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1 **Spectral induced polarization characterization of**
2 **non-consolidated clays for varying salinities - an**
3 **experimental study**

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7 **Key Points:**

- 8 • The quadrature conductivity of clays behaves non-monotonously with increasing
9 salinity
- 10 • Some polarization mechanisms may cease to act or decrease significantly at a spe-
11 cific salinity
- 12 • The quadrature to surface conductivity ratio is lower for clays than for other min-
13 erals

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14 **Abstract**

15 Clay material characterization is of importance for many geo-engineering and environ-
 16 mental applications, and geo-electrical methods are often used to detect them in the sub-
 17 surface. Spectral induced polarization (SIP) is a geo-electric method that non-intrusively
 18 measures the frequency-dependent complex electrical conductivity of a material, in the
 19 mHz to the kHz range. We present a new SIP dataset of four different types of clay (a
 20 red montmorillonite sample, a green montmorillonite sample, a kaolinite sample, and an
 21 illite sample) at five different salinities (initially de-ionized water, 10^{-3} , 10^{-2} , 10^{-1} , and
 22 1 mol/L of NaCl). We propose a new laboratory protocol that allows the repeatable char-
 23 acterization of clay samples. The complex conductivity spectra are interpreted with the
 24 widely used phenomenological double-Pelton model. We observe an increase of the real
 25 part of the conductivity with salinity for all types of clay, while the imaginary part presents
 26 a non monotonous behavior. The decrease of polarization over conduction with salin-
 27 ity is interpreted as evidence that conduction increases with salinity faster than polar-
 28 ization. We test the empirical petrophysical relationship between σ''_{surf} and σ'_{surf} and
 29 validate this approach based on our experimental data and two other datasets from the
 30 literature. With this dataset we can better understand the frequency-dependent elec-
 31 trical response of different types of clay. This unique dataset of complex conductivity
 32 spectra for different types of clay samples is a step forward toward better characteriza-
 33 tion of clay formations in situ.

34 **1 Introduction**

35 Clay minerals are ubiquitous in the Earth's subsurface and can be found in many
 36 geological formations, from hard clay rocks to disseminated clay aggregates or lenses in
 37 other sedimentary rocks. These minerals are frequently the main components of extended
 38 sedimentary stratigraphic layers. Illite and smectite alone may constitute around 30%
 39 of all sedimentary rocks (Garrels & Mackenzie, 1971). Clay materials are fine-grained
 40 soil materials (particle size below $2 \mu\text{m}$) characterized by a large fraction of nanopores,
 41 high specific surface area (between 10 and 1000 m^2/g), and a large negative surface charge
 42 (between -0.15 and -0.10 Cm^{-2}) (e.g., Michot & Villieras, 2006), thus large cationic ex-
 43 change capacity (CEC, between 0.03 and 1.5 meq g^{-1}) and low permeability (typically
 44 below 10^{-16}m^2) (Revil & Leroy, 2004). These properties make clay formations suitable
 45 to be, e.g.: cap rocks forming geo-reservoirs, aquitards defining the geometry of hydrosys-

46 tems, or potential hosts for waste repositories. Studying the transport and mechanical
47 properties of clay materials is crucial for many geoenvironmental and environmental appli-
48 cations, such as: oil and gas (e.g., Morsy & Sheng, 2014), geothermal energy exploration
49 and production (e.g., Corrado et al., 2014), critical zone research (e.g., Chorover et al.,
50 2007), nuclear waste storage (e.g., Gonçalves et al., 2012; Ortiz et al., 2002), hydroge-
51 ology (e.g., Parker et al., 2008; Konikow et al., 2001), civil engineering (e.g., Islam et al.,
52 2020), among others.

53 Clay formations are geological formations composed of a majority of clay minerals. Clay
54 minerals are hydrous aluminium phyllosilicates, that is, silicates organized in stacks of
55 tetrahedral (T) silica sheets and aluminium octahedral (O) sheets called platelets (Bergaya
56 & Lagaly, 2006). The T and O sheets present an overall negative electrical charge at their
57 surfaces because of deprotonated oxygen atoms and isomorphic substitutions in the crys-
58 tal lattice (Leroy & Revil, 2004). Due to these charges on the clay surface, cations (e.g.:
59 Ca^{2+} , Na^+ , Mg^{2+} , K^+) can be adsorbed in the interlayer space of illite, smectite and
60 chlorite minerals between platelets; and on the external surface in the electrical double
61 layer (EDL) made of the Stern and diffuse layer (Leroy & Revil, 2009). The differences
62 between clay minerals depend on the kind of tetrahedral and octahedral stacks (1:1 for
63 TO or 2:1 for TOT) and adsorbed cations in the interlayer space (e.g., K^+ for illite or
64 Na^+ and Ca^{2+} for montmorillonite) (Brigatti et al., 2006). The clay platelets are then
65 organized in tactoids, that is, stacks of platelets having different geometries, which form
66 aggregates (Bergaya & Lagaly, 2006). There are four main groups of clay minerals: kaoli-
67 nite, illite, smectite, and chlorite.

68 The total specific surface area of a kaolinite tactoid, typically $10\text{-}20\text{ m}^2/\text{g}$, is consider-
69 ably lower than the total specific surface area of an illite and montmorillonite tactoid
70 (typically $100\text{-}200\text{ m}^2/\text{g}$ for illite and $750\text{-}800\text{ m}^2/\text{g}$ for Na-montmorillonite)(Hassan et
71 al., 2006; Revil & Leroy, 2004; Tournassat et al., 2011, 2015). Clay formations can be
72 constituted of a mixture or stratifications of different clay minerals (e.g., inter-stratified
73 illite-smectite). In the present work, we focus on the three more common groups: kaoli-
74 nite (1:1), illite (2:1), and smectite (2:1, montmorillonites are part of the smectite fam-
75 ily). As presented previously, kaolinite, illite and smectite groups present many differ-
76 ent characteristics in terms of structure (e.g., number of stacked platelets, tactoid size
77 and shape), physicochemical properties (e.g., surface charges, CEC), mechanical prop-
78 erties (e.g., plasticity, resistance to stress, swelling-shrinking), and also electrical prop-

79 erties. It is therefore crucial to electrically discriminate these minerals between each other
80 in order to characterize the properties of the formation or predict its behavior if submit-
81 ted to stress (e.g., hydraulic, mechanic, thermic).

82 In geophysics, the most common methods to identify the presence of clay minerals non-
83 intrusively in the field are electrical and electromagnetic methods (e.g., Auken et al., 2017):
84 direct current electrical resistivity tomography (ERT) (e.g., Batayneh, 2006), induced
85 polarization (IP) (e.g., Okay et al., 2013; Lévy et al., 2019a), time-domain electromag-
86 netics (TDEM) (e.g., Finco et al., 2018), frequency-domain (FDEM) electromagnetics
87 (e.g., Spichak & Manzella, 2009), and ground penetrating radar (GPR) (e.g., Looms et
88 al., 2018). However, if clays are usually associated to high electrical conductivity zones,
89 they can be mistaken with highly mineralized pore water when only the real electrical
90 conductivity is considered. One way to avoid this misinterpretation is to use the com-
91 plex conductivity (inferred from IP), that is the real and imaginary parts of the conduc-
92 tivity, or its spectral behavior, i.e. the dependence with frequency of the conductivity,
93 to extract more information than from a single frequency measurement.

94 The spectral induced polarization (SIP) method can investigate the conduction and po-
95 larization of geological materials over a large range of frequencies: from the mHz to the
96 kHz (e.g., Kemna et al., 2012; Revil et al., 2012). Indeed, in addition to the resistivity,
97 the SIP method gives the chargeability of the investigated porous medium, which describes
98 its capability to reversibly store electrical charges (e.g., Revil et al., 2012; Tabbagh et
99 al., 2021). The chargeability is very sensitive to the pore structure and electrical surface
100 properties (Leroy & Revil, 2009). When SIP measurements are coupled with a relevant
101 petrophysical model, they can provide information on the nature and behavior of elec-
102 trical phenomena (conduction and polarization) happening at the pore scale (Revil, 2012),
103 helping to interpret field scale geophysical electrical measurements in terms of mineral-
104 ogy, pore structure, water content, and permeability distribution (Okay et al., 2013; Ghor-
105 bani et al., 2009).

106 The frequency-dependent electrical response of clay minerals has been recently studied
107 in well-controlled conditions in the laboratory. Many clayey materials have been stud-
108 ied, from mixtures containing quartz sand and clays (e.g., Breede et al., 2012; Okay et
109 al., 2014; Wang & Slater, 2019), synthetic clay suspensions (e.g., Leroy et al., 2017a),
110 to natural clays and clayrocks (e.g., Lévy et al., 2018; Jougnot et al., 2010). These mea-

111 surements have been performed in saturated (e.g., Lévy et al., 2019b) or partially water-
112 saturated (e.g., Cosenza et al., 2008; Ghorbani et al., 2009; Jougnot et al., 2010) con-
113 ditions.

