits an hysteresis between drainage and imbibition and that it can vary non-monotonically with saturation.
 87 Up to this date, neither existing datasets, nor numerical models are entirely consistent.

88 The current contribution aims to reconcile the experimental SP data from *Linde et al.* [2007], *Mboh*
 89 *et al.* [2012] and *Allègre et al.* [2010] by using the same processing steps. We emphasise that the water/air
 90 interfaces have to be included in the modelling process so that it can properly describe the unsaturated SP
 91 response.

92 **2 State of the art**

93 We present in this section the theoretical background of the electrokinetics and particularly of the stream-
 94 ing potential coefficient. We describe the different theories and models of the streaming potential as a func-
 95 tion of saturation. Then we show measurements of the streaming potential coefficient as a function of the
 96 water-saturation.

97 **2.1 Theoretical background**

98 The electrokinetic effect is due to fluid flow in porous media because of a particular distribution of ions
 99 within the electric double layer, which can induce a streaming electric current when water flows, which is
 100 counterbalanced by a conduction current. The general equation coupling the different flows is:

$$\mathbf{J}_i = \sum_{j=1}^N \mathcal{L}_{ij} \mathbf{X}_j \quad (1)$$

101 which links the forces \mathbf{X}_j to the macroscopic fluxes \mathbf{J}_i , through transport coupling coefficients \mathcal{L}_{ij} [*Onsager,*
 102 1931]. Notice that boldface is used to denote vector quantities.

In seismoelectrics the coupling between the hydraulic flow and the electric flow is induced by seis-
 mic wave propagation, which leads to a relative motion between the fluid and the rock matrix. The theory
 for the coupled electromagnetics and acoustics of porous media was developed by *Pride* [1994]. The trans-

port relations (Pride, 1994, Eqs. 250 and 251) are:

$$\mathbf{J}_e = \hat{\sigma}(\omega)\mathbf{E} + \hat{\mathcal{L}}(\omega) (-\nabla P + \omega^2 \rho^f \mathbf{u}_s), \quad (2)$$

$$\mathbf{J}_f = \hat{\mathcal{L}}(\omega)\mathbf{E} + \frac{k(\omega)}{\eta} (-\nabla P + \omega^2 \rho^f \mathbf{u}_s), \quad (3)$$

103 where an $e^{-i\omega t}$ time dependence has been assumed. The electrical fields and mechanical forces that induce
 104 the electric current density \mathbf{J}_e and the fluid volume flux $\mathbf{J}_f = -i\omega \mathbf{w}_f$ are, respectively, \mathbf{E} and $(-\nabla P +$
 105 $i\omega^2 \rho^f \mathbf{u}_s)$, where P is the pore-fluid pressure, \mathbf{u}_s and \mathbf{w}_f are respectively the solid and fluid displacements,
 106 \mathbf{E} is the electric field, ρ^f is the pore-fluid density, η the dynamic viscosity of the fluid [Pa s], and ω is the
 107 angular frequency.

The electrokinetic coupling $\hat{\mathcal{L}}(\omega)$ describes the coupling between the seismic and electromagnetic fields and is complex and frequency-dependent [Pride, 1994; Reppert et al., 2001]:

$$\hat{\mathcal{L}}(\omega) = \mathcal{L}_0 \left[1 - i \frac{\omega}{\omega_c} \frac{m}{4} \left(1 - 2 \frac{d^l}{\Lambda} \right)^2 \left(1 - i^{3/2} d^l \sqrt{\frac{\omega \rho^f}{\eta}} \right)^2 \right]^{-\frac{1}{2}}, \quad (4)$$

108 where m and Λ are geometrical parameters of the pores (Λ is defined in Johnson et al. [1987] and m is in
 109 the range 4–8), d^l the Debye length. The electrokinetic coupling is an important parameter: if this coupling
 110 is zero, then there is no seismo-electric nor electro-seismic conversion.

The electrokinetic coupling is related to the streaming potential coefficient \hat{C}_s as

$$\hat{\mathcal{L}}(\omega) = -\hat{\sigma}(\omega)\hat{C}_s(\omega); \quad (5)$$

with σ the rock conductivity. The frequency-dependence of the streaming potential coefficient [Jou-
 niaux and Bordes, 2012] can be measured as the ratio between the electric field induced by an applied pres-
 sure gradient, when the electric current density \mathbf{J}_e is zero as:

$$\hat{C}_s(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} \quad (6)$$

111 This coefficient has been studied on synthetic samples [Packard, 1953; Cooke, 1955; Groves and Sears, 1975;
 112 Sears and Groves, 1978; Chandler, 1981; Reppert et al., 2001; Schoemaker et al., 2007, 2008], and recently
 113 on sand [Tardif et al., 2011], and on unconsolidated materials [Glover et al., 2012]. However the effect of

114 water-saturation has been studied only on steady-state streaming potential coefficient, which is related to the
115 steady-state electrokinetic coupling.

The steady-state electrokinetic coupling is defined as:

$$\mathcal{L}_0 = -\sigma C_0 \left(1 - 2 \frac{\tilde{d}}{\Lambda}\right), \quad (7)$$

where the streaming potential coefficient C_0 (or SPC) ($V Pa^{-1}$) is defined when the electric current density \mathbf{J}_e

$$\mathbf{J}_e = -\sigma \nabla V - \mathcal{L}_0 \nabla P, \quad (8)$$

116 is zero.

When the surface conductivity can be neglected compared to the fluid conductivity, and assuming a laminar fluid flow and identical hydraulic and electric tortuosity, the streaming coefficient is described by the well-known Helmholtz-Smoluchowski equation [e.g., *Dukhin and Derjaguin*, 1974]:

$$C_0 = \frac{\Delta V}{\Delta P} = -\frac{\mathcal{L}_0}{\sigma} = SPC = \frac{\epsilon_f \zeta}{\eta \sigma^f}. \quad (9)$$

117 The relevant parameters influencing the SPC are the fluid relative permittivity ϵ_f , the fluid viscosity
118 η , the fluid conductivity σ^f and the zeta potential ζ , itself depending on rock, fluid composition, and pH .
119 The effect of these parameters has been modeled using Lattice-Boltzmann simulations within a large range
120 of salinity and compared to measured SPC [*Fiorentino et al.*, 2016].

Depending on the type of rocks the surface conductivity may not be negligible as for clay for example. Then the streaming potential coefficient can be written as:

$$C_0 = \frac{\epsilon_f \zeta}{\eta(\sigma^f + \sigma_s)}, \quad (10)$$

121 **with σ_s the surface conductivity ($S m^{-1}$) which can be inferred from $\sigma_s = 2\Sigma_s/R$, with R the hydraulic
122 radius of the rock or the pore radius and Σ_s the surface conductance (S) [*Rutgers, 1940; Alkafef and Alajmi, 2006; Wang and Hu, 2012*]. In Fontainebleau sand σ_s is less than $2 \times 10^{-4} S m^{-1}$ [*Guichet et al., 2003*].
123 **For quartz or sandstone typical values of Σ_s range from 8.9×10^{-9} to $4.2 \times 10^{-8} S$ [*Block and Harris,***
124**

125 **2006]** and 2.5×10^{-9} S for clays [Revil and Glover, 1998]. The surface conductivity can neither be ne-
 126 glected in clay layers, nor when the hydraulic radius is of the order of the Debye length. This latter case
 127 can be encountered when the fluid is not very conductive, as below $2 \times 10^{-3} \text{ S m}^{-1}$ in sandstones [Pozzi
 128 and Jouniaux, 1994]. In that case the streaming potential coefficient can be lowered compared to the ex-
 129 pected value. Since the hydraulic radius can be indirectly connected to the permeability, the effect of sur-
 130 face conductivity can explain some observations of permeability-dependence of the streaming potential
 131 coefficient [Jouniaux and Pozzi, 1995].

Another way to take into account σ_s without knowing the surface conductivity nor the conductance [Jouniaux et al., 2000], but knowing the rock conductivity σ possibly with a surface component and the formation factor F is:

$$C_0 = \frac{\epsilon_f \zeta}{\eta \sigma_{\text{eff}}} = \frac{\epsilon_f \zeta}{\eta F \sigma}. \quad (11)$$

132 2.2 Streaming potential coefficient modelling for unsaturated conditions

133 The effect of water-saturation on the SPC is still discussed, both through modelling and through the
 134 interpretation of the observations, although the effect of saturation on electrical properties is well known [Archie,
 135 1942; Carrara et al., 1999; Tsakiroglou and Fleury, 1999; Zhou et al., 2002; Bekri et al., 2003; Jouniaux et al.,
 136 2006; Kim et al., 2013]. Most of the models for the SPC can be written as a product between the SPC at full
 137 saturation C_{sat} and a function of saturation $S(S_w)$ as

$$C_0(S_w) = C_{\text{sat}} S(S_w) \quad (12)$$

Perrier and Morat [2000] were the first to propose that the SPC depends on the relative permeability, and proposed that SPC depends on the relative permeability k_r as:

$$C_0(S_w) = C_{\text{sat}} \frac{k_r(S_w)}{S_w^n}, \quad (13)$$

138 with S_w the water saturation, and n the second Archie exponent [Archie, 1942], where k_r is the relative per-
 139 meability defined as: $k_r(S_w) = (S_w - 0.1/0.9)^2$. Later Revil et al. [2007] proposed a similar formula as

140 proposed by *Perrier and Morat* [2000], assuming that the excess countercharge density scales inversely with
 141 water saturation.

Then *Jackson* [2010] developed a model for the SPC for unsaturated conditions through a capillary tubes model, including water or oil as fluid. *Jackson* [2010] showed that the electrokinetic coefficient depends on the relative permeability, the relative charge density, and the fluid content, assuming that Archie's law is valid, as:

$$C_0(S_w) = C_{\text{sat}} \frac{k_r(S_w) Q_r(S_w)}{S_w^n}, \quad (14)$$

142 with Q_r the relative excess charge density: $Q_r(S_w) = Q(S_w)/Q(S_w = 1)$. *Jackson* [2008, 2010] showed
 143 that the relative excess charge density depends on the pore-scale distribution of fluid and charge, and that
 144 it does not scale inversely with the water saturation. *Jackson* [2010] showed that the relative excess coun-
 145 tercharge density increases with decreasing water saturation in water-wet models, because water is first emp-
 146 tied from the large capillaries. As a result, the water progressively occupies a larger amount of small cap-
 147 illaries. All these models describe a monotonous decrease of the SPC from C_{sat} to zero with decreasing sat-
 148 uration, but it has been shown that the relative SPC C_r (i.e., normalized to C_{sat}) could be higher than 1,
 149 taking into account the specific flow and electrolyte properties [*Jackson, 2010*].

Allègre et al. [2012] modelled both Richards' equation for hydrodynamics and the Poisson's equation for electrical potential for unsaturated conditions using a 1-D finite element method, which was never reported for unsaturated conditions. They concluded, based on laboratory experiments and using these equations, that the unsaturated electrokinetic coefficient should have a non-monotonic behaviour:

$$C_0 = C_{\text{sat}} S_e [1 + \beta(1 - S_e)^\gamma], \quad (15)$$

where the effective saturation is:

$$S_e = \frac{S_w - S_{wr}}{1 - S_{wr}}, \quad (16)$$

150 and β and γ are two adjusted parameters, β depending on the initial flow conditions, particularly on the wa-
 151 ter velocity at the beginning of the drainage phase. Table 1 summarises the values of $C_0(S_w)/C_{\text{sat}} = S(w)$
 152 gathered from the literature.

2.3 Streaming potential coefficient observations for unsaturated conditions

The first experimental study on SP dependence on water content was carried out by Guichet et al (2003). They measured the SP associated to water flow during an experiment performed by injecting inert gas into a column filled with Fontainebleau sand (>99% quartz rich sand). The results, corrected from pH and electrical conductivity variations (Fig.1), suggested a monotonous and linear behaviour of the SPC as a function of the water saturation. They therefore proposed a linear relation, via:

$$C_0(S_e) = C_{sat}S_e. \quad (17)$$

154 *Linde et al.* [2007] measured SP signals associated to a gravity-driven drainage experiment and reported pres-
 155 sure head and outflow measurements. They concluded that the SP recordings could be modelled using the
 156 model from *Revil et al.* [2007]. We further discuss the results from this study in section 3. *Allègre et al.* [2010]
 157 reported the first continuous recordings of SP measured during a drainage experiment. Two main important
 158 observations were presented: 1) the SPC can be one order of magnitude larger than its value at saturation
 159 (C_{sat}); 2) its behaviour can be non-monotonic (first increasing then decreasing) with decreasing water sat-
 160 uration (Fig.2). The SPC reaches a maximum value that depends on the water flow velocity. No existing mod-
 161 els could support the dataset. The non-monotonic behaviour of the SPC is partly supported by the observa-
 162 tions from *Revil et al.* [2007] and *Revil and Cerepi* [2004] as discussed in *Allègre et al.* [2011], once the SPC
 163 value measured at saturation from *Revil and Cerepi* [2004] is properly included (Fig. 3).

164 *Vinogradov and Jackson* [2011] published SP data acquired during multiphase flow (e.g., water/air or
 165 water/oil) imbibition and drainage experiments. They used brine/undecane and brine/nitrogen mixtures. The
 166 SP measurements were provided at isolated water saturation values ranging from 0.2 to 0.5. One measure-
 167 ment was provided for saturated conditions (Fig. 4), but no data points were available for saturation between
 168 0.5 and 1. It was therefore difficult to conclude whether the SPC behaviour is non-monotonic in that case.