114 However, as pointed out by Leroy & Revil (2009) and Leroy et al. (2017a), there is a lack
115 of SIP laboratory studies on individual clay minerals. Indeed, measuring the frequency-
116 dependent electrical response of individual clay minerals is of great importance to bet-
117 ter understand their specific conduction and polarization and to improve their geophys-
118 ical imaging. This is needed in order to move towards a full discrimination of clay min-
119 erals when interpreting field electrical measurements. This can only be achieved by bet-
120 ter understanding the electrical signal of each individual type of clay. In this paper, we
121 intend to characterize the electrical signal of a variety of clay samples at multiple fre-
122 quencies (from mHz to kHz) and at multiple salinities (from initially de-ionized water
123 to 1 mol/L of NaCl) using laboratory SIP measurements on three groups of clay min-
124 erals: illite, smectite, and kaolinite.

125 In the present contribution, we first present the method and some theoretical background
126 for the SIP of clay materials. Then, we detail the protocol we propose in order to ob-
127 tain the clay samples, characterize them, perform the SIP measurements, and post-treat
128 them. We present the results on four clay samples (two smectite samples, a kaolinite sam-
129 ple, and an illite sample) at five different salinities (initially de-ionized water, 10^{-3} , 10^{-2} , 10^{-1} ,
130 and 1 mol/L of NaCl) and analyze them using a phenomenological model. Finally, we
131 discuss our results with respect to the existing literature.

132 **2 Theory**

133 **2.1 Characteristics of kaolinite, illite, and montmorillonite**

134 As mentioned earlier, clay minerals have a strong electrical conductivity response
135 due to the high surface conductivity associated with the high electrical charge on their
136 surface (Revil & Leroy, 2004; Revil, 2012). This particularity, in addition to the hetero-
137 geneities of the surface electrical properties of clay minerals (Leroy & Revil, 2004), makes
138 clay systems quite complex but also, interesting to characterize electrically.

139 Kaolinite is a 1:1 clay, composed of a succession of silica tetrahedral (T) and aluminum
140 octahedral (O) sheets (see Figure 1a) whereas illite and montmorillonite (member of the
141 smectite group) are 2:1 clays made up of a succession of TOT sheets (see Figure 1b) (Leroy

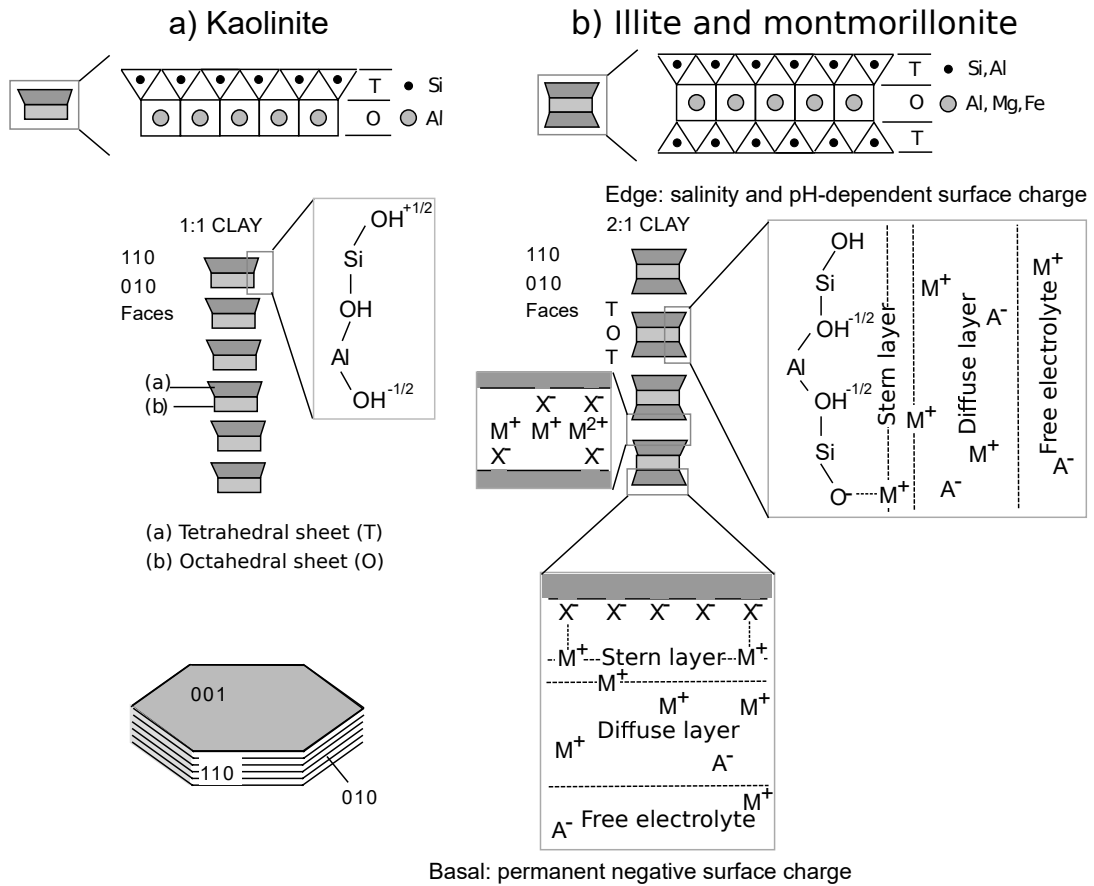


Figure 1. Sketch of a (a) kaolinite and an (b) illite or montmorillonite clay tactoid showing the different types of surface sites on the basal and edge surfaces as well as the electrical double layer around them (electrical double layer not shown for kaolinite) and the interlayer space between TOT sheets (modified from Leroy & Revil, 2009).

142 & Revil, 2009). The thickness of a TOT platelet is around 9.5 Å, its length is around
143 50-100 nm for illite and 50-1000 nm for montmorillonite (Tournassat et al., 2015). For
144 kaolinite, the thickness of a TO platelet is around 7 Å and its length lies between around
145 200 nm to more than 1000 nm (Tournassat & Steefel, 2015). The number of stacked lay-
146 ers of a kaolinite tactoid ranges from 10 to more than 200 whereas this number ranges
147 between 1 and 2, 6 and 10, and 5 and 20 for Na-montmorillonite, Ca-montmorillonite
148 and illite, respectively (Tournassat et al., 2015; Tournassat & Steefel, 2015; Leroy et al.,
149 2017a). The height of a kaolinite tactoid ranges between 7 and 150 nm and the height
150 of an illite and montmorillonite tactoid lies between 5 and 20 nm, and, 1 and 10 nm, re-
151 spectively (Hassan et al., 2006; Tournassat et al., 2011; Tournassat & Steefel, 2019). It
152 results that the total specific surface area of a kaolinite tactoid is considerably lower than
153 the total specific surface area of an illite and montmorillonite tactoid (typically, 10-20
154 m²/g versus 100-200 m²/g and 750-800 m²/g, respectively).

155 Consequently, clay minerals generally present a high aspect ratio with different morpholo-
156 gies: kaolinite and well-crystallized illite have a tendency toward hexagonal and elongated
157 hexagonal morphologies respectively, whereas montmorillonite and less well-crystallized
158 illite have mostly irregular platy or lath-shaped morphologies. The surface charge of the
159 lateral (or edge) surface of kaolinite, illite and montmorillonite (to a lesser extent due
160 to the influence of the basal surface) are controlled by the aluminol and silanol (>Al-
161 OH and >Si-OH) surface sites and are thus sensitive to salinity and pH (Tombácz & Szek-
162 eres, 2006). When salinity and pH increase, the charge on these surfaces is generally more
163 negative due to the >Si-O- surface sites. On the other hand, the basal surface of illite
164 and montmorillonite is permanently negative and less sensitive to salinity and pH because
165 it mainly results from the isomorphic substitutions in the crystal lattice (e.g., Si⁴⁺ by
166 Fe³⁺ or Al³⁺ ions in the T-sheet or Al³⁺ by Mg²⁺ or Fe²⁺ ions in the O-sheet). Most
167 of the isomorphic substitutions in these minerals occur in the O-sheet. Because the spe-
168 cific surface area of the basal surface of these 2:1 clays is more than one order of mag-
169 nitude higher than the specific surface area of the lateral surface (typically 760 m²/g vs
170 20 m²/g) (Tournassat et al., 2011), the basal surface may control the surface electrical
171 properties of illite and montmorillonite. The CEC method can be used to measure the
172 surface properties and then the surface charge of illite and montmorillonite, if the spe-
173 cific surface area is known (Okay et al., 2014). For kaolinite, the CEC is very sensitive
174 to pH and salinity due to the pH and salinity dependent surface charge of the lateral sur-

175 face. When a clay particle is put in water, an EDL mostly made of counterions builds
176 up to compensate the external negative surface charge (Leroy et al., 2015; Tsujimoto et
177 al., 2013). The internal negative surface charge of montmorillonite is compensated by
178 cations in the interlayer space. The pore space is then made of the EDL and the free elec-
179 trolyte. The EDL is thought to be composed of two portions, the Stern and the diffuse
180 layer. The Stern layer is only made of counterions (cations for clays) and is thought to
181 be fixed to the surface of the mineral (see Figure 1). The diffuse layer is made mostly
182 of counter-ions that are more mobile than those of the Stern layer. When a clay parti-
183 cle and its surrounding electrolyte is submitted to a frequency dependent electrical field
184 (for frequencies typically lower than 1 MHz), cations and anions around the clay par-
185 ticle separate, giving rise to different types of polarization mechanisms.

186 In the literature, three different polarization mechanisms have been proposed for clay
187 samples in the mHz to the kHz frequency range: Maxwell-Wagner polarization, EDL po-
188 larization, and membrane polarization (e.g., Kemna et al., 2012; Chen & Or, 2006; Leroy
189 & Revil, 2009; Bückner & Hördt, 2013; Bückner et al., 2019). The Maxwell-Wagner polar-
190 ization mechanism is due to a charge build-up at boundaries between phases with dif-
191 ferent electrical properties (conductivity, permittivity) in geologic materials and happens
192 at the highest frequencies (in the kHz range) for SIP. The EDL polarization happens when
193 ions in the Stern and diffuse layers migrate around the surface of the mineral guided on
194 the orientation of the time varying external electric field, leading to a charge separation
195 in the EDL at the particle scale (Leroy et al., 2017a). This polarization mechanism typ-
196 ically occurs at the mid frequencies for SIP (below the kHz range). Finally, the mem-
197 brane polarization mechanism happens when pore throats block electrical charges (an-
198 ions for clays, due to their negative electrical charge) mobilizing due to repulsive EDLs
199 and a time varying external electric field, and thus charges separate in ion selective zones.
200 This polarization mechanism happens in the lowest frequencies for SIP (typically in the
201 mHz to the Hz range). With all these polarization mechanisms the question is open on
202 what is the active polarization mechanism in clay samples at a given frequency of the
203 injected sinusoidal electrical field.

204 **2.2 Background on spectral induced polarization**

205 The SIP geophysical method consists of a sinusoidal electric current injection in
206 a rock sample and the measurement of a resulting electrical potential difference between

207 two electrodes at multiple frequencies (from mHz to kHz). In addition to the electrical
 208 conductivity (or resistivity, $\rho^* = 1/\sigma^*$) of the sample, the phase-lag between injected
 209 and measured signal gives information about the petrophysical and surface electrical prop-
 210 erties of clay samples at the pore scale (e.g., Leroy et al., 2017a; Kemna et al., 2012; Re-
 211 vil et al., 2012).

212 The frequency dependent complex conductivity $\sigma^*(\omega)$ is inferred from SIP. The angu-
 213 lar frequency ω (rad/s) is related to the frequency f (Hz) by $\omega = 2\pi f$. There are two
 214 ways to express the complex conductivity, either by real σ' (S m^{-1}) and imaginary com-
 215 ponents σ'' (S m^{-1}), or amplitude $|\sigma|$ (S m^{-1}) and phase φ (rad):

$$\sigma^*(\omega) = |\sigma|e^{i\varphi} = \sigma' + i\sigma'', \quad (1)$$

216 where $i = \sqrt{-1}$ represents the imaginary unit. The resulting electric signal of a rock
 217 sample depends on the electrical properties of the pore water and the rock matrix itself.
 218 Following Waxman & Smits (1968), we assume then that the measured electrical con-
 219 ductivity (a complex quantity) is a result of the bulk pore water electrical conductivity
 220 (σ_w) in the rock acting in parallel to the surface conductivity (σ_{surf}^*) of the geologic ma-
 221 terial:

$$\sigma^* = \frac{\sigma_w}{F} + \sigma_{surf}^*, \quad (2)$$

222 where F is the electrical formation factor, sensitive to the electrically connected poros-
 223 ity and the shape of the grains. For clays, surface conduction is particularly strong due
 224 to their high specific surface area and surface charge, resulting in a strong EDL (Leroy
 225 & Revil, 2004). Weller et al. (2013) took equation 2 and proposed a linear relation be-
 226 tween the real part of the measured conductivity, water conductivity, and surface con-
 227 ductivity:

$$\sigma'_{surf}(\sigma_w) = \sigma'(\sigma_w) - \frac{\sigma_w}{F}. \quad (3)$$

228 Following the notation of Weller et al. (2013), we have:

$$\sigma'' = \sigma''_{surf}. \quad (4)$$

229 Börner (1992) proposes to link the real and imaginary surface components as:

$$l = \frac{\sigma''_{surf}}{\sigma'_{surf}}. \quad (5)$$

230 2.3 Double-Pelton phenomenological model

231 In order to model SIP data there are several types of models available, some are
 232 physical models and some are phenomenological. Physical models are often complex and
 233 require a thorough knowledge of a plethora of physical and chemical properties of the
 234 rock sample in question. Phenomenological models are able to reproduce large datasets
 235 and do not require much knowledge on the physical and chemical properties of the rock
 236 sample that is being studied. We use a phenomenological double-Pelton model to fit our
 237 data. We use one Pelton model to describe the complex conductivity (the inverse of the
 238 complex resistivity) of the clay and the other Pelton model to explain the high frequency
 239 signal due to inductive and capacitive noise and also clay polarization. Our double-Pelton
 240 model consists of two individual Pelton (Pelton et al., 1978) electrical signals summed
 241 up together. The double-Pelton model originates from the Cole-Cole and Debye mod-
 242 els (Cole & Cole, 1941). The double-Pelton model is defined by:

$$\rho^*(\omega) = \rho_0 \left[1 - m_1 \left(1 - \frac{1}{1 + (i\omega\tau_1)^{c_1}} \right) - m_2 \left(1 - \frac{1}{1 + (i\omega\tau_2)^{c_2}} \right) \right], \quad (6)$$

243 where ρ ($\Omega \cdot m$) is the electrical resistivity of the sample (inverse of the electrical conduc-
 244 tivity σ), c (-) is the Cole-Cole exponent, τ (s) refers to the relaxation time, and m (mV/V)
 245 is the chargeability of the material. In general, ρ_0 is thought of as a direct current (DC)
 246 or low frequency term. In the case of $c=0.5$, the Pelton model becomes a Warburg model.
 247 Therefore, when in equation 6 we have $c_1 = 0.5$ and $c_2 = 0.5$, we obtain a double-Warburg
 248 model.

249 3 Materials and methods

250 3.1 CEC and XRD of clay samples

251 We performed the CEC measurements and the X-ray diffraction (XRD) charac-
 252 terization of all the clay types used in this work, to have the surface properties and the
 253 mineralogical composition of the samples. We present the results of the XRD analysis

Table 1. Results of XRD analysis, showing the exact mineral content of each clay sample.

Clay sample	Smectite	Illite	Kaolinite	Gypsum	Quartz	Microcline	Albite	Calcite	Magnetite
	%	%	%	%	%	%	%	%	%
Kaolinite sample	4	3	84		10				
Illite sample		67	10			10		12	
Green mont. sample	90	1		<i>tr*</i>	1	3	1	4	
Red mont. sample	66				11	18	3		1

*tr**: traces.

254 in Table 1. As for the CEC results, we obtained: 22 meq/100 g for the kaolinite sam-
255 ple, 47 meq/100 g for the illite sample, 132 meq/100 g for the green montmorillonite sam-
256 ple, and 135 meq/100 g for the red montmorillonite sample. From Table 1, we see that
257 none of our clay samples are 100% pure. The XRD measurements were obtained using
258 a Philips Xpert machine from clay powder and glycolated samples. The bulk clay pow-
259 der samples were quantitatively analyzed with randomly oriented preparations follow-
260 ing Brindley & Brown (1980) and Moore & Reynolds (1989). Furthermore, following the
261 modified Chung method (Chung, 1974; Hillier, 2003) an analysis on glycolated oriented
262 preparations was done in order to correct the measurements on the clay powder sam-
263 ples. The CEC measurement consists of replacing a cation present on the clay surface
264 with another cation (Ma & Eggleton, 1999). Methods differ on the exchanged cation,
265 the exchange solution (according to the AFNOR standard NF X31-108 and Khaled &
266 Stucki, 1991), and if there are consecutive exchanges in the procedure (Ciesielski & Ster-
267 ckeman, 1997; Meier & Kahr, 1999). For the CEC measurements presented in this pa-
268 per, we determined the amount of recovered Mg^{2+} ions after a second exchange (Khaled
269 & Stucki, 1991).