169 *Mboh et al.* [2012] reported streaming potential and water pressure measurements performed during
 170 a drainage experiment. The authors proposed to remove a trend from the SP data to ensure zero electrical
 171 potential difference at the end of the experiment (i.e., in no flow conditions) and the the value. The correc-
 172 tion also guarantied the SP signal to fit eq. 13 for saturated conditions. The resulting corrected SPC curves

173 were supported by the model from *Revil et al.* [2007]. This data set is analyzed from scratch in the follow-
174 ing section.

175 *Jougnot and Linde* [2013] performed a few drainage and imbibition experiments providing both SP and
176 hydrodynamic measurements. They observed some features in the SP signals that they attributed to electrode
177 issues. They compared their data set to the one from *Mboh et al.* [2012] and proposed that SP data should
178 be corrected from electrode effects such as leakage, especially when the medium is quite unsaturated. *Allègre*
179 *et al.* [2014] utilized another apparatus to measure self-potentials signals during drainage and imbibition cy-
180 cles. They argued that non-zero SP signals could occur for unsaturated conditions and proposed a water out-
181 flow based model to fit their data set. The measurements did not show any evidence for electrode leakage
182 that proved to be extremely stable over time, even for very low saturation values. They suggested that wa-
183 ter/air interfaces could be responsible for such variations. The influence of water/air interfaces on SP mea-
184 surements is fully discussed in section 4.

185 **3 Cross-analysis of streaming-potential data**

186 **3.1 Background**

187 Among the contributions on SP measurements published in the literature, we chose to combine the data
188 from *Linde et al.* [2007], *Allègre et al.* [2010] and *Mboh et al.* [2012], that we refer to as experiments I, II,
189 and III in the following. The three datasets were acquired under similar experimental conditions and exclu-
190 sively relate to drainage experiments performed in sand. The raw SP and hydrodynamic data available for
191 each study were used. We included an original dataset acquired using the experimental setup described in
192 *Allègre et al.* [2014] and designed for drainage/imbibition cycles experiments. We refer to this work as ex-
193 periment IV in the results section. We chose to focus on SP data recorded during non-steady state exper-
194 iments, since the dynamics of the water flow is a key parameter. We therefore did not include SPC measure-
195 ments performed in consolidated samples in quasi-static conditions [e.g., *Revil and Cerepi*, 2004; *Vinogradov*
196 *and Jackson*, 2011] .

197 3.2 Experimental procedures

198 The drainage experiment proposed by *Linde et al.* [2007] was performed in a 135 cm long and 35 mm
199 wide poly-vinyl chloride tube. The medium was a fine grain quartz sand saturated with tap water, whose the
200 electrical conductivity was $\sigma_w = 0.051$ S/m. The bulk electrical conductivity of the saturated mixture was
201 $\sigma_{sat} = 0.012$ S/m. The water pressure was monitored with ten tensiometers spread along the column (Fig.
202 5). The SP data were measured with 17 non-polarizable electrodes. The water contents were not measured.
203 The experimental course was described as: 1) a drainage phase was triggered by applying a pressure bound-
204 ary condition of 9.1 cm high water column at the lower end of the column, while the upper end was open
205 to atmosphere; 2) this lower boundary condition was removed after 6 hours, allowing a free gravity-driven
206 drainage phase to occur.

207 *Allègre et al.* [2010] experiment consisted in draining a 1.3 m long and 10 cm wide plexiglass column
208 filled with quartzic sand initially saturated with chemically equilibrated water. A constant pressure head of
209 2 cm was applied at the bottom of the column to drive the drainage experiment. The procedure stopped when
210 no outflow was recorded. The water pressure heads, water contents and SP data were monitored at ten lev-
211 els inside the column during the experiment (Fig. 5).

212 The experiment by *Mboh et al.* [2012] was performed in a 217.5 cm long and 5 cm wide plastic tube.
213 The medium was also a quartz sand, compacted on a portion of the column (117.5 cm). The water pressure
214 were measured using 6 tensiometers, and 10 SP electrodes were located along the column (Fig. 5). The pro-
215 tocol was designed in three steps: 1) the system was monitored at the hydrodynamic equilibrium (i.e., no
216 flow occurring) for 22 minutes; 2) a Mariotte reservoir was used to apply a constant head at the top for 38
217 minutes; 3) the reservoir is opened allowing a falling head experiment, followed by a drainage phase of the
218 column.

219 The experiment described by *Allègre et al.* [2014] was designed to monitor self-potential signals as-
220 sociated with drainage and imbibition cycles. The authors used a 30 cm long and 10 cm wide plexiglass col-
221 umn filled with saturated quartz sand. The singular experiment included here consisted of a step-by-step drainage
222 phase, followed by a step-by-step imbibition phase. The pressure heads and self-potentials were measured

223 at two locations along the column. The procedure consisted in incrementally decreasing the bottom pressure
 224 boundary condition to allow drainage. The imbibition phase mimics these steps by incrementally increas-
 225 ing the boundary condition until the initial condition was reached. The water contents were computed from
 226 solving the flow equation (details in the next section). The SP signals were measured between electrodes lo-
 227 cated along the column and a reference electrode located at the very bottom, in the saturated part of the sys-
 228 tem. Using a reference electrode remaining in the water provides a stable potential. This common reference
 229 allows to infer any dipole differences afterwards.

230 3.3 Hydrodynamic modelling

The hydrodynamic conditions of the experiments need to be constrained so that one can compute the
 SPC from the computed water pressure differences. Unsaturated flow through a homogeneous porous medium
 is well described by the Richards equation [Richards, 1931], which is formulated in 1D in its mixed form
 as,

$$\frac{\partial \theta(h)}{\partial t} - \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} - 1 \right) \right] = 0, \quad (18)$$

231 where $\theta(h)$ is the volumetric water content in $\text{m}^3 \cdot \text{m}^{-3}$, depending on the pressure head h (m). The param-
 232 eter K is the hydraulic conductivity ($\text{m} \cdot \text{s}^{-1}$), t is time (s), and z is the vertical coordinate (m), positive down-
 233 ward. The retention properties and a relative permeability model are necessary to solve eq. 18. Various mod-
 234 els are available to assess those properties and the studies presented here rely on a few different ones.

Linde et al. [2007] used the *van Genuchten* [1980] model which describes the behaviour of h as a func-
 tion of the water content as,

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1 + (\alpha_v |h|)^n)^m}, \quad (19)$$

235 where S_e is the effective water saturation, θ_s is the water content at saturation, which equals porosity ϕ , θ_r
 236 is the residual water content. The parameter α_v (m^{-1}) relates to the air entry pressure, and n and m are two
 237 empirical coefficients.

Substituting eq. 19 in the capillary model from *Mualem* [1976] yields to the following relative permeability model,

$$K(S_e) = K_s S_e^L \left[1 - (1 - S_e^{1/m})^m \right]^2, \quad (20)$$

with K_s the hydraulic conductivity at saturation (m/s). The values of m and n are linked by: $m = 1 - 1/n$. Usually, this decoupled model is used to improve the results of the parameter optimization of the inverse problem [van Genuchten and Nielsen, 1985]. The parameters used in *Linde et al.* [2007] are reported in Table 3. Associating α_v to m and n values in eq. 19 yields to a large air entry pressure. The resulting capillary fringe is almost 40 cm (Fig.6). The capillary fringe is a zone in which water pressure heads can be negative, but which remains saturated (Bear 1972).

Allègre et al. [2010] and *Allègre et al.* [2012] used the model of *Brooks and Corey* [1964] to address the retention behaviour of the medium as,

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} \left(\frac{h_a}{|h|} \right)^\lambda, & \text{if } \frac{h_a}{|h|} < 1 \\ 1, & \text{if } \frac{h_a}{|h|} > 1 \end{cases} \quad (21)$$

The parameter λ is an estimate of the pore size distribution, characterizing the medium granulometry, the larger the value of λ the more homogeneous the medium. The second hydrodynamic parameter h_a is the air entry pressure [Brooks and Corey, 1964] which can be related to α_v in eq. (19). The relative permeability behaviour followed the law of *Mualem* [1976] which leads to,

$$K(S_e) = K_s \cdot S_e^{L+2+\frac{2}{\lambda}}, \quad (22)$$

The parameters used by *Allègre et al.* [2010] and *Allègre et al.* [2012] are reported in Table 3.

The hydrodynamic measurements from *Linde et al.* [2007] and *Allègre et al.* [2010] were modelled using the code proposed by *Allègre et al.* [2012], that solves the electric and hydrodynamic forward problems simultaneously in one dimension. Hydrodynamic behaviour from *Mboh et al.* [2012] and *Allègre et al.* [2014] were modelled using Hydrus-1D (www.pc-progress.com), in both cases using the eqs. (19) and (20) for retention and permeability models. The parameter values from the two studies are reported in Table 3.

The figures 6a-h show the measured and simulated pressure heads for the experiments I, II and III, as well as the respective vertical profile of saturation inferred from the modelling results. Additional modelling

252 feature include the cumulative outflow measured by *Linde et al.* [2007], which is a good proxy to check the
253 robustness of the modelling *a posteriori*.

254 Even though the experimental conditions were similar for all experiments, one can observe that the
255 dynamics varies a lot from one to another. While 10 hours were necessary for experiment I to stop, it took
256 approximately 14 hours for experiment III, and about 200 hours for experiment II. The maximum water flow
257 was therefore much smaller during experiment II.

258 The investigated range of saturation is quite similar as far as the entire column is concerned. However,
259 *Allègre et al.* [2010] and *Mboh et al.* [2012] had electrodes located in the part of the medium where the sat-
260 uration significantly decreased (fig. 6c,i) whereas the saturation investigated by *Linde et al.* [2007] SP mea-
261 asurements ranged between 0.85 and 1 (Fig. 6f).

262 **3.4 Streaming potential measurements**

263 During each experiment, streaming potentials were measured between one electrode and a reference
264 located within the saturated part of the column. Additional SP differences can be inferred at any other elec-
265 trode locations by subtraction of the raw measurements. The figure 7 compiles the raw SP measurements
266 from experiments I and II. *Mboh et al.* [2012] corrected raw SP signals using a linear relation designed to
267 address a linear drift between the beginning and the end of the experiment. Following a basic procedure widely
268 reported in the literature [e.g., *Allègre et al.*, 2010; *Jougnot and Linde*, 2013], we started our analysis back
269 from the raw data and shifted them to zero at the experiment start time (Fig. 7a). Shifting the signals to zero
270 assesses that SP do not exist until water is in motion. *Mboh et al.* [2012] SP correction also intended to ac-
271 count for non-zero electric potential differences at the end of their experiment (i.e., no flow conditions).

272 *Jougnot and Linde* [2013] analysed *Mboh et al.* [2012] dataset in combination with one dataset of their
273 own which was acquired during drainage and imbibition experiments. They argued that electrode drifting
274 can be responsible for non-related SP signals, such as non-zero potential differences. *Zhang et al.* [2014] showed
275 with numerical simulations that non-zero SP could be observed in no flow conditions without the need for
276 the electrodes to be responsible for it. We later argue that the behaviour of water/air interfaces appearing when

277 the medium is unsaturated can be in fact responsible for *a priori* non-related SP signals. *Jougnot and Linde*
 278 [2013] also wrote that electrode effects were responsible for the behaviour of SP signals observed by *Allègre*
 279 *et al.* [2010]. *Allègre et al.* [2015] and *Fiorentino et al.* [2016] argued that water/air interfaces could be a plau-
 280 sible cause for that behaviour. The importance of water/air interfaces is further developed in section 4. Since
 281 *Jougnot and Linde* [2013] demonstrated that the electrodes they used could be unstable over the course of
 282 their experiment, we decided not to include their data in this section.

283 SP differences for electrode couples were inferred from raw measurements by subtraction of the raw
 284 signals (Fig. 7b-c). The experiment III shows consistently decreasing SP as water saturation decreases (Fig-
 285 ures 7c), until the dipoles stabilized. The behaviour of SP signals during experiment II is more chaotic with
 286 electrodes dipoles showing both decreasing and increasing values when saturation decreases (Fig. 7b).

287 Experiments II and III experienced very different flow dynamics. The figure 8a-b shows the total pres-
 288 sure differences computed at the location of SP electrode couples. The recovery of total pressure differences
 289 (i.e., pressures differences coming back to equilibrium) which drives the flow, was quite fast in the case of
 290 experiment III (Fig.8a). Such a recovery was not reached after 150 hours in the case of experiment II (Fig.8b).
 291 The impact of flow dynamics was argued to be of significant effect on the resulting SP response [*Allègre*
 292 *et al.*, 2015].

293 3.5 Streaming-potential modelling

294 The numerical approach of *Allègre et al.* [2012] allowed us to model the SP responses of experiments
 295 I and III. A constant SPC, equal to C_{sat} , and the model from *Guichet et al.* [2003] (eq. 17) were tested in
 296 the procedure. For both studies, the original modelling was performed using the SPC model from *Revil et al.*
 297 [2007]. For experiment I, the hydrodynamic modelling showed that the SP signals were measured within the
 298 part of the column that remained saturated during the experiment (Fig. 6f). The modelling results consequently
 299 show that the SP signals can be fairly estimated assuming a constant SPC, that equals C_{sat} (Fig. 9). Using
 300 the SPC model from *Guichet et al.* [2003] also leads to a good estimation of SP values. The influence of the
 301 SPC model is limited in that case since the saturation remains in the range [0.85; 1], and the electrical po-
 302 tential is less sensitive to saturation variations. The small SP amplitudes observed by *Linde et al.* [2007] ($|\Delta V|$

303 < 1.1 mV) probably result from the small value of the saturated SPC, $C_{sat} = -7.9 \times 10^{-7} \text{ V.Pa}^{-1}$. The
 304 SP signals measured in the transition zone, where $0.85 < S_w < 1$ (at 25, 35, 60 cm), exhibit a similar be-
 305 haviour than the other dipoles located in the saturated part. The experiment I does not show a significant sen-
 306 sitivity of SP signals to water content variations. Additionally, several models including a constant SPC can
 307 fairly predict the measurements.