270 3.2 Preparation of clay samples

271 We developed a laboratory protocol that allowed us to have clay mixtures we could
272 knead and place inside a sample holder, while ensuring a good reproducibility of the data.
273 Plasticity is our criteria for a parameter to keep between all clay types, salinities and mea-
274 surements. When we talk about plasticity, we need to take a look at the Atterberg lim-
275 its in clays. The liquid and plastic limits are water contents that mark the limits of plas-
276 tic behavior of clays (White, 1949). We chose a water content within those limits for each
277 clay, to avoid a clay mixture too liquid (more water than the liquid limit), or a sample
278 too dry that crumbles into pieces (smaller water content than the plastic limit). Wag-
279 ner (2013) presents a table of liquid and plastic limits for illite, kaolinite, smectites, and
280 others. Note that Mitchell & Soga (2005) explain that the availability of ions and the
281 valence of the ions present in the pore water of the clay samples may affect these lim-
282 its. As presented in Table 2, we see a decrease of porosity at the highest salinities in our
283 clay samples, in accordance with Mitchell & Soga (2005).

284 Figure 2 describes the procedure used to prepare the clay samples. In order to obtain
285 the adequate plasticity, we first combine water and clay powder at higher water contents
286 than the objective (Figure 2a and b). We left the clay powder in contact with water for
287 at least 24 hours to have a good imbibition process, and we then mix the whole mixture
288 mechanically using a drill until we reach a homogeneous mixture (Figure 2c). In order
289 to obtain the desired water content, we eliminate the water excess through evaporation
290 by letting the clay mixture dehydrate on a polyurethane foam (Figure 2d). We use a polyurethane
291 foam to have a homogeneous evaporation process, that is, to allow evaporation from the
292 bottom, top and sides of the clay mixture. The mass of the mixture is monitored at ev-
293 ery step to determine the evolution of water content at each step of the process. After
294 obtaining the desired water content, we take the clay mixture out of the foam, knead it
295 and locate it in our sample holder (Figure 2e). Once in place, we perform the SIP mea-
296 surement of the clay sample twice, from 1 mHz to 20 kHz (see the following section and
297 Figure 2f). We acknowledge that a total chemical equilibrium might not be achieved when
298 measuring the SIP signal in the clay samples, but we assume that the difference between
299 the SIP signal we measure and a true equilibrated sample is negligible. After the mea-
300 surements are over, we take out the sample from the sample holder and dry it in an oven
301 at 105° C during 25h (Figure 2g). By measuring the mass at every step of the process,
302 we can calculate the water content (presented in Table 2) at each step and therefore de-

303 termine the porosity of our clay sample during the SIP measurement. The calculated porosi-
 304 ties of the clay mixtures are presented in Table 2. These porosities help us keep a check
 305 on the water vs clay powder ratios of our samples. The porosity calculations present some
 306 experimental uncertainties, these porosity values are a good estimate but should not be
 307 over-interpreted.

308 Note that as the water content changed in the samples, so did the salinities. We orig-
 309 inally started all samples with five different salinities: De-ionized water (D.W.), 1×10^{-3} ,
 310 1×10^{-2} , 1×10^{-1} , and 1 M (mol/L) of NaCl. To account for the water content de-
 311 crease due to the evaporation procedure, we recalculated the salinities in our sample dur-
 312 ing the SIP measurements for all the salinities from 1×10^{-3} to 1 M of NaCl. Table 2
 313 presents the corrected salinities using a simple proportion equivalence. From these post-
 314 dehydration salinity values we calculated the bulk water electrical conductivity, follow-
 315 ing the procedure proposed in Leroy et al. (2015), using:

$$\sigma_w = e10^3 N_A \sum_{i=1}^N z_i \beta_i^w C_i^w, \quad (7)$$

316 where β_i^w (in $\text{m}^2\text{s}^{-1}\text{V}^{-1}$) is the ionic mobility of an ion i in the bulk water, C_i^w (in mol
 317 dm^{-3}) is its concentration, and z_i is its valence. Also, N_A is the Avogadro number ($6.022 \times$
 318 10^{23}mol^{-1}), and e is the elementary charge (1.602×10^{-19} C). It is worth noting that
 319 the ionic mobility values used in equation 7 have been corrected for the temperature and
 320 salinity, as presented in Leroy et al. (2015). It should be noted that the low-salinity wa-
 321 ter conductivity values may be underestimated because we do not consider clay disso-
 322 lution as well as cation leaching from the interlayer space for the calculation of the ion
 323 concentrations.

324 3.3 SIP measurement setup

325 We conducted the SIP measurements on the clay samples using the SIP-FUCHS
 326 III equipment (Radic Research, www.radic-research.de). The setup for the measurements
 327 is presented in Figure 3a. The SIP-FUCHS III sends a sinusoidal current into the sam-
 328 ple through the injection unit and then the so-called current electrodes (C1 and C2 in
 329 Figure 3b) by imposing a chosen potential difference. The second unit measures the re-
 330 sulting voltage through the so-called potential electrodes (P1 and P2 in Figure 3b). The
 331 communication between the units (injection and measurement) and the system is done

Table 2. Post-dehydration calculated salinities, porosities, and gravimetric water contents (m_{fluid}/m_{solid}) for all the SIP-measured clay samples.

Initial Salinity	(D.water)	(10^{-3} M NaCl)	(10^{-2} M NaCl)	(10^{-1} M NaCl)	(1 M NaCl)
Clay type	Final salinity (M NaCl)	Final salinity (M NaCl)	Final salinity (M NaCl)	Final salinity (M NaCl)	Final salinity (M NaCl)
Kaolinite sample	D.W.	1.53×10^{-3}	1.54×10^{-2}	1.91×10^{-1}	1.76
Illite sample	D.W.	1.92×10^{-3}	1.80×10^{-2}	1.82×10^{-1}	1.91
Green montmorillonite sample	D.W.	1.39×10^{-3}	1.53×10^{-2}	1.46×10^{-1}	1.54
Red montmorillonite sample	D.W.	1.64×10^{-3}	1.71×10^{-2}	1.54×10^{-1}	1.51
Clay type	Porosity	Porosity	Porosity	Porosity	Porosity
Kaolinite sample	0.54	0.59	0.57	0.56	0.47
Illite sample	0.52	0.56	0.54	0.56	0.42
Green montmorillonite sample	0.65	0.68	0.68	0.71	0.57
Red montmorillonite sample	0.67	0.62	0.61	0.62	0.51
Clay type	Water content	Water content	Water content	Water content	Water content
Kaolinite sample	0.48	0.51	0.55	0.54	0.44
Illite sample	0.49	0.41	0.46	0.43	0.40
Green montmorillonite sample	1.02	0.96	0.91	0.93	0.85
Red montmorillonite sample	0.71	0.63	0.60	0.66	0.67

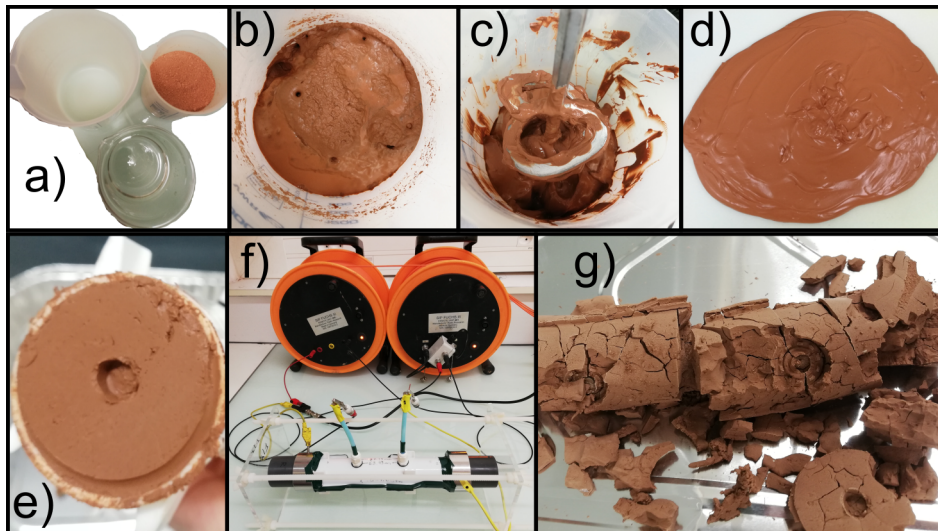


Figure 2. Laboratory protocol to create clay samples: a) Combination of clay powder and water. b) Saturation of clay powder for at least 24 h. c) Homogenization of mixture with drill. d) Excess water evaporation until correct plasticity is reached. e) Setting clay in sample holder. f) SIP measurements. g) Clay sample drying.

332 through optic cables to reduce electromagnetic noise. The SIP-FUCHS III outputs the
 333 amplitude of the measured impedance (Ω), the phase shift between injected and mea-
 334 sured signal (mrad), and their respective errors, for each measured frequency.