308 The same approach was used for experiments III (Fig. 10) and experiment IV (Fig. 11). The data from
 309 experiment III are not corrected as mentioned in previous section. As for experiment I, the SP are modelled
 310 following the approach from *Allègre et al.* [2012] associated with a constant SPC and *Guichet et al.* [2003]
 311 SPC model. If the trend of SP signals is pretty well described in both cases, the amplitudes of the dipoles
 312 from 73 cm to 109 cm are underestimated (Fig. 10). The dipoles from 73 to 109 cm correspond to water
 313 saturation ranging from 0.2 to 0.3. The SP measurements from *Mboh et al.* [2012] are therefore much more
 314 sensitive to water saturation than those from experiment I.

315 The experimental SPC curves from experiment III are compared to those from *Allègre et al.* [2010] ex-
 316 periment in figure 12. The shape of the SPC from experiment III is significantly altered if no SP correction
 317 is applied (Fig. 12a-c). One can notice the significant scattering when the water saturation goes very low,
 318 and increasing SPC, which is due to too small pressure difference when using eq. (9). The relative SPC curves
 319 from experiment III now exhibit value larger than 1, which is a feature shared with *Allègre et al.* [2010] re-
 320 sults. Although the relative SPC can show non-monotonous behaviour for $0.6 < S_w < 0.9$ (e.g., $C_{r/9,8}$
 321 and $C_{r/7,6}$ in fig. 12c), it generally decreases when saturation decreases. Interestingly, the relative SPC val-
 322 ues for experiment II are lower for larger water flow (Fig. 12d), The upper dipole shows higher velocity since
 323 the decrease of the water saturation happens for this dipole at the beginning of the drainage. so I would write
 324 the reverse which could be be related to the amount and dynamic of water/air interfaces (see next section).

325 Experiment IV was performed with a shorter column (fig.11e), which explains why the drainage phases
 326 lasted less than those of experiment III. A few millivolts SP signals was produced overall, which is simi-
 327 lar to experiment III. Figure 11 presents all of six drainage phases. Although phases d_1 and d_2 produces a
 328 pressure drop and an outflow (Figs. 11a-b), an extremely weak, almost not measurable SP was created. The

329 phases d_3 and d_4 produced measurable SP drops, that were followed by a recovery phase to zero potential.
 330 The following phases are associated to few mV amplitude SP with no recovery. The beginning of phase d_5
 331 defines a sort of a water saturation threshold beyond which no recovery occurs anymore. Again, the stabi-
 332 lization of SP signals as soon as the medium is sufficiently unsaturated can easily be related to the influence
 333 of water/air interfaces. *Allègre et al.* [2014] demonstrated that their electrodes were extremely stable during
 334 the experiment and not responsible for that stabilization of SP signals. The next section addresses the im-
 335 portance of the water/air interfaces in the SP response for unsaturated conditions.

336 **4 Importance of the interface water/air**

337 We saw that the SPC can show a non-monotonous behaviour with the water saturation, and that clas-
 338 sical models assuming a monotonous behaviour can not be used for unsaturated conditions. For unsaturated
 339 conditions two interfaces have to be taken into account: the interface between the matrix and the water, and
 340 the interface between the water and the air. Indeed both interfaces are charged and are described as electric
 341 double layer or triple layer, and can contribute to the streaming potential through the electrokinetic coupling.
 342 Depending on the quantity, mobility, and evolution of these interfaces, according to different conditions of
 343 fluid flow such as drainage or imbibition, these contributions can show different behaviours. We describe be-
 344 low these interfaces, and show some recent results of the modelling of both interfaces using the Lattice Boltz-
 345 mann approach.

346 **4.1 Rock/water interface**

347 The interface between rock and water is related to the existence of an electrical double layer between
 348 the rock and the fluid. Minerals forming the rock develop an electric double-layer when in contact with an
 349 electrolyte, usually resulting from a negatively charged mineral surface. An electric field is created perpen-
 350 dicular to the surface of the mineral which attracts counterions (usually cations) and repulses anions in the
 351 vicinity of the pore matrix interface. The electric double layer (Fig. 13) is made up of the Stern layer, where
 352 cations are adsorbed on the surface, and the Gouy diffuse layer, where the number of counterions exceeds
 353 the number of anions [*Adamson, 1976; Davis et al., 1978; Hunter, 1981*].

The distribution of the electrical potential ϕ within the electrical double layer, perpendicular to the solid surface can be calculated resolving the Poisson's equation:

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_f} \quad (23)$$

where ϵ_f is the dielectric constant of the fluid. The fluid contains M_i ionic species with valence z_i ($i=1, \dots, M_i$) and number density N_i^b (the number of species- i ions per unit volume) in the bulk solution far from any charged surface. The charge density ρ can be expressed using a Boltzmann distribution for the ionic species within the fluid:

$$\rho = \sum_{i=1}^M e z_i N_i^b \exp\left(-\frac{e z_i \phi}{kT}\right) \quad (24)$$

where k is the Boltzmann constant, $-e$ is the charge of an electron, T is the temperature. It is often assumed that the Poisson-Boltzmann equation governing the equilibrium charge clouds can be linearized. Assuming $e\phi/kT \ll 1$, the Poisson's equation becomes:

$$\nabla^2 \phi = (d^l)^{-2} \phi \quad (25)$$

with d^l the Debye length, which is a measure of the thickness of the double diffuse layer, typically of the order of a few nm:

$$\frac{1}{(d^l)^2} = \sum_{i=1}^M \frac{e^2 z_i^2 N_i^b}{\epsilon_f kT} \quad (26)$$

The electrical potential ϕ at a distance x from a charged surface is therefore

$$\phi(x) = \zeta \exp\left(-\frac{x}{d^l}\right) \quad (27)$$

354 and ζ is called the zeta potential and is the electrical potential at the shear plane (for further details see *Pride*
355 [1994]). The zeta potential itself depends on rock, fluid composition, and pH [*Ishido and Mizutani*, 1981;
356 *Jouniaux et al.*, 1994, 2000; *Jouniaux and Pozzi*, 1995; *Lorne et al.*, 1999; *Guichet et al.*, 2006; *Maineult et al.*,
357 2006b; *Jaafar et al.*, 2009; *Vinogradov et al.*, 2010].

358 The charge density at the surface of the minerals results from surface complexation reactions. The quartz
359 surface can be modelled with silanol $>SiOH$ group [*Davis et al.*, 1978]. The potential-determining ions

360 OH^- and H^+ are adsorbed onto the surface of the mineral and determine the charge density on the inner
 361 plane (see figure 13). Therefore the surface charge depends on the pH. There exists a pH for which the total
 362 surface charge is zero: this is the point of zero charge and pH is called pH_{pzc} [Davis and Kent, 1990;
 363 Sposito, 1989]. The charge is positive for $pH < pH_{pzc}$ and negative for $pH > pH_{pzc}$. In this case this
 364 electrokinetic effect is zero. The pH_{pzc} for quartz is in the range $2 < pH_{pzc} < 4$ [Parks, 1965; Lorne
 365 *et al.*, 1999]. The calcite surface can be modelled with $> CaOH$ and $> CO_3H$ groups. Carbonate ions
 366 and Ca^{2+} are the determining-potential ions. The electrokinetic behavior on carbonates is more complicated.
 367 The pH_{pzc} varies from 7 to 10.8 according to the authors [VanCappellen *et al.*, 1993].

368 It is possible to model simple interfaces and to calculate zeta potential in simple cases [Guichet *et al.*,
 369 2006]. This modeling can be performed assuming the triple-layer-model (TLM) which distinguishes three
 370 planes to describe the electric double layer: the inner Helmholtz plane for counter ions directly bound to the
 371 mineral (assumed to be chemically adsorbed), the outer Helmholtz plane for weakly bound counter ions (as-
 372 sumed to be physically adsorbed), and a d -plane associated with the smallest distance between the mineral
 373 surface and the counter ions in the diffuse layer. It has been proposed that the slipping plane lies near the
 374 distance of closest approach of dissociated ions and that the ζ potential can be calculated as the potential
 375 on this plane [Davis and Kent, 1990].

376 At a given pH the most influencing parameter on the streaming potential coefficient is the fluid con-
 377 ductivity. It has been proposed that $C_0 = -1.2 \times 10^{-8}(\sigma^f)^{-1}$ [Allègre *et al.*, 2010], based on data col-
 378 lected in the literature on sandstones and sands (Fig. 14), which leads to a zeta potential equal to -17 mV
 379 assuming Eq. (9) and that zeta potential, dielectric constant, and viscosity do not depend on fluid conduc-
 380 tivity. These assumptions are not exact, but the value of zeta is needed for numerous modellings which usu-
 381 ally assume the dielectric constant and viscosity independent of the fluid conductivity. Luong and Sprik [2014]
 382 also proposed that the zeta potential is constant over a large range of electrolyte concentration. A recent study,
 383 taking into account the viscosity and permittivity relationship with the electrolyte concentration, deduced a
 384 constant apparent zeta potential of -21 mV, from the comparison of modelling and experimental data set from
 385 the literature [Fiorentino *et al.*, 2016]. Therefore an average value of **an apparent zeta** -20 mV for the needed
 386 input value in modellings is fairly exact, at least for media with no clay nor calcite, and in the fluid conduc-

387 tivity range excepting very high values. Another formula is often used [*Pride and Morgan, 1991*] based on
 388 quartz minerals rather than on sands and sandstones, which may be less appropriate for field applications
 389 **when this formula is used in the models without taking into account the effect of the fluid conductivity**
 390 **on all the parameters leading to biased values of the streaming potential coefficients..**

391 The streaming current is due to the motion of the diffuse layer induced by a fluid pressure difference
 392 along the interface. **It has been proposed that the streaming current could be used to deduce the perme-**
 393 **ability [*Jouniaux, 2011; Wang et al., 2016*].** This streaming current is then balanced by the conduction cur-
 394 rent, leading to the streaming potential which is proportional to the zeta potential (eq.9): the knowledge of
 395 the electric double layer of the rock/water interface and its zeta potential is therefore essential. In the same
 396 way the knowledge of the water/air interface is essential and is described below.

397 **4.2 Water/air interface**

398 Recently *Allègre et al.* [2015] showed that the interface between water and air should also be taken into
 399 account, since this interface is negatively charged, as the interface between the rock matrix and the water.

400 The interface developed between water and air is negatively charged (Fig. 15), the associated zeta po-
 401 tential being negative and ranging from -65 mV to -35 mV in distilled water [e.g., *Graciaa et al., 1995;*
 402 *Takahashi, 2005*]. For a water electrical conductivity of 10^{-2} S/m (equivalent to NaCl concentration of 10^{-3}
 403 mol/l) and for pH=7, the zeta potential ranges from -30 mV to -40 mV [e.g., *Yang et al., 2001; Creux et al.,*
 404 *2007*]. We can note that sand/water interfaces are also negatively charged, the associated zeta potential be-
 405 ing equal to -20 mV. When relative motion occurs at the shear plane of the air/water interface, this results
 406 in a streaming current density identical in sign to the current classically created at water/grain interfaces. On
 407 the contrary, if the water/air interfaces are dragged, and there is no relative motion, no additional stream-
 408 ing current will occur.

409 **4.3 Evolution of the water/air interface during a drainage**

410 One should consider that the streaming current depends on the amount of charges mobilized during
 411 a flow. The excess countercharge density depends on the electrical characteristics of the rock/water interface

412 and it has been shown that the matrix/water interfacial area decreases monotonously with decreasing water-
413 saturation (Fig. 16) [Culligan *et al.*, 2006].

414 However the excess countercharge density should also depend on the water/air interfaces in the case
415 of multi-phase flow (water/air/rock). During a drainage phase the surface-area of the water/air interfaces does
416 not decrease with decreasing water-saturation, but first rises to a maximum, and finally decreases. This be-
417 haviour has been observed during drainage experiments (Fig. 17) [Culligan *et al.*, 2004], and has been also
418 modelled [e.g., Reeves and Celia, 1996; Berkowitz and Hansen, 2001]).

419 We argue that the behaviour of the unsaturated SPC is related to the surface-area of the water/air in-
420 terfaces, since it displays a non-monotonous behaviour as a function of water saturation. This quantity af-
421 fects the cohesion of the material: the larger the surface-area of the interfaces, the larger the cohesive stress
422 of the material. It has been shown that the cohesive stress first increases with decreasing water saturation
423 (capillary regime), then reaches a maximum value (within the funicular regime), and finally decreases with
424 further decreasing saturation [e.g., Mitarai and Nori, 2006] (see Fig. 18). During a drainage experiment of
425 a sand column, the upper dipoles first undergo a capillary phase followed by a funicular phase. The upper-
426 most sand may be subject to a pendular regime.

427 However to quantify the relative importance of the contribution of the surface-area of the water/air in-
428 terface to the surface-area of the matrix/water interface, we developed a two-phase lattice Boltzmann mod-
429 elling, whose first results are described in the following section.

430 **4.4 Two-phase modelling of steaming potential**

431 The streaming potential coefficient has been modelled solving the Navier-Stokes equation and the Poisson-
432 Boltzmann equation, using the lattice Boltzmann method in a 2D capillary channel [Fiorentino *et al.*, 2016].
433 This method allows to model the electrokinetic coupling at a small scale. The flow of an electrolyte within
434 a channel is simulated, as well as the accumulation of charges at the rock/water and water/air interfaces. Then
435 these results are coupled through the computation of the electric field induced by the water flow, via a sec-
436 ond Lattice Boltzmann model solving the Poisson-Boltzmann equation. The macroscopic streaming poten-

437 tial coefficient is deduced from averaging the electric field on the entire channel and from the pressure dif-
 438 ference allowing the fluid flow. The presence of water and air within the channel has been studied through
 439 several cases: a- the water and the air flows are parallel; b- the air is entrapped within the pores; c- the air
 440 flows through bubbles [Fiorentino et al., 2017]. The zeta potential of both interfaces is set at $-20mV$.

441 **4.4.1 Air flow parallel to the channel**

442 The water content is decreased by increasing the air content in the middle of the channel: the inter-
 443 face water/air is therefore parallel to the interface matrix/water, and the diameter of this air corridor is in-
 444 creasing while the water saturation is decreasing. In this case the surface area of the water/air interface is
 445 continuous and constant whatever is the water saturation, except at full water saturation. The streaming po-
 446 tential coefficient is calculated as a function of the water saturation: C_{EK}^{all} involves all the sites of the chan-
 447 nel, C_{EK}^w involves the sites within the water excluding the sites within the air which is not a conducting phase.
 448 The streaming potential coefficient is increasing with increasing water saturation, up to the full water sat-
 449 uration for which the interface water/air does not exist anymore, leading to a decrease of the streaming po-
 450 tential coefficient (Fig.19). These results show a non monotonous behaviour of the streaming potential co-
 451 efficient with the water saturation, without involving an increase of the surface area of the water/air inter-
 452 face. The increase of the SPC with increasing saturation is linked to the increase of the fluid velocity at the
 453 interface water/air which is moving towards the centre of the channel when the water saturation is increas-
 454 ing. Therefore the positive charge excess of the water/air interface is enhanced by a larger velocity, leading
 455 to an increase of the SPC.

456 **4.4.2 Flow with entrapped bubbles**

457 Air bubbles are entrapped on the wall of the channel, with an increasing size for a decreasing water
 458 saturation. The resulting SPC is also non monotonous with the water saturation with a possible increase within
 459 the range 95% to 80% water saturation (Fig.20). In this case the fluid velocity is decreasing with decreas-
 460 ing water saturation, and the charge density and the surface area of the water/air interface is increasing, re-
 461 sulting in such a behaviour of the SPC.

462 **4.4.3 Flowing bubbles**

463 Air injection in the channel is simulated by flowing an increasing number of bubbles in the centre of
464 the channel, that finally merge together. The streaming potential coefficient shows a non monotonous behaviour
465 with water saturation, linked to a decrease of the fluid velocity with decreasing water saturation, and to an
466 increasing charge density and surface area of the water/air interface with decreasing water saturation (Fig.21).
467 The step in SPC between 55% and 50% is linked to the fact that two bubbles merge into one bubble. The
468 value of the SPC at 82% (star) corresponds to a configuration with more than two bubbles and shows a higher
469 value compared to the SPC value at 82% with two bubbles. The SPC values (dots) involve a zeta potential
470 of $-20mV$ for both matrix/water and water/air interface, whereas the SPC values (crosses) are calculated
471 with a null zeta potential at the interface water/air. The results are therefore very different when the inter-
472 face water/air is not taken into account. The non monotonous behaviour of the SPC can hardly be seen when
473 the water/air interface is neglected: the main contribution to the SPC comes from the water/air interface.

474 Therefore these numerical results show that the water/air interface is the main contribution in the elec-
475 trokinetic signal for unsaturated conditions, even if the surface area of this interface is constant. An increase
476 of this interface further contribute to the electrokinetic signal. It has to be noted that we made the assump-
477 tion that the negative charges causing the zeta potential at the interface air/water are placed in the air phase
478 and stay in the air. They do not contribute to the calculation of the SPC. If these negative charges were in
479 the water, they would contribute to the local electric charge density. In the case of flowing bubbles these charges
480 would move and induce an electric current balancing the electric current due to the excess positive charges.
481 Then the enhancement of the SPC with decreasing saturation would be linked to the difference of velocity
482 between air and water which is near zero. Therefore for flowing bubbles the SPC would not be increased
483 with decreasing saturation, whereas for fixed bubbled the SPC would still first increase with decreasing sat-
484 uration and then decrease with further decreasing saturation. We discuss in the following section the effect
485 of different behaviour of the streaming potential coefficient on seismoelectric conversions for unsaturated
486 conditions.

487 5 Consequences on seismoelectric conversions for nonsaturated cases

488 We now describe how the behaviour of the streaming potential coefficient for unsaturated conditions
 489 is taken into account in the modelling of the seismoelectric conversions. Then we summarize the seismo-
 490 electric observations for unsaturated conditions.

491 5.1 Seismoelectric modelling for unsaturated conditions

492 An extension of Pride's equations aiming to take into account unsaturated materials, in the case of a
 493 water-air mixture has been developed by *Warden et al.* [2013]. The effective medium theory is used to ex-
 494 press mechanical properties such as the bulk and shear moduli and dynamic viscosity (see Table 2). The medium's
 495 permittivity is derived using the Complex Refractive Index Method, while its conductivity is obtained by ex-
 496 tending the conductivity derived by *Pride* [1994] (Equation 242) to partial saturation conditions; this expres-
 497 sion takes the surface conductivities into account. This approach is combined with the strategy introduced
 498 by *Strahser et al.* [2011], thus writing the dynamic seismoelectric coupling under partial saturation condi-
 499 tions as a function of the saturation-dependent Streaming Potential Coefficient (SPC).

500 In order to express the static seismoelectric coupling \mathcal{L}_0 under partial saturation conditions, the SPC
 501 at full saturation in Equation 7 is replaced by the saturation-dependent SPC given in Equation 12. One also
 502 needs to replace the rock effective conductivity at full saturation in Equation 7 with a saturation-dependent
 503 effective conductivity. Using Archie's second law, that is, neglecting surface conductivities:

$$\sigma = \frac{\sigma^f}{F} S_w^n = \sigma^f \phi^m S_w^n = \sigma^f \frac{\phi}{\alpha_\infty} S_w^n \quad (28)$$

504 Therefore, $\mathcal{L}_0(S_w)$ can be written as:

$$\mathcal{L}_0(S_w) = -\frac{1}{F} \frac{\epsilon_f \zeta}{\eta} \left(1 - 2 \frac{\tilde{d}}{\Lambda}\right) S_w^n S(S_w) \quad (29)$$

505 with S_w a function of saturation being possibly different (see Table 1).

506 By implementing this approach in the GMRT method by *Garambois and Dietrich* [2002], *Warden et al.*
 507 [2013] studied the interface responses (IR) created by a saturation contrast, and evaluated the influence of
 508 the presence of a capillary fringe. They concluded that an IR created by a saturation contrast between sand
 509 and sandstone may be easier to detect than a seismoelectric conversion occurring at the same boundary be-
 510 tween sand and sandstone with the two units fully saturated. Moreover, they proved that the conversions de-
 511 pend on the type of saturation transition existing between the partially saturated and fully saturated units,
 512 as it is depicted in Fig. 22. The extension for the electrokinetic coefficient using different $S(S_w)$ to handle
 513 partially saturated media was later used to perform computational simulations of the interface responses at
 514 different saturations in a CO₂ geological deposition site [*Zyserman et al.*, 2015], and to analyze the contam-
 515 ination of a fresh water aquifer by dense non-aqueous liquids [*Munch and Zyserman*, 2016]. In the former,
 516 it was observed that the IR are sensitive to CO₂ saturations ranging between 10% and 90%, and that the CO₂
 517 saturation at which the IR maxima are reached depends on the models employed for $S(S_w)$. Moreover, the
 518 simulations predict that the IR's are still sensitive to different CO₂ saturations for a sealed CO₂ reservoir
 519 covered by a clay layer. For the latter, it was observed that the predicted IR's are sensitive to different con-
 520 taminants saturation only when the thickness of the contaminated layer is larger than a threshold value de-
 521 pending on the properties of the non-aqueous fluid and the saturation function $S(S_w)$; in Fig. 23 this situ-
 522 ation is depicted.

523 Other authors, e.g., *Jardani et al.* [2010]; *Revil and Jardani* [2010]; *Revil and Mahardika* [2013] pro-
 524 posed a model alternative to Eq.(29) for the electrokinetic coupling at partial saturation; instead of work-
 525 ing with the zeta potential, they based the coupling on the excess of electrical charge present in the pore wa-
 526 ter. However, their model also employs a still not validated -to the authors' knowledge- relationship between
 527 the mentioned excess charges and the rock permeability; this point is discussed by *Jouniaux and Zyserman*
 528 [2015], so that this approach should not be used unless the relation between the excess charge density and
 529 the permeability is proved. Within this frame, *Revil and Mahardika* [2013] studied two-phase flow conditions
 530 and proposed a numerical application for water flooding of a non-aqueous phase liquid (NAPL, oil) contam-
 531 inated aquifer where they observed that seismoelectric conversions mostly take place at the NAPL (oil)/water
 532 invasion front and could be used to remotely track its position; *Sava et al.* [2014] proposed a method to im-

533 age the soil electrical resistivity between a set of wells, by mapping the interfaces between different forma-
 534 tions by means of seismoelectrics, and afterwards deriving the electrical resistivity using crosswell electric
 535 tomography. They concluded that the proposed methodology could resolve the fine structure of resistivity
 536 between the wells.

537 **5.2 Seismoelectric observations for unsaturated conditions**

538 The effect of moisture on seismoelectrics was studied in laboratory through experiments performed on
 539 samples. However it is difficult to deduce a behaviour of the transfer function as a function of the water-saturation,
 540 because of different conditions in the laboratory experiments.

541 The seismoelectric (SE) potential was measured to increase with increasing moisture from 1 to 17 %
 542 on samples of limestone, sandstone, aleurolites and marl. At moisture in excess of 15 % a slight decrease
 543 was observed in some samples. The inflection of this curve was shifted toward higher moisture values in pro-
 544 portion to the increase in the concentration of the solution [*Gaskarov and Parkhomenko, 1974*]. A sharp in-
 545 crease at low water content was observed in other studies, and could then be constant at increasing water
 546 content on dolomite, marl and sandstones, or could decrease on tegillate loam, morainic loam, and limestones
 547 for a frequency of the seismic source around 25 kHz [*Parkhomenko and Tsze-San, 1964; Parkhomenko and*
 548 *Gaskarov, 1971; Ageeva et al., 1999*]. However, at low frequencies (400 Hz compared to 25 kHz) no decrease
 549 of the SE effect was observed with increasing water saturation. Only *Ageeva et al. [1999]* performed mea-
 550 surements at low frequencies (400 Hz), but they normalized the SE signal to the response of the source of
 551 the elastic waves (the test transducer, in V), so that the coseismic transfer function (Eq. 30) cannot be de-
 552 duced.

Seismo-electric conversions in the field can be observed at different conditions of water-content. The
 water content of the soil can be deduced from electrical resistivity survey or georadar survey. *Strahser et al.*
 [2011] observed seismo-electric conversions in the field, as a function of water-saturation, and proposed a trans-
 fer function between the electric field and the acceleration as a function of the water-saturation. These au-
 thors proposed to modify the transfer function developed by *Garambois and Dietrich [2001]*, in the low fre-
 quency assumption valid at seismic frequencies, meaning at frequencies lower than the Biot's frequency sep-

arating viscous and inertial flows. In this case, and assuming the Biot's moduli $C \ll H$, *Garambois and Dietrich* [2001] showed that the SE field \mathbf{E} is proportional to the grain acceleration for longitudinal fast P waves:

$$\mathbf{E} \simeq -\frac{\mathcal{L}_0}{\sigma} \rho^f \ddot{\mathbf{u}} = \frac{\epsilon_f \zeta}{\eta \sigma^f} \rho^f \ddot{\mathbf{u}}. \quad (30)$$

Based on their field observations *Strahser et al.* [2011] proposed that in the low frequency domain, taking into account the water saturation, the SE field and the seismic field are related as:

$$\mathbf{E} \simeq \frac{\epsilon \zeta}{\eta \sigma^f} S_e^{(0.42 \pm 0.25)n} d_f \ddot{\mathbf{u}}. \quad (31)$$

553 These observations could not be performed in a large range of water-content, leading to relatively scattered
554 data.

555 Recently the effect of water saturation on coseismic SE signals was studied on sand [*Bordes et al.*, 2015].
556 Experiments were performed during imbibition and drainage for several cycles, and the water-content was
557 measured by capacitance probes. These authors developed as seismic source a steel ball hitting a granite cylinder
558 in contact with the sand [*Sénéchal et al.*, 2010], showing a main frequency content of about 1.5 kHz and
559 inducing direct P wave [*Barrière et al.*, 2012]. The electric signal was recorded by electrodes dipoles (10
560 cm apart) along the P wave propagation. The authors estimated the transfer function of the electric field (elec-
561 tric field over acceleration) by picking the arrival in time domain, and by a spectral analysis using contin-
562 uous wavelet transform. Both methods showed that these ratios are of the order of $2-7 \times 10^{-4} \text{ V m}^{-2} \text{ s}^{-2}$
563 (depending on the offset to the source) and are rather constant in the water saturation range 0.2–0.9 for im-
564 bibition and drainage experiments. None of the tested models for the water-saturation dependence of the SPC
565 could model correctly a constant transfer function in this range of saturation.

566 **6 Discussion and conclusions**

567 Measurements of SP for unsaturated conditions published in the literature do not always show the same
568 trend, because they can depend on the conditions of the experiment. Whether the experiment consists of a
569 drainage phase, of an imbibition phase, or uses air injection, results in very different pressure behaviours (Fig.
570 8), and leads to a different SP response. We show that the raw SP data should not be corrected for a drift
571 if the electrodes are stable in a saturated medium. The apparent drift of the SP signals is due to water/air

572 interfaces, which are negatively charged such as rock/water interfaces. Such a drift is therefore part of the
 573 useful signal.