335 The current electrodes C1 and C2 are stainless steel cylinders that we use also as cov-
 336 ers for the sample holder, while we use home-made non-polarizable electrodes for P1 and
 337 P2. We made our own Cu-CuSO₄ non-polarizable electrodes, following the procedure
 338 proposed by Kremer et al. (2016). They consist of a copper wire inserted in a plastic tube
 339 filled with a saturated solution of copper sulfate and gelatin, plugged by a porous filter
 340 at the bottom. We used a near cylindrical sample holder of length 22.9 cm and radius
 341 2.1 cm, with electrode separation of 7.4 cm, that is separated roughly by a third of the
 342 sample holder's total length (Figure 3b); this pseudo-Wenner configuration has been used
 343 previously by Ghorbani et al. (2009), and Jougnot et al. (2010). The geometrical fac-
 344 tor to convert measured impedances to conductivities has been determined using finite
 345 elements numerical methods, this approach has been used previously by Jougnot et al.
 346 (2010).

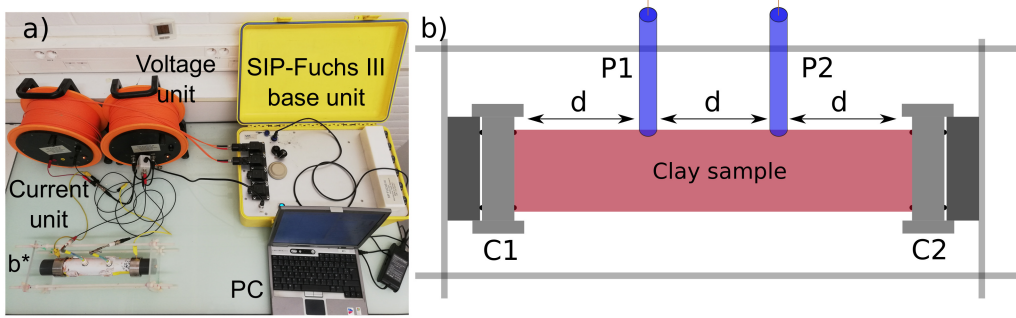


Figure 3. a) Laboratory set-up for SIP measurements on our clay samples with the sample holder, injecting and measuring units (orange), SIP-FUCHS III, and a computer to store the data. b) Sample holder sketch with the external structure. C1 and C2 are two cylindrical plates, our current electrodes that inject a sinusoidal electric current. P1 and P2 are a pair of non-polarizable electrodes that measure the resulting electrical potential difference, they are equally distanced from the current electrodes, making a pseudo-Wenner array.

347 We created an external structure to hold the sample holder (Figure 3b) in order to achieve
 348 repeatability in our measurements. Indeed, we needed the ability to close the sample holder
 349 at the exact same position and with the same pressure between measurements. As re-
 350 peatability test, we built two identical sample holders, made two individual green mont-
 351 morillonite samples, and measured the SIP signal in both samples. The repeatability of
 352 the measurements shows a 4.7% difference on the real part of the electrical conductiv-
 353 ity and a 0.47% difference on the imaginary part at 1.46 Hz. For the whole spectrum,
 354 we see a maximum percentage difference of 4.8% on the real part of the electrical con-
 355 ductivity (at 2.9 mHz) and 11.89% for the imaginary part (at 45.8 mHz). In average,
 356 for the whole spectrum, we see a difference of 4.6% for the real part of the spectrum, and
 357 1.5% for the imaginary part. See the supplementary information file, to visualize the re-
 358 peatability test. We acknowledge that the difference between the real part of the con-
 359 ductivity between both samples is surprising (although negligible). We think that such
 360 difference lies on the fact that we are dealing with two different clay samples in two dif-
 361 ferent sample holders. A minimal difference between these two will correspond to a min-
 362 imal difference between their signals.

3.4 Optimization of the double-Pelton model

For the optimization procedure, we use our SIP data as input, that is, conductivity amplitude ($S\ m^{-1}$) and phase (rad), and then fit a double-Pelton model (see equation 6). In this paper, we optimize for seven parameters: ρ_0 , m_1 , m_2 , τ_1 , τ_2 , c_1 , and c_2 . The cost function is:

$$\Phi = \frac{\sum_{i=1}^{N_a} (A_{mes}^i - A_{mod}^i)^2}{\sum_{i=1}^{N_a} (A_{mes}^i - \langle \mathbf{A}_{mes} \rangle)^2} + \frac{\sum_{i=1}^{N_p} (P_{mes}^i - P_{mod}^i)^2}{\sum_{i=1}^{N_p} (P_{mes}^i - \langle \mathbf{P}_{mes} \rangle)^2}, \quad (8)$$

where, A_{mes} represents the measured amplitude vector, $\langle \mathbf{A}_{mes} \rangle$ represents the mean of the measured amplitude vector, A_{mod} , the modeled or calculated amplitude vector, via the double-Pelton model, N_a is the number of amplitude data points that have been preserved, P_{mes} is the measured phase vector, $\langle \mathbf{P}_{mes} \rangle$ is the mean of the measured phase vector, P_{mod} is the modeled or calculated phase vector, and N_p is the number of phase data points that have been kept. The strategy we used was to first optimize with a simulated annealing approach, that has been explained in detail in Maineult (2016). For the parameters m_1 , m_2 , c_1 , and c_2 , we let them vary between [0 - 1], for ρ_0 we usually use $[\bar{\rho} \pm (0.2 \cdot \bar{\rho})\ \Omega \cdot m]$, for τ_1 we usually use $[10^{-3} - 10^6]$ s, and finally for τ_2 we use $[10^{-10} - 10^1]$ s. Here, $\bar{\rho}$ is the arithmetic mean electrical resistivity for all frequencies. We later optimize the double-Pelton parameters using a simplex optimization procedure (Caceci & Cacheris, 1984). This same strategy has been used in Maineult et al. (2017). As input of the simplex code we use our measured SIP data (amplitude and phase) and as initial model we use the result of the simulated annealing method. The simulated annealing step allows us to explore the parameter space preventing to get trapped in a local minimum, but this is done in a discrete manner. When we know the vicinity of the solution, we use the Simplex optimization procedure to refine the solution.

Moreover, we fixed a double-Warburg model for the red and green montmorillonite samples, as well as the kaolinite sample. A double-Warburg model is a double-Pelton model but with $c_1 = 0.5$ and $c_2 = 0.5$. In the case of these three types of clay samples, we turned the optimization code and obtained values of c_1 and c_2 near 0.5. Therefore, we opted that for these three types of clay samples, we would fix c_1 and c_2 , and we would only optimize for the remaining five parameters, that is: ρ_0 , m_1 , m_2 , τ_1 , and τ_2 . It is worth mentioning that we tried fixing c_1 and c_2 for the illite sample as we also obtained val-

ues near 0.5, but we obtained poor fits with $c_1 = 0.5$ and $c_2 = 0.5$. We assume then that the illite sample does not behave as a double-Warburg, but as a double-Pelton. The rest of the clay samples (kaolinite, red and green montmorillonite samples) do behave as double-Warburg models. The results of our fits are presented later on in this article, in Table 4.

3.5 Differentiation of clay minerals

In order to compare our SIP datasets, we calculated the normalized measured conductivity differences ($\Delta\sigma'_N$ or $\Delta\sigma''_N$) between each clay type for every salinity at 1.46 Hz, for both the real and imaginary parts of the complex conductivity. We chose 1.46 Hz because frequencies near 1 Hz represent a widely used choice in geophysics (Zanetti et al., 2011). Also, as it will be presented in the results and discussion sections, the local maximum polarization phenomena happens near 10^0 Hz. To choose this particular frequency, we also took into account that the highest measured errors in the data happened at the lowest frequencies (mHz range), because less stacking is possible, due to the long time periods for each measurement. The noisiest data happened at the highest frequencies (kHz range). Indeed, according to Huisman et al. (2016) the electromagnetic coupling effects happen at the highest frequency range of our SIP measurements, in the kHz range. Therefore, when choosing near 1 Hz, we should get the most accurate data. We calculate Δx_N values between each clay type at 1.46 Hz, for the datasets shown in Figure 4. To calculate the Δx_N we use:

$$\Delta x_N(f = 1.46 \text{ Hz}) = 100 \times \frac{x_1 - x_2}{\frac{x_1 + x_2}{2}}, \quad (9)$$

where x_N , x_1 and x_2 can be substituted by the real and imaginary parts of the conductivity (so either $\Delta\sigma'_N$ or $\Delta\sigma''_N$), in such a way that the operation is done either for the real part or the imaginary part of the conductivity, separately. Additionally, x_1 and x_2 represent either the real or imaginary part of the conductivity at 1.46 Hz of an individual type of clay. The idea is to quantify if we are able to distinguish between two different clay minerals in a laboratory setting. That is, if the $\Delta\sigma'_N$ or $\Delta\sigma''_N$ value is low (e.g. below 10%) that means we are hardly able to differentiate two specific clay minerals at the laboratory scale, then at the field scale it would seem impossible to differentiate such clay minerals. Conversely, if we have a high $\Delta\sigma'_N$ or $\Delta\sigma''_N$ (e.g. above 100%) it would

not mean that we could automatically differentiate two different clay minerals at the field scale.