574 Relevant unsaturated SPC curves can be inferred from raw observations if the experiments investigate
 575 a large saturation range. We showed that the model tested in *Linde et al.* [2007] is based on SP measurements
 576 performed at saturation ranging from 0.85 to 1, and that these signals [*Linde et al.*, 2007] can be fairly well
 577 simulated using a constant SPC equal to C_{sat} (Fig. 9). Therefore, one should not rely on this study to in-
 578 terpret SP measurements out of that saturation range. The SPC models from *Revil et al.* [2007] and *Linde*
 579 *et al.* [2007] models, assuming that the excess of charge in the diffuse layer to saturation ($Q_{v,sat}$) scales
 580 $1/S_w$, is not supported by these observations if $S_w < 0.85$.

581 The underlying physics of a non-monotonous behaviour of the SPC is related to water/air interfaces
 582 as shown by the results of the lattice Boltzmann numerical simulations. Whether the water/air interfaces pro-
 583 gresses as an air flow parallel to the channel, or as a flow with entrapped bubbles, or as flowing bubbles,
 584 the results predict a non-monotonous behaviour of the SPC with the water saturation. The main contribu-
 585 tion to the SPC comes from the charged water/air interface, and not from the rock/water interface, assum-
 586 ing the same zeta potential for both interfaces. Two competing effects are involved: the decrease of the fluid
 587 velocity with decreasing water saturation, and the increase of the charge density and the surface area of the
 588 water/air interface with decreasing water saturation. A non monotonous behaviour of the SPC also appears
 589 without any increase of the surface area of the water/air interface with decreasing water saturation.

590 One should use a non-monotonous SPC in order to model seismoelectric conversions. This assump-
 591 tion allows a larger SPC value for saturation ranging from 0.6 to 1 leading to larger amplitudes of seismolec-
 592 tric conversions However, seismoelectric conversions occurring for unsaturated conditions do not only rely
 593 on the saturation dependence of the SPC [*Bordes et al.*, 2015; *Warden et al.*, 2013], and observations and mod-
 594 elling are still not always coherent.

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Reference	$C_{s0}(S_w)/C_{sat}$
<i>Perrier and Morat</i> [2000]	S_e^2/S_w^n
<i>Guichet et al.</i> [2003]	S_e
<i>Jackson</i> [2010]	$S_e^{(L+2+2/\lambda)} Q_r(S_w)/S_w^n$
<i>Allègre et al.</i> [2012]	$S_e(1 + 32(1 - S_e)^{0.4})$

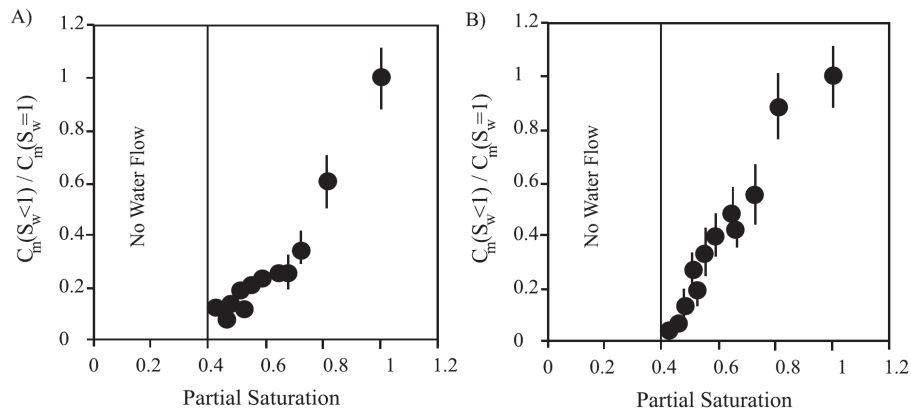
974 **Table 1.** Streaming Potential Coefficient behaviours as a function of water-saturation. The effective saturation S_e is defined
975 in eq.16 in which S_{wr} denotes the residual saturation, n is Archie's saturation exponent, L and λ are the Mualem's parameters
976 in the relative permeability formula *Mualem* [1976].

Parameter	S_w dependence	Expression
K_f (Pa)	YES	<i>Brie et al.</i> [1995]: $K_f(S_w) = (K_{eau} - K_{air})S_w^5 + K_{air}$
ρ_f (Kg/m ³)	YES	Arithmetic average: $\rho_f(S_w) = (1 - S_w)\rho_{air} + S_w\rho_{eau}$
η (Pa.s)	YES	<i>Teja and Rice</i> [1981]: $\eta(S_w) = \eta_{air}(\eta_{eau}/\eta_{air})^{S_w}$
b_1 (N.s/m)	NO	Computed for water only with Einstein-Stokes' law.
ϵ (F/m)	YES	CRIM: $\epsilon = \epsilon_0[(1 - \phi)\sqrt{\kappa_{quartz}} + \phi S_w\sqrt{\kappa_{eau}} + \phi(1 - S_w)\sqrt{\kappa_{air}}]^2$
α_∞	NO	Hydraulic (geometric) tortuosity.
Λ (m)	NO	Characteristic length of the microstructure.
ω_t (rad/s)	YES	$\omega_t = \frac{\eta(S_w)}{Fk_0\rho_f(S_w)}$
C_{em} and $C_{os}(S)$	NO	Computed for water only using Pride's expressions.
σ (S.m)	YES	$\sigma(S_w, \omega) = \frac{1}{F}(\sigma_f S_w^n + 2\frac{C_{em} + C_{os}(\omega)}{\Lambda})$

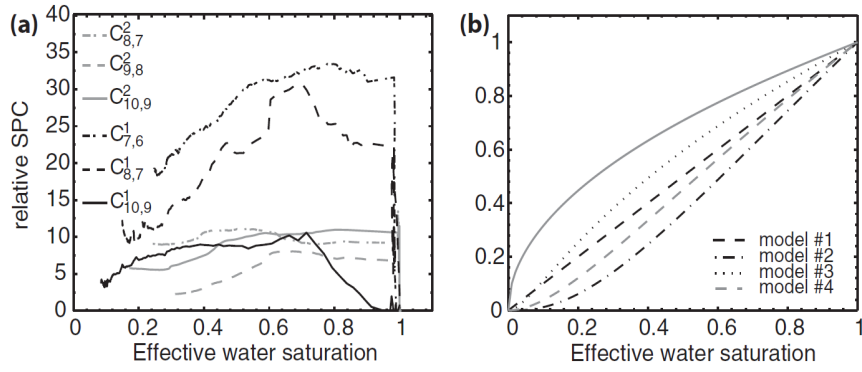
Table 2. *Effective properties for a water-air mixture, from Warden et al. [2013]*

978 **Table 3.** Parameters used in eqs. 19, 20, 21 and 22. The parameters m_{theta} and m_K are the values of m used in eqs. 19 and
 979 20 respectively.

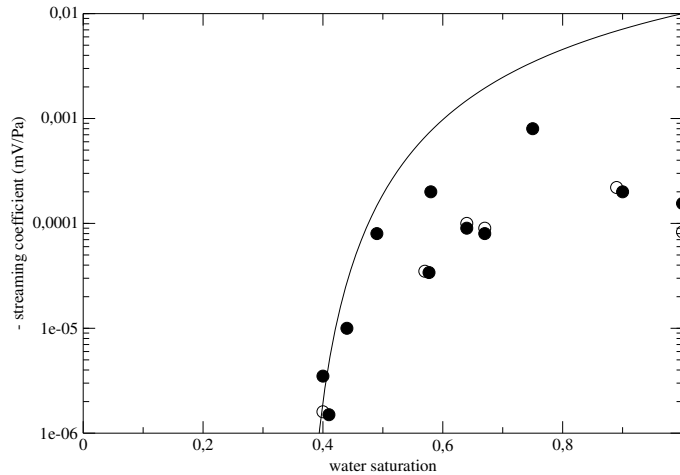
Experiment	n	m_θ	m_K	λ	α_v [cm ⁻¹]	K_s [cm/s]	L	h_a [cm]	θ_s	θ_r
[Linde <i>et al.</i> , 2007]	10	0.9	0.87	/	0.0151	0.0068	0.5	/	0.34	0.05
[Allègre <i>et al.</i> , 2010]	/	/	/	3.88	/	0.0017	0.5	40	0.355	0.11
[Mboh <i>et al.</i> , 2012]	3.879	/	/	/	0.02	0.0031	0.5	/	0.33	0.01-0.1
[Allègre <i>et al.</i> , 2014]	4.35	/	/	/	0.022 (drainage)	0.0041	0.5	/	0.41	0.01
					0.044 (imbibition)					



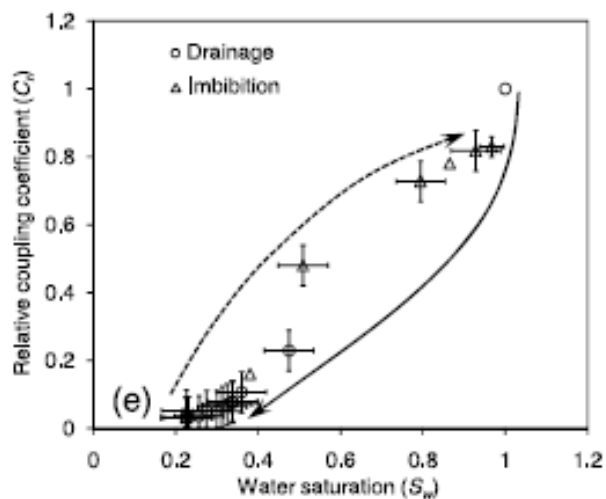
980 **Figure 1.** a) Normalized streaming potential coefficient $C_{s0}(S_w)/C_{s0}(S_w = 1)$ versus water saturation. The zeta-potential
 981 is assumed to be insensitive to water saturation, and is calculated using equation 17. The gas injected is argon. The experi-
 982 mental results are corrected for pH and fluid electrical conductivity. Variations in zeta-potential are corrected to a pH value
 983 of 8 and a fluid electrical conductivity value of of 140 mS/cm, using $\zeta = -0.0146 \ln(\sigma_f) - 0.0854$ (from Guichet *et al.*
 984 [2003]). b) Normalized streaming potential coefficient $C_{s0}(S_w)/C_{s0}(S_w = 1)$ versus water saturation as in a), using
 985 $\zeta = 20 \log_{10}(\sigma_f)$ (from Guichet *et al.* [2003])



986 **Figure 2.** a) SPC measured during a drainage of a sand, on 6 dipoles with electrodes distance of 10 cm, showing a non-
 987 monotoneous behaviour as a function of the water saturation (from *Allègre et al.* [2010]); b) current models from *Guichet*
 988 *et al.* [2003] (black dashed), *Perrier and Morat* [2000] (black dotted), and *Revil et al.* [2007] (grey dotted dashed). Note the
 989 difference in Y-axis scale.

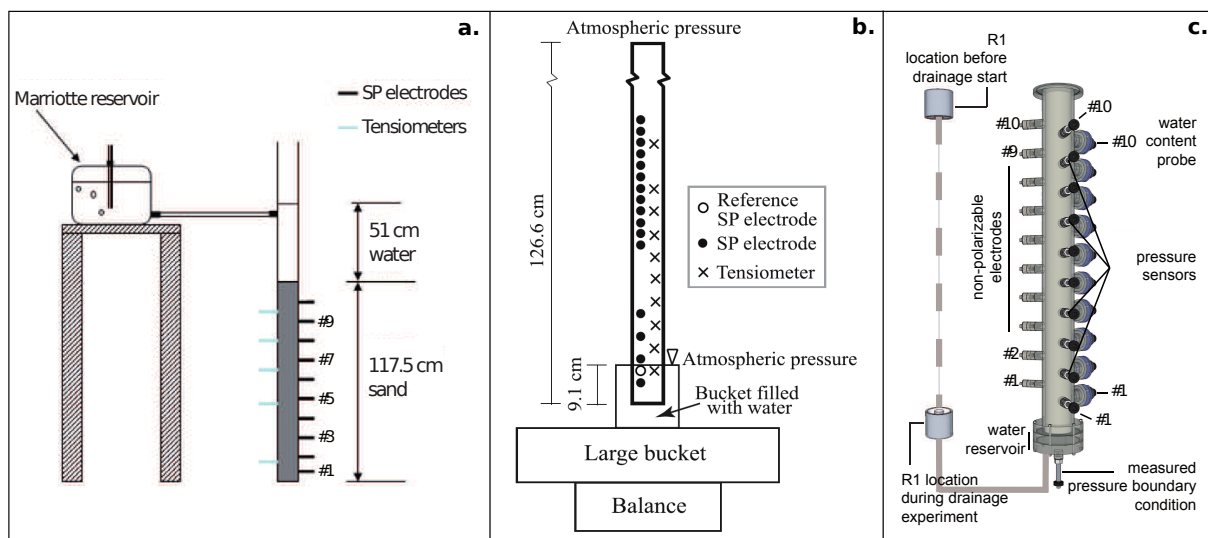


990 **Figure 3.** Streaming potential coefficient measured for sample E3 (black circles) and E39 (empty circles) from *Revil et al.*
 991 [2007] (Fig. 7b) including measurements at full saturation ($=1$) not reported by *Revil et al.* [2007] and shown in *Revil and*
 992 *Cerepi* [2004] (Fig. 3) on same samples with the same water conductivity 0.93 S/m. The model from *Revil et al.* [2007] (con-
 993 tinuous line) with $n=2.7$; $S_w^r=0.36$; $\lambda=0.87$, eq.112 and 113 calculated with the value at saturation extrapolated from the
 994 values obtained at various saturation to 10^{-2} mV/Pa, which is two orders of magnitude above the measured values. From
 995 *Allègre et al.* [2011]



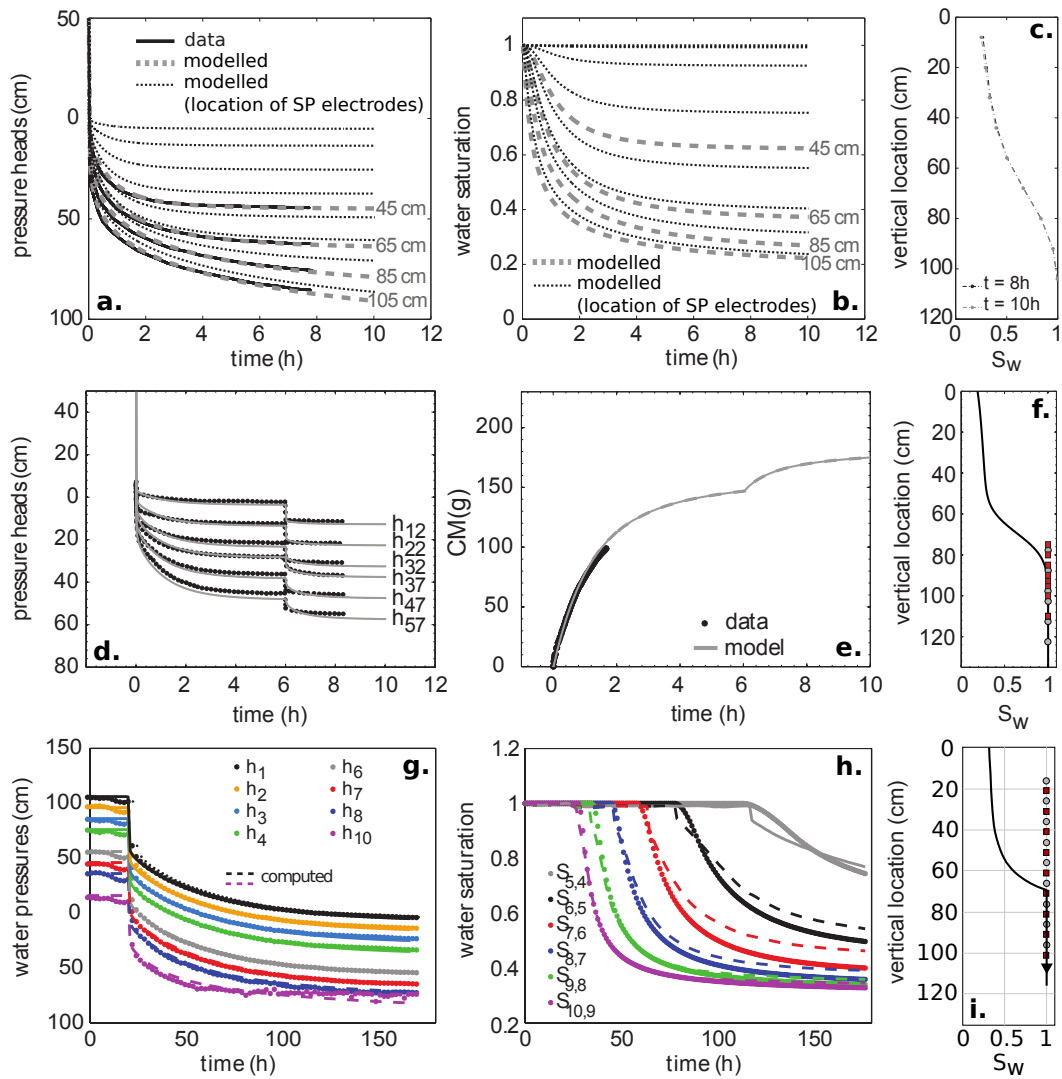
996 **Figure 4.** Streaming potential measured with brine/nitrogen on St Bees sample by *Vinogradov and Jackson* [2011] (fig. 3e).

997 For the drainage no measured values are available between 0.5 water-saturation and full saturation.

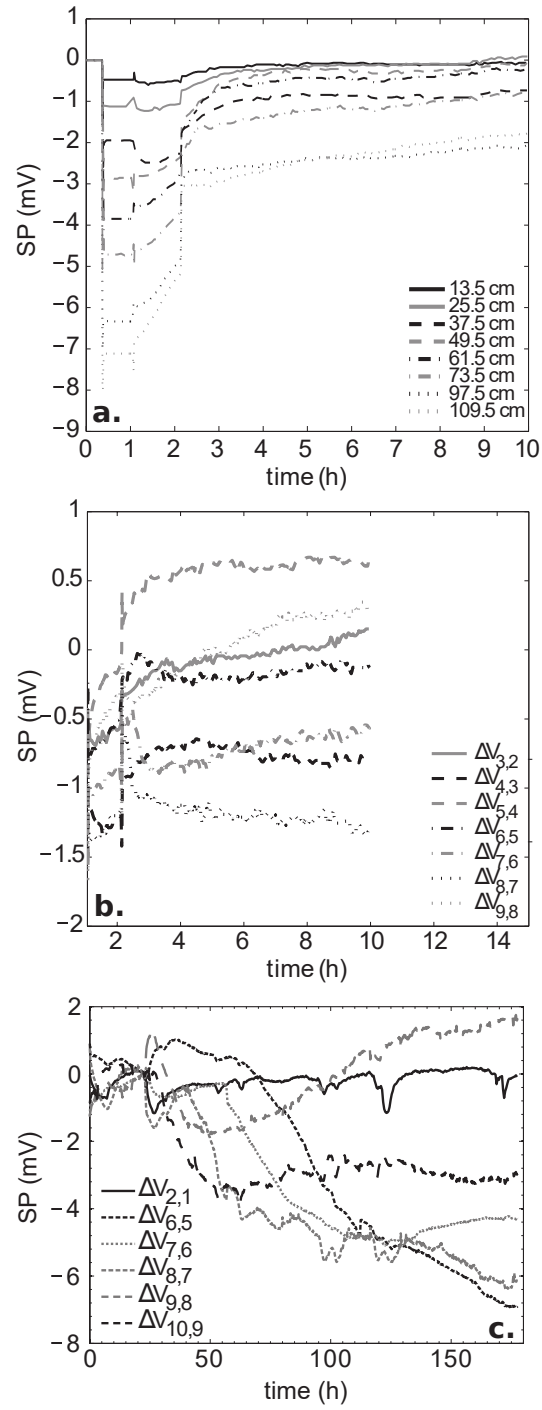


998 **Figure 5.** Experimental apparatus from *Mboh et al.* [2012] (a), from *Linde et al.* [2007] (b) and from *Allègre et al.* [2010]

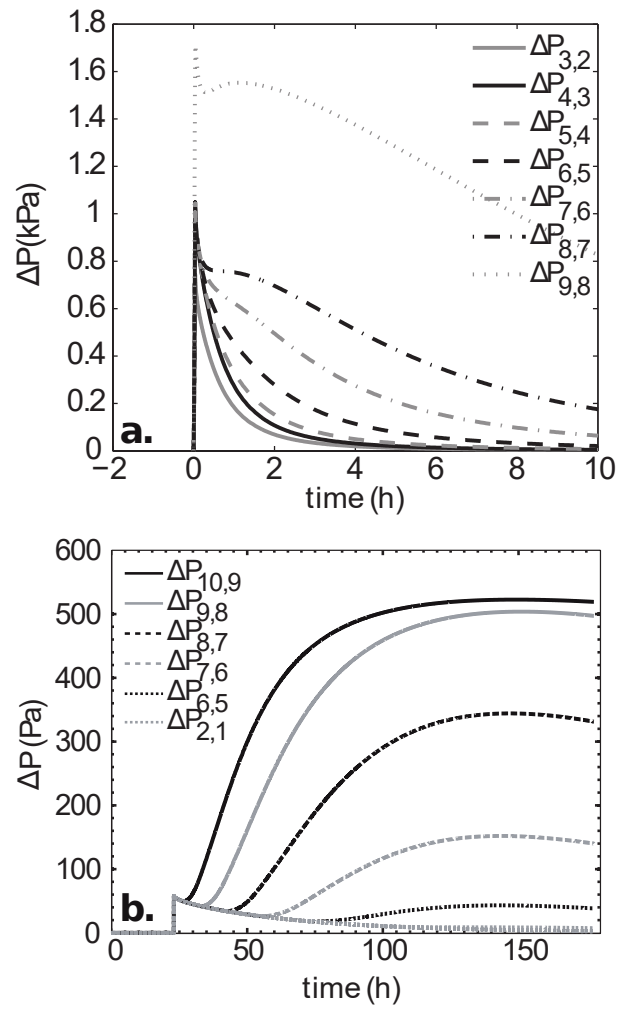
999 (c).



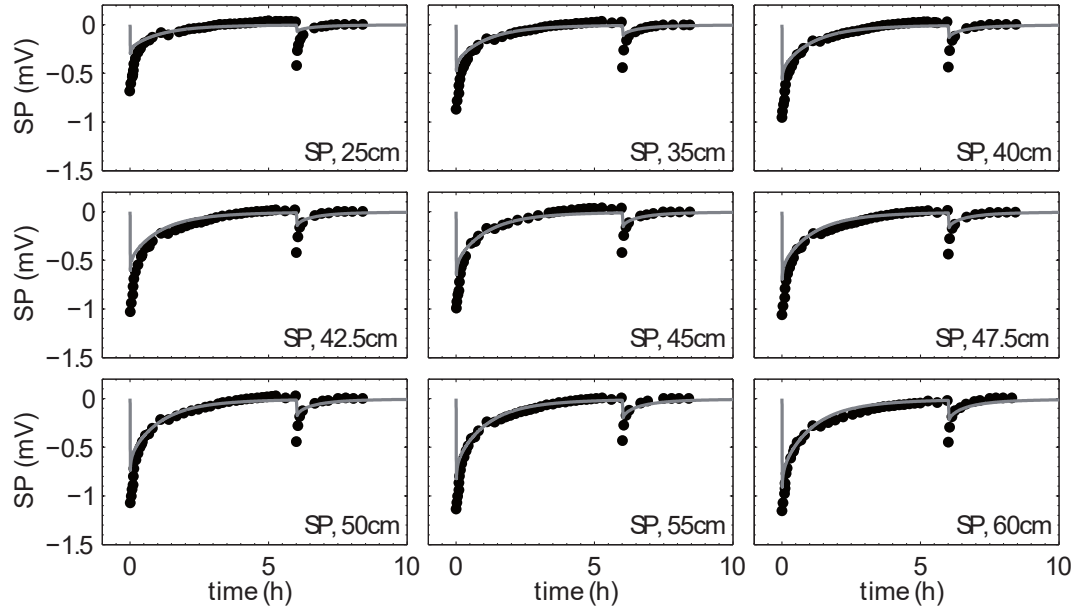
1000 **Figure 6.** Measured and computed pressure heads time-series, water saturation time-series and vertical saturation profiles
 1001 for (a-c) *Mboh et al.* [2012] and (g-i) *Allègre et al.* [2010] experiments. The measured and computed cumulative outflow
 1002 are shown instead of saturations for *Linde et al.* [2007] study (d-f). Pressure heads are both computed at the locations of
 1003 tensiometers and SP electrodes for *Mboh et al.* [2012] experiment (b). The vertical saturation profiles are inferred from com-
 1004 puted saturations at the end of each experiment. Red squares and gray circles indicate the locations of SP electrodes and
 1005 tensiometers respectively.



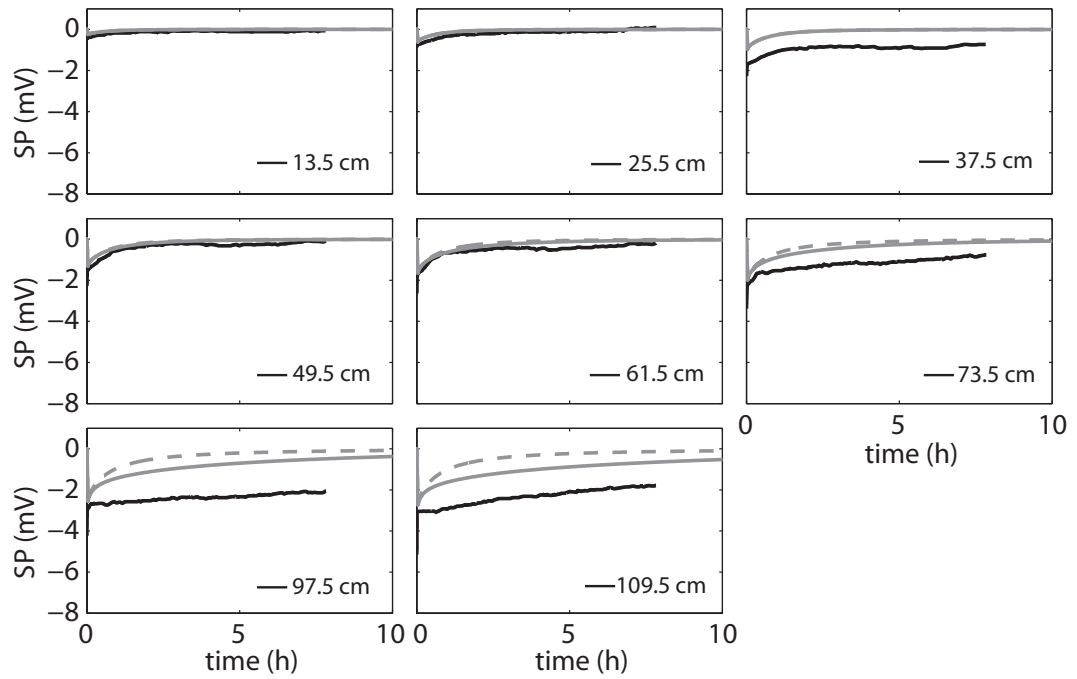
1006 **Figure 7.** (a) Raw SP measurements during the drainage experiment from *Mboh et al.* [2012] shifted to zero at $t = 0$.
 1007 (b) SP differences computed for couples of consecutive electrodes. (c) SP differences computed for couples of consecutive
 1008 electrodes from *Allègre et al.* [2010]. The indices i indicate the number of each electrode. All electrodes are numbered from 1
 1009 to 10 from the bottom to the top of the column.