4 Results

We obtained a large SIP dataset in the laboratory. To make our interpretation of this dataset more accessible, we decomposed their analysis into several subsections. First, we will present the complex conductivity values at 1.46 Hz vs. the calculated water conductivity, to get a quick view of the electric behavior of the clay samples at varying salinities. After that, we present the normalized spectrum of the real part of the complex conductivity per clay type; we show the evolution with salinity. We then present the full spectra of the complex conductivity for all clay samples and all salinities. Afterwards, we present the results of our double-Pelton fits, and the obtained parameters. We finally present a quantitative differentiation between clay samples at the same salinity. We filtered all of our datasets with a 5% percent filter. That is, if the error of the measured amplitude is larger than 5%, we remove the data point from our dataset. We performed our SIP measurements at five salinities on four types of clay: montmorillonite samples (red and green), a kaolinite sample and an illite sample (see Table 2). Additionally, we performed SIP measurements at three salinities (initially de-ionized water, 1×10^{-2} , and 1 M of NaCl) on two extra types of clay: beige montmorillonite sample and a Boom clay sample. Boom clay is a natural clayrock used for nuclear waste storage (Ortiz et al., 2002). The results of these additional types of clay are shown as supplementary information in this article.

4.1 Results at varying salinities at 1.46 Hz

We collected SIP measurements of four different types of clay (red and green montmorillonite samples, an illite sample, and a kaolinite sample) with the SIP-FUCHS III system. We used frequencies from 10^{-3} to 10^4 Hz. The calculated water conductivity values (following equation 7) presented in Figure 4, correspond to those of the post-dehydration salinities (Figures 2d and e). We chose to present the data points at 1.46 Hz, because the highest measured errors and the noisiest data are present at the lowest and highest frequencies, respectively. It should be noted that the low salinity (initially 10^{-3} M NaCl) calculated water conductivity values may be underestimated because we did not consider clay dissolution as well as cation leaching from the interlayer space of montmorillonite.

452 In Figure 4a we observe that the real conductivity increases with an increase in the con-
 453 ductivity of the fluid saturating our clay mixtures for all salinities for all types of clay.
 454 In addition, Figure 4a shows that both montmorillonite samples exhibit higher surface
 455 conductivity than the illite and kaolinite samples. Due to their difference in surface elec-
 456 trical properties (see section 2.1), it is a bit surprising to see that the kaolinite and il-
 457 lite samples may have the same surface conductivity here. This may be due to the fact
 458 that the kaolinite sample is not pure and contains 4% in weight of more conducting smec-
 459 tite and 3% in weight of more conducting illite (see Table 1).

460 With the imaginary conductivity we see a different behavior. For the red and green mont-
 461 morillonite samples, we see a peak of the imaginary conductivity at the second to high-
 462 est salinity (corresponding to a water conductivity in the 10^0 S m⁻¹ range). For the kaoli-
 463 nite and illite samples, we see a similar behavior, however, we see the peak in the range
 464 of 10^{-1} S m⁻¹ for the water conductivity. The imaginary conductivity amplitude is also
 465 roughly one order of magnitude higher for the montmorillonite samples than for other
 466 clay samples. Due to their higher CEC and stronger EDL, the montmorillonite samples
 467 polarize more than the illite and kaolinite samples. In addition, the zeta potential of Na-
 468 montmorillonite in a NaCl solution is higher in magnitude than the zeta potential of il-
 469 lite and kaolinite in a NaCl solution (Sondi et al., 1996; Leroy & Revil, 2004; Leroy et
 470 al., 2015). Consequently, membrane polarization effects may be higher for Na-montmorillonite
 471 than for illite and kaolinite. It results that more salt is necessary to decrease the imag-
 472 inary conductivity of montmorillonite compared to illite and kaolinite at high salinity.
 473 Note that although we collected SIP data at five different salinities, the de-ionized wa-
 474 ter dataset are not presented in Figure 4. We chose not to present those data points be-
 475 cause knowing or controlling the conductivity of the pore water at that salinity proved
 476 to be very complex, and out of the scope of this paper. However, the datasets of de-ionized
 477 water are presented in the following parts of this paper.

478 Equation 2 was adjusted to the σ' values at 1.46 Hz (for 10^{-3} -1 M NaCl) by consider-
 479 ing that the formation factor and the surface conductivity are independent from the pore
 480 water conductivity. For this adjustment, more weight was attributed to the values for
 481 the two highest pore water conductivities as they are expected to be less sensitive to the
 482 surface conductivity (see Weller et al., 2013). This procedure provides a single surface
 483 conductivity per sample presented in Table 3 and seems to overestimate its values for
 484 the lowest pore water conductivity. As expected, we see larger values of σ'_{surf} for both

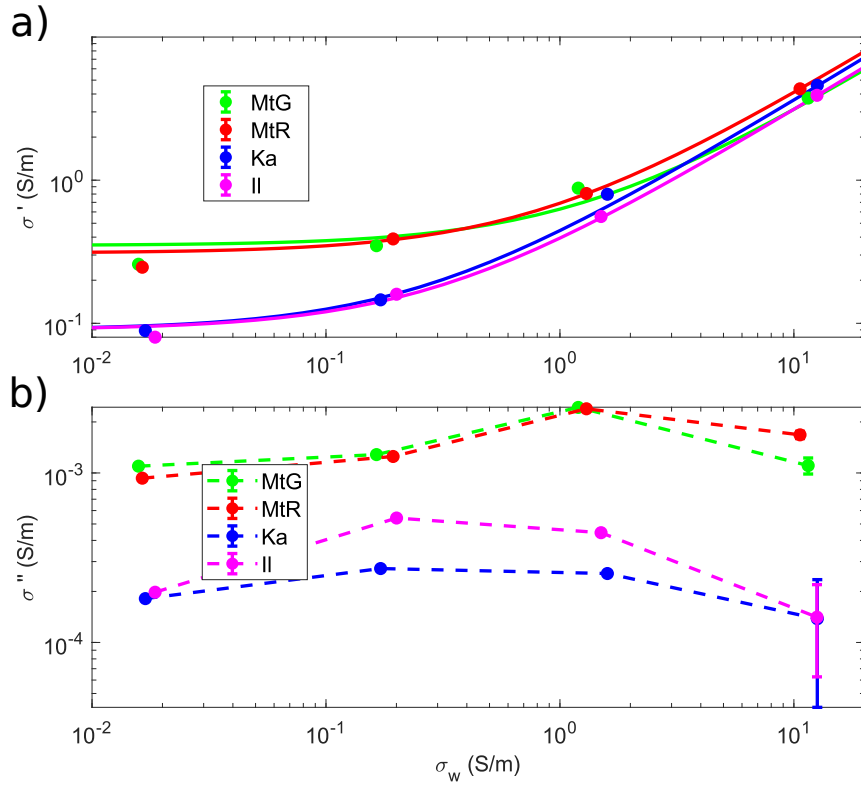


Figure 4. Measured (filled circles) real (a) and imaginary (b) conductivity of the four clay samples as a function of calculated water conductivity, at a frequency of 1.46 Hz. MtG represents the green montmorillonite sample, MtR the red montmorillonite sample, Ka the kaolinite sample, and Il the illite sample. The bold line on (a) is the calculated $\sigma'(\sigma_w)$ from equation 2, the parameters we fit are presented in Table 3.

Table 3. Formation factors (F) and σ'_{surf} fitted from equation 2 for the real conductivity values at 1.46 Hz, CEC and specific surface area (Ss) of the clay samples.

Clay type	F [-]	σ'_{surf} [Sm^{-1}]	CEC [meq/100 g]	Ss* [m^2/g , BET]
Kaolinite sample	2.82	0.09	22	16.94
Illite sample	3.29	0.09	47	101.60
Green mont. sample	3.60	0.35	132	77.71
Red mont. sample	2.63	0.31	135	71.09

*Specific surface area measured through the BET (Brunauer-Emmett-Teller) method for each sample. BET cannot probe the interlayer space of montmorillonites.

485 montmorillonite samples, because these clay samples have a more important surface elec-
486 tric charge and specific surface area than the illite or kaolinite samples. We recognise the
487 formation factor values we obtained have some uncertainty and are only meant as a mean
488 of the electrical formation factor for each type of clay sample, as we are dealing with clay
489 muds with varying porosities and not hard rocks with a specific formation factor. We
490 present the σ' calculated values from the σ'_{surf} and F fitted values in Figure 4a. It is
491 worth mentioning that the specific surface areas measured using the BET (Brunauer-
492 Emmett-Teller) technique might not be representative of the true values for the mont-
493 morillonites mineral. Indeed, previous work from the literature indicate this technique
494 is not able to properly probe interlayer space (e.g., Tournassat et al., 2003; Hassan et
495 al., 2006). In order to do so, other methods such as wet-state methylene blue (MB) should
496 be used (Weller et al., 2015a). Another possibility to better determine the real specific
497 surface area could be through a calculation of the specific surface area based on the XRD
498 characterisation of the samples. According to the literature the specific surface area of
499 montmorillonites should be in the range of 390-780 m^2/g (see Tournassat et al., 2013).