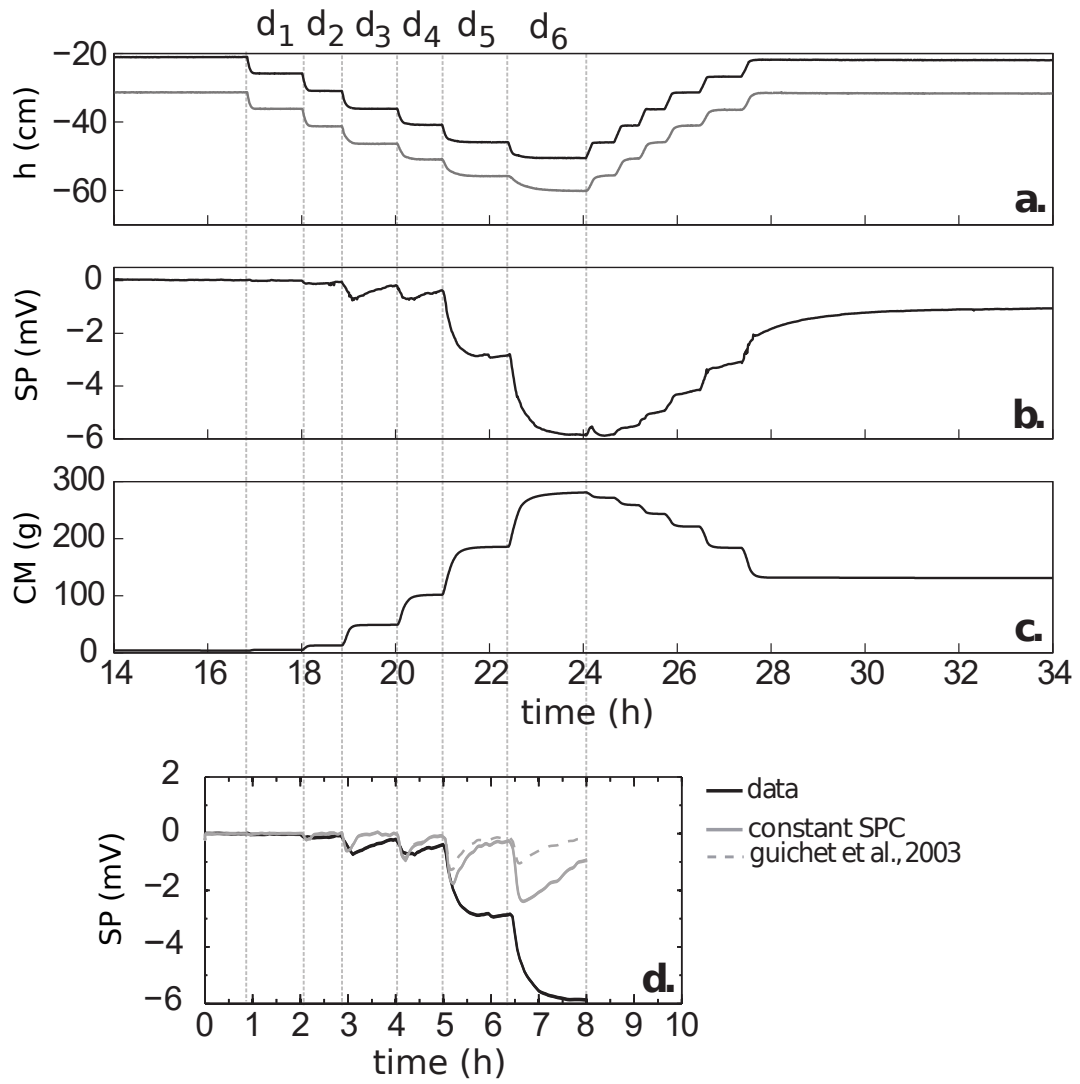
1010 **Figure 8.** Total water pressure differences ΔP inferred from computed h time-series (fig. 6) for (a) *Mboh et al.* [2012] and
 1011 (b) *Allègre et al.* [2010] drainage experiments. Each each curve corresponds to the pressure difference at the locations of two
 1012 consecutive SP electrodes (fig. 5).



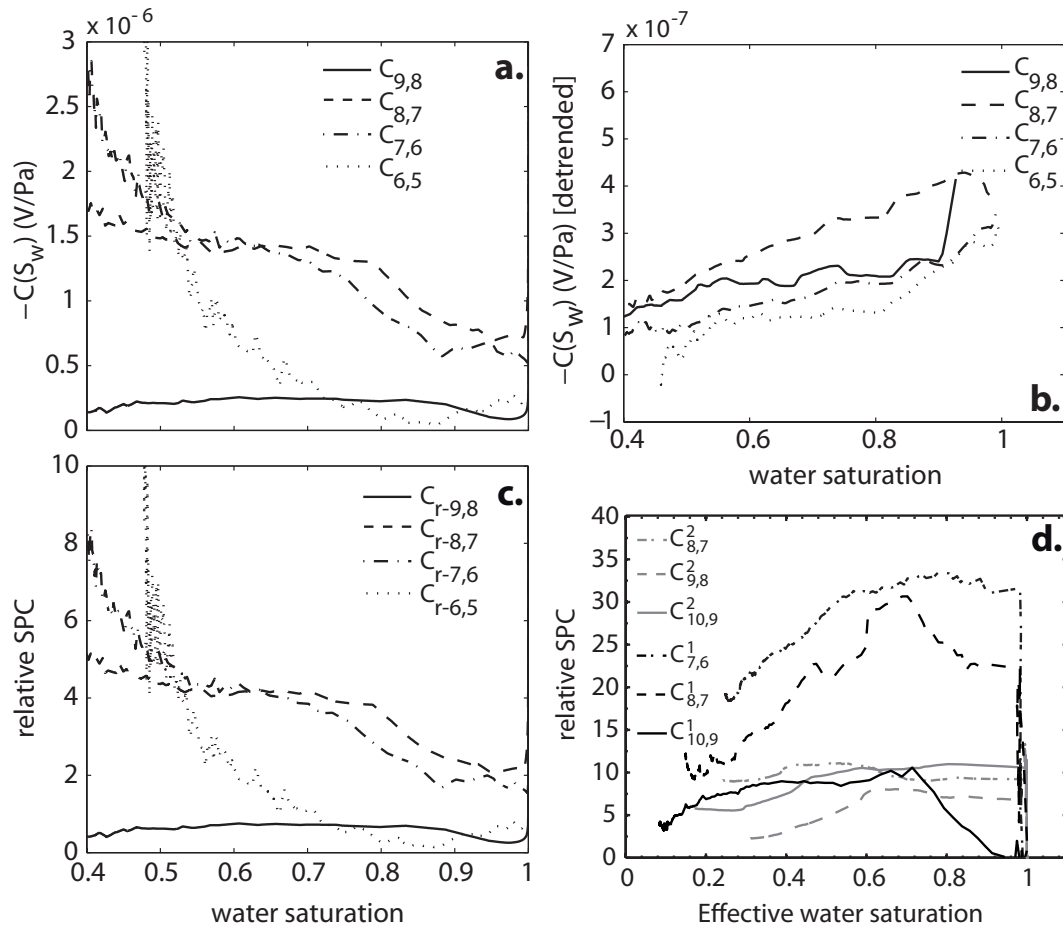
1013 **Figure 9.** Measured SP from *Linde et al.* [2007] during the drainage experiment (black dots) : **the first stage of the**
 1014 **drainage experiment consisted of draining the saturated sand column where the lower boundary condition consisted**
 1015 **of a fixed head, the second stage of the experiment began after six hours when the lower boundary was removed to**
 1016 **ensure a free drainage.** Simulated SP (gray line) calculated using the procedure from *Allègre et al.* [2012] with a constant
 1017 SPC (C_{sat}). Despite a constant SPC, the measurements are fairly reproduced regardless the dipole location within the column.
 1018 This good fit is explained by the limited saturation range ($0.85 < S_w < 1$) investigated during the experiment (see text for
 1019 details).



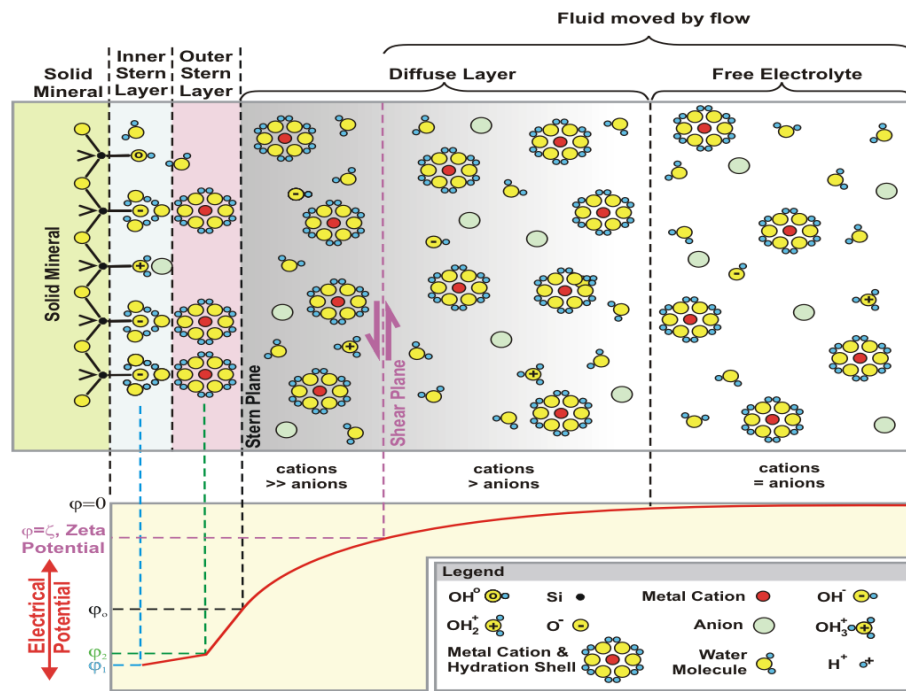
1020 **Figure 10.** Measured SP differences from *Mboh et al.* [2012] drainage experiment (black) inferred from raw signals (see
 1021 text for details), and simulated (gray) using the procedure from *Allègre et al.* [2012] with a constant SPC (C_{sat} , dashed line)
 1022 and the SPC model from *Guichet et al.* [2003] (solid line). The measurements are well reproduced in terms of both shape and
 1023 amplitude for lower location within the column where the range of saturation is limited. A simple SPC model does seem well
 1024 suited for all the dipoles.



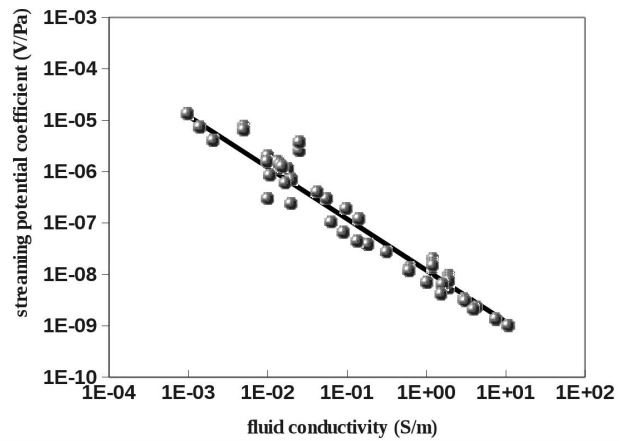
1025 **Figure 11.** Step-by-step drainage and imbibition experiment performed with the experimental setup from Allègre *et al.*
 1026 [2014]. The drainage phases are triggered by decreasing the pressure boundary conditions by 5 cm pressure steps. (a) Mea-
 1027 sured pressure heads, (b) measured self-potentials, (c) measured cumulative outflow. (d) Close-up view on the six drainage
 1028 phases, noted d_1 to d_6 .



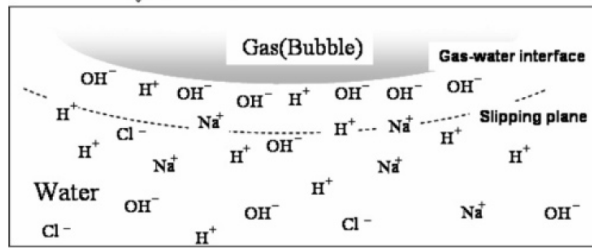
1029 **Figure 12.** Streaming potential coefficient curves inferred from *Mboh et al.* [2012] dataset using (a) uncorrected SP differ-
 1030 ences (fig.7b) and (b) corrected SP differences (see details in the text). (c,d) Relative SP coefficient for *Mboh et al.* [2012] and
 1031 *Allègre et al.* [2010] experiments.