500 4.2 Normalized real conductivity

501 In Figure 5 we show the normalized real conductivity for all clay samples. For nor-
 502 malization value we used the amplitude of the conductivity at 1.46 Hz, per clay type,
 503 per salinity. We observe that overall the signal of the normalized real conductivity gets
 504 flattened as the salinity increases. In other words, we see less of a change in the normal-
 505 ized real conductivity within the measured frequency range as the salinity of the fluid
 506 increases. We interpret this as evidence that at the highest salinity, pore conduction dom-
 507 inates over the surface conduction, and we are able to see this evolution with salinity.
 508 The normalized value presented in Figure 5 could be interpreted as a ratio of alternat-
 509 ing current (AC) conduction vs. close to direct current (DC) conduction. Even though
 510 we see an overall decrease with salinity of $\sigma'/\sigma_{1.46}$. This decrease could be interpreted
 511 as evidence that the DC conduction increases faster with salinity than the AC conduc-
 512 tion due to polarization. We used a frequency of 1.46 Hz as normalization value because,
 513 as mentioned previously in the paper, as it is the closest value to 1 Hz; a widely used choice
 514 in field geophysics. Also, in field geophysics, the measurements (i.e. electrical resistiv-
 515 ity tomography) are thought of as DC measurements. A true DC value would make use
 516 of the lowest measured frequency.

517 4.3 Effect of the salinity on the spectra

518 Figure 6 shows the real conductivity spectra of each clay per salinity, with the double-
 519 Pelton model superimposed onto the dataset. We see for all of the clay samples that as
 520 the salinity increases, the real conductivity also increases. We do however notice that
 521 the data seems more dispersed for the kaolinite and illite samples, meaning, the differ-
 522 ence between maximum and minimum conductivities seems bigger for the kaolinite and
 523 illite samples, than for the montmorillonite samples.

524 Figure 7 shows the imaginary conductivity spectra of each clay per salinity, with the double-
 525 Pelton model predictions superimposed onto the dataset. For the montmorillonite sam-
 526 ples we see the overall highest polarization at the second to highest salinity. Finally, for
 527 the kaolinite and illite samples, we see the highest polarization at the middle salinity (10^{-2}
 528 M of NaCl salinity range), this is better seen for the illite sample.

529 The errorbars become larger in the highest salinity measurements. This is expected from
 530 the measurement itself. Indeed, measuring low phases, that is, very small time differences

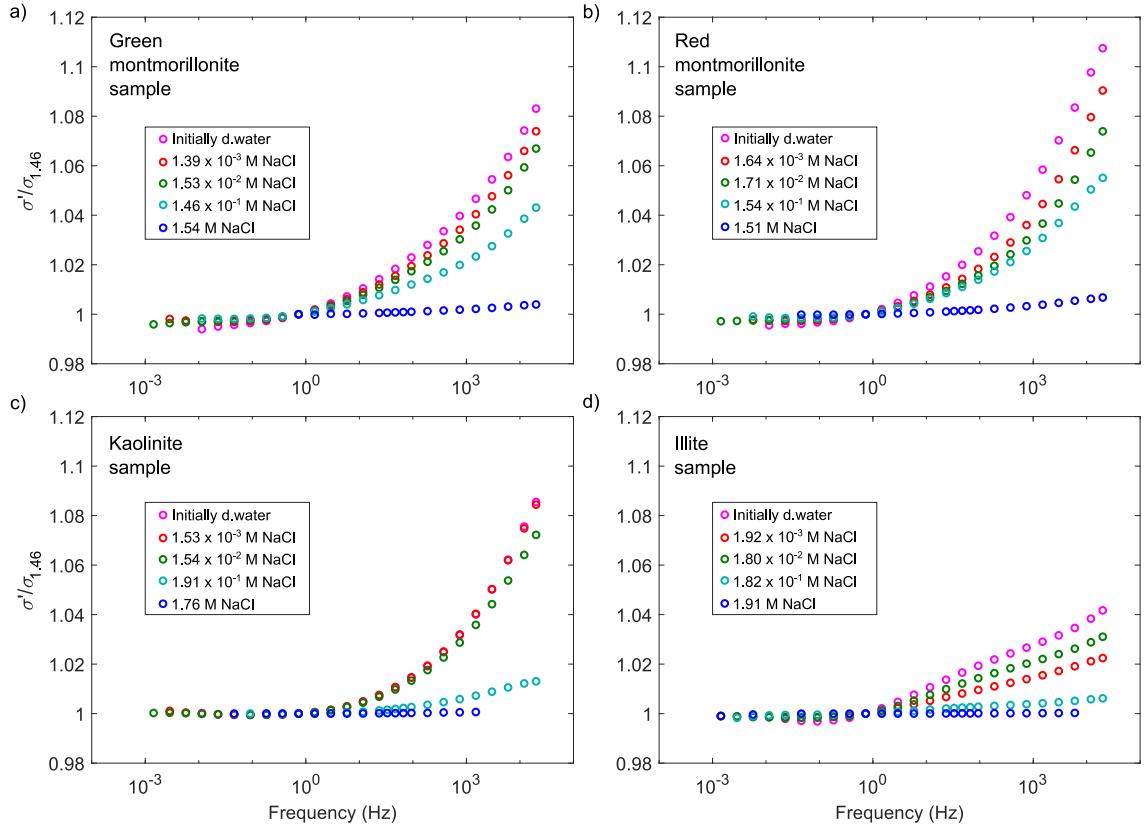


Figure 5. Normalized real conductivity for all salinities per clay type: a) green montmorillonite sample, b) red montmorillonite sample, c) kaolinite sample, and d) illite sample. All these spectra have been normalized by the conductivity amplitude at 1.46 Hz.

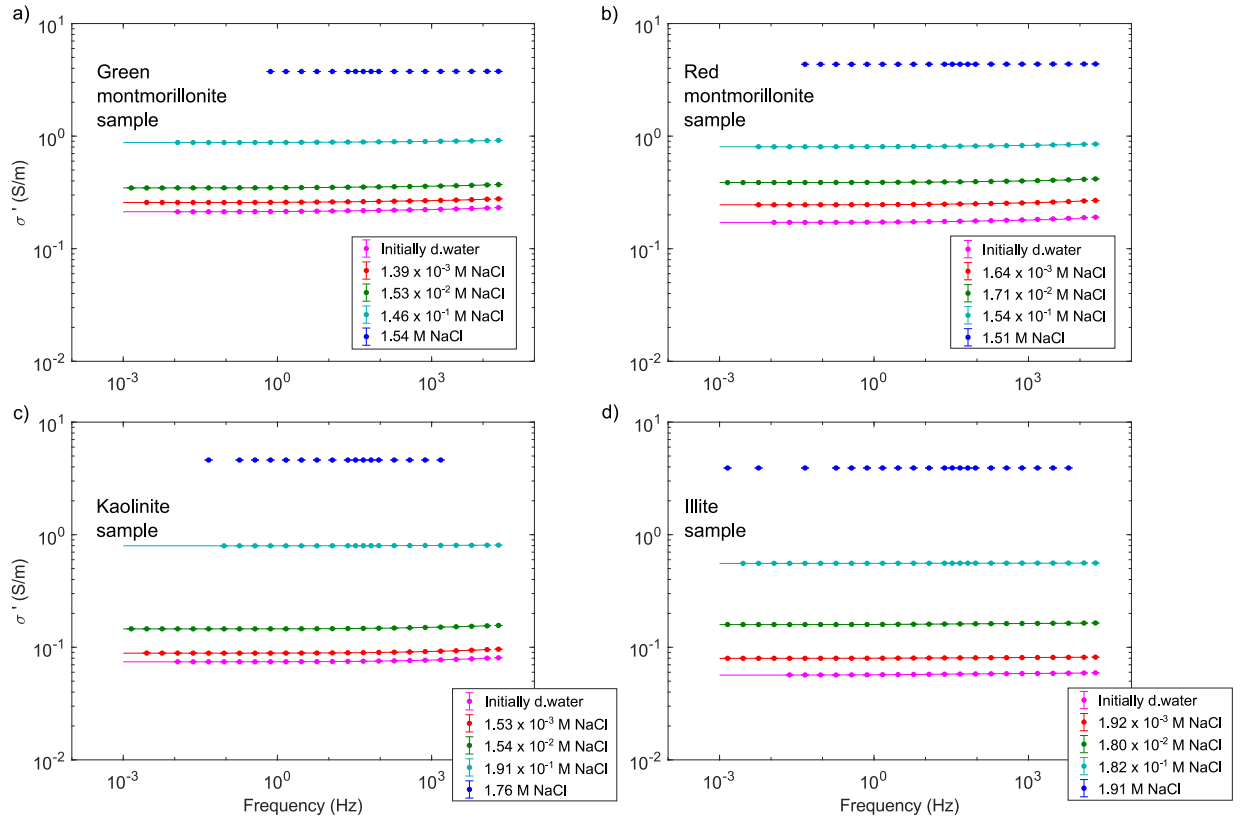


Figure 6. Real part of the complex conductivity per salinity of: a) green montmorillonite sample, b) red montmorillonite sample, c) kaolinite sample, and d) illite sample. The calculated salinity values at which the SIP measurements were collected are presented in the legends of each subplot. Dots with errorbars represent the measured SIP data, and the line represents the double-Pelton model predictions for each dataset.

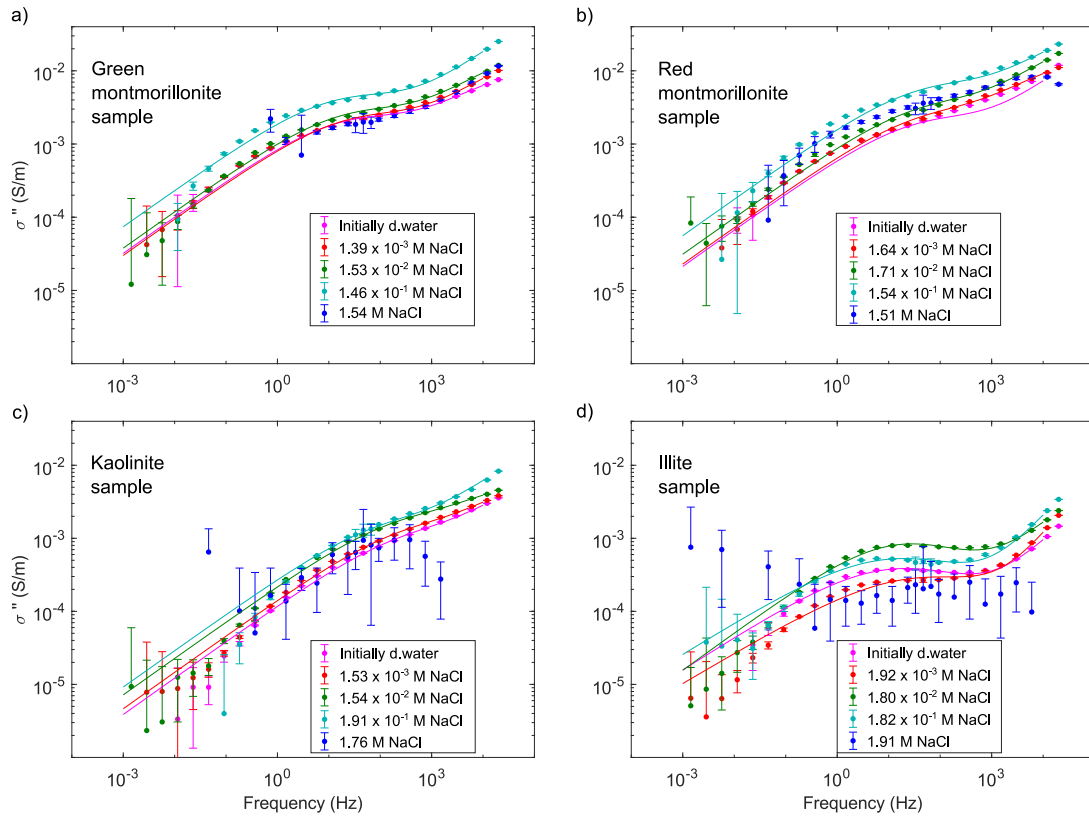


Figure 7. Imaginary part of the complex conductivity per salinity of: a) green montmorillonite sample, b) red montmorillonite sample, c) kaolinite sample, and d) illite sample. The calculated salinity values at which the SIP measurements were collected are presented in the legends of each subplot. Dots with errorbars represent the measured SIP data, and the line represents the double-Pelton model predictions for each dataset.

531 between the injected current and the resulting measured voltage signal, is a real chal-
 532 lenge for the electronics involved in SIP measurements (Zimmermann et al., 2008). Nev-
 533 ertheless, it is possible to distinguish a clear tendency with frequency, in most of the spec-
 534 tra, except for the illite and kaolinite samples at the highest salinity.

535 **4.4 Double-Pelton model fits and variation of Pelton parameters with** 536 **varying salinities**

537 In Figure 8 we present the principle of the double-Pelton model decomposition. We
 538 sum two individual Pelton signals (see equation 6), the resulting signal is the one that
 539 we fit our data with. Note that we ran more than 3 simulated annealing optimizations
 540 to check for the repeatability of the solution and in all cases we found the same solution.
 541 It is also worth mentioning that we use filtered data for this process, for which the er-
 542 rorbars are negligible. We assume that the high frequency peak (in blue) happens due
 543 to partly an inductive and capacitive effect (Huisman et al., 2016) plus polarization of
 544 the clay (Leroy & Revil, 2009; Okay et al., 2014; Leroy et al., 2017a). We assume that
 545 the mid-frequency peak (in red) corresponds solely to the polarization of clay.

546 In Table 4 we have summarized the optimized Pelton parameters of both the red and
 547 blue peaks (Figure 8). Furthermore, as mentioned previously, we used a double-Warburg
 548 model ($c_1=0.5$ and $c_2=0.5$) for all clay samples except the illite sample, that was fitted
 549 with a double-Pelton (fitted c_1 and c_2). We present fully the double-Pelton parameters
 550 as we believe it will be of interest to the community to have access to Pelton param-
 551 eters of individual types of clays at varying salinities, for possible forward-modeling op-
 552 portunities.

553 For the four lowest salinity datasets, we observe how at the highest fitted salinity, there
 554 is a considerable decrease in the chargeability (m_1) parameter for the lower frequency
 555 local maxima. For all datasets we see chargeability values (in each individual local max-
 556 ima) in the same magnitude order. We also see an increase on DC electrical conductiv-
 557 ity with increasing salinity, as expected. Note that we present values of electrical con-
 558 ductivity, instead of resistivity (as shown in the double-Pelton model, equation 6), as the
 559 complex conductivity is only the inverse to the complex resistivity. As for the illite sam-
 560 ple, we see that for c_1 all values linger near 0.5, but not quite 0.5. Finally, we see that

Table 4. Double-Pelton parameters obtained from the optimization procedure of section 3.4 to reproduce SIP signal on the four studied clay types.

Clay type	Salinity [M NaCl]	σ_0 [S m ⁻¹]	m_1 [mV/V]	τ_1 [μ s]	c_1	m_2 [mV/V]	τ_2 [μ s]	c_2	RMS [-]
Kaolinite	D.W.	0.074	40.14	333	0.5	345	0.327	0.5	1.78×10^{-3}
	1.53×10^{-3}	0.089	40.68	332	0.5	249	0.599	0.5	1.82×10^{-3}
sample	1.54×10^{-2}	0.146	34.86	413	0.5	142	1.483	0.5	1.52×10^{-3}
	1.91×10^{-1}	0.797	5.66	842	0.5	350	0.014	0.5	2.63×10^{-2}
Illite	D.W.	0.057	34.26	10110	0.45	682	0.063	0.66	4.82×10^{-3}
	1.92×10^{-3}	0.080	20.00	3261	0.42	740	0.143	0.84	5.26×10^{-3}
sample	1.80×10^{-2}	0.159	22.57	7662	0.51	515	0.021	0.56	6.18×10^{-3}
	1.82×10^{-1}	0.557	5.11	10369	0.44	342	0.043	0.76	7.21×10^{-3}
Green mont.	D.W.	0.213	37.40	4418	0.5	158	1.917	0.5	4.75×10^{-3}
	1.39×10^{-3}	0.257	32.55	3432	0.5	249	0.56	0.5	4.23×10^{-3}
sample	1.53×10^{-2}	0.347	28.27	3957	0.5	198	0.803	0.5	2.72×10^{-3}
	1.46×10^{-1}	0.877	18.48	5758	0.5	504	0.052	0.5	3.87×10^{-3}
Red mont.	D.W.	0.171	42.32	2266	0.5	958	0.048	0.5	9.61×10^{-2}
	1.64×10^{-3}	0.245	30.87	2046	0.5	200	1.88	0.5	3.78×10^{-3}
sample	1.71×10^{-2}	0.387	27.47	2033	0.5	306	0.452	0.5	3.85×10^{-3}
	1.54×10^{-1}	0.805	25.76	1846	0.5	188	0.528	0.5	7.41×10^{-3}

561 the relaxation times for the second (high frequency) local maxima are mostly below the
 562 μ s range, and that for the second local maxima, these are considerably above.

563 **4.5 Differentiation of clay minerals**

564 After calculating