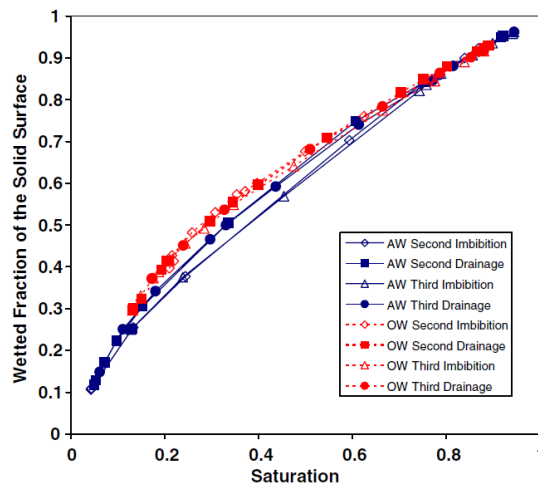
1032 **Figure 13.** Electric double layer, first published in [Glover and Jackson, 2010]. The solid mineral presented is the case of
 1033 silica. At pH above the isoelectric point the cations are adsorbed within the Stern layer; there is an excess of cations in the
 1034 diffuse layer. The zeta potential is defined at the shear plane. The fluid flow creates a streaming current which is balanced by
 1035 the conduction current, leading to the streaming potential.



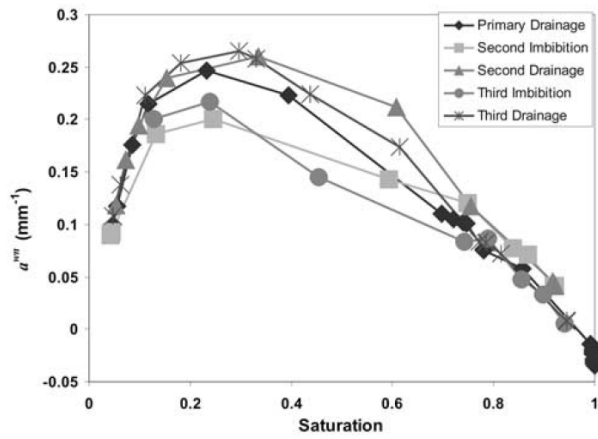
1036 **Figure 14.** Streaming potential coefficient from data collected (in absolute value) on sands and sandstones at pH 7-8 (when
 1037 available) from *Ahmad* [1964]; *Li et al.* [1995]; *Jouniaux and Pozzi* [1997]; *Lorne et al.* [1999]; *Pengra et al.* [1999]; *Guichet*
 1038 *et al.* [2003]; *Perrier and Froidefond* [2003]; *Guichet et al.* [2006]; *Ishido and Mizutani* [1981]; *Jaafar et al.* [2009]. The
 1039 regression (black line) leads to $C_{s0} = -1.2 \times 10^{-8} \sigma_f^{-1}$. A zeta potential of -17 mV can be inferred from these collected
 1040 data (from *Jouniaux and Ishido* [2012]; *Allègre et al.* [2010]).



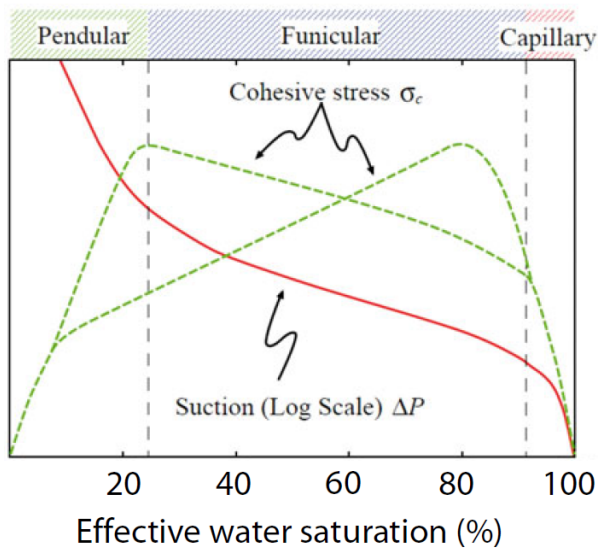
1041 **Figure 15.** Electric double layer at the interface gas/water (from *Takahashi* [2005]). The ions from water are attracted by
 1042 the interface charged by H^+ and OH^- . The zeta potential is defined as the potential on the slipping plane.



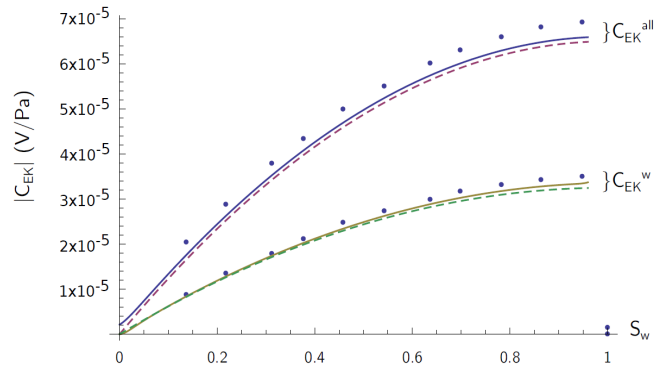
1043 **Figure 16.** Interfacial areas matrix/water measured during drainage experiments by *Culligan et al.* [2006].



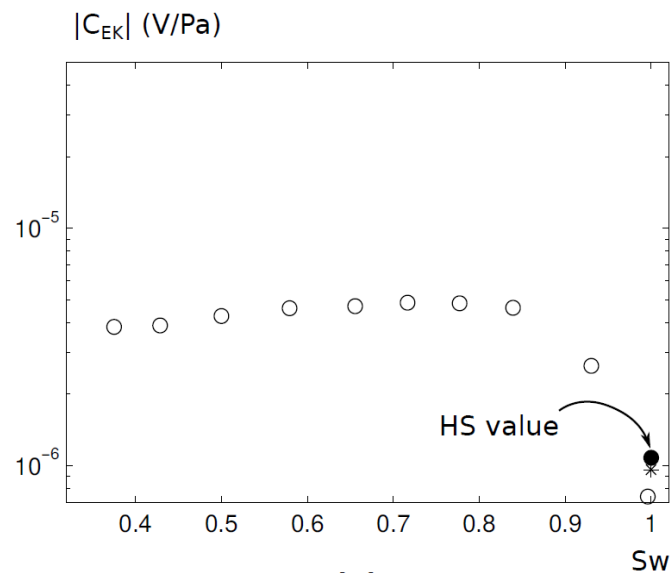
1044 **Figure 17.** Interfacial area water/air measured during drainage experiments by *Culligan et al.* [2004]. Slightly negative
 1045 values are due to numerical error in the image analysis routine or wrong identification of a small number of pixels.



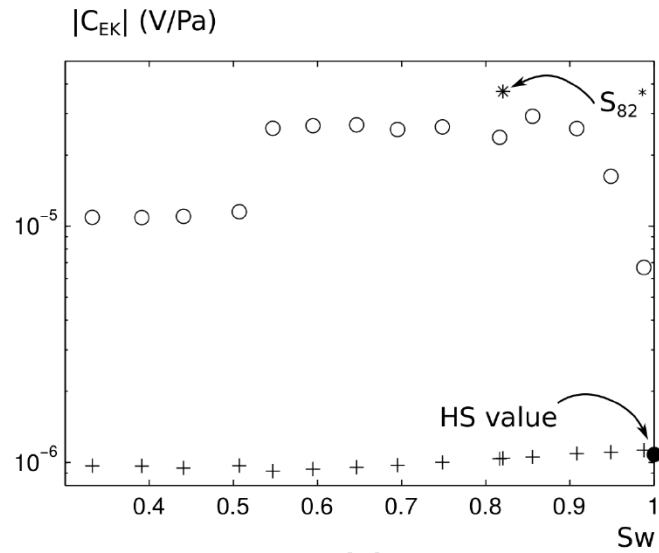
1046 **Figure 18.** (Schematic variations of the cohesive stress as a function of the water saturation (modified after *Mitarai and*
 1047 *Nori* [2006]).



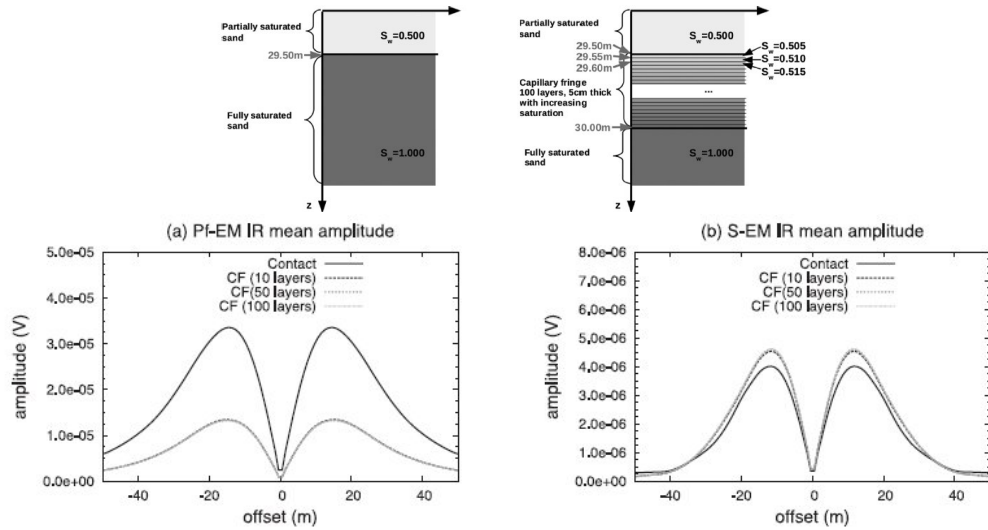
1048 **Figure 19.** Streaming potential coefficient simulated in a capillary channel with an increasing air corridor in the middle
 1049 of the channel when the water saturation S_w decreases (after ?). The streaming potential coefficient is increasing with water
 1050 saturation, linked to increasing fluid velocity, up to full water saturation where the SPC decreases, linked to the fact that the
 1051 interface water/air does not exist anymore.



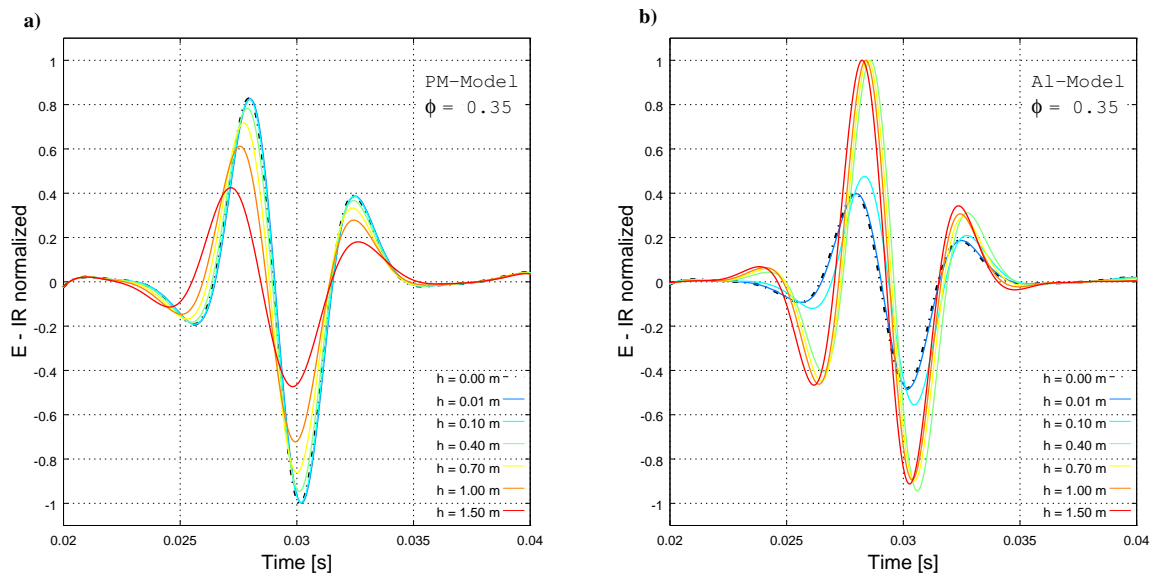
1052 **Figure 20.** Streaming potential coefficient simulated in a capillary channel with an increasing entrapped bubbles on the
 1053 wall of the channel for a decreasing water saturation (after *Fiorentino et al. [2017]*). The streaming potential coefficient shows
 1054 non monotonous behaviour with water saturation, linked to a decreasing of the fluid velocity with decreasing water saturation,
 1055 and to an increasing charge density and surface area of the water/air interface with decreasing water saturation.



1056 **Figure 21.** Streaming potential coefficient simulated in a capillary channel with increasing flowing bubbles for a decreasing
 1057 water saturation (after ?). The streaming potential coefficient shows non monotonous behaviour with water saturation, linked
 1058 to a decreasing of the fluid velocity with decreasing water saturation, and to an increasing charge density and surface area of
 1059 the water/air interface with decreasing water saturation. The step in SPC between 55% and 50% is linked to the fact that two
 1060 bubbles merge into one bubble. The dots involve a zeta potential of $-20mV$ for both matrix/water and water/air interface; the
 1061 crosses are calculated with a null zeta potential at the interface water/air.



1062 **Figure 22.** Comparison of the mean amplitudes of the interface response induced by compressional waves (bottom left)
 1063 and shear waves (bottom right), for a sharp saturation transition (top left model) between the two considered regions and for
 1064 a gradual saturation transition, as given for the capillary fringe shown in the top right model. The IR response induced by
 1065 the S-wave is stronger for the capillary fringe than for the sharp saturation transition, while the IR response generated by the
 1066 compressional wave is stronger for the sharp concentration transition than for the capillary fringe.



1067 **Figure 23.** Electric field interface response E-IR dependence on the thickness of the contaminated layer h for: a) PM-
 1068 Model and b) AI-Model (meaning Perrier-Morat model and Allègre model respectively, see Table 1). In the former, $S(S_w)$ is
 1069 a monotonic function of water saturation, in the latter a non monotonic one. Notice that for both models the responses related
 1070 to the absence of contamination ($h = 0$ m) and $h = 0.1$ m are coincident, as expected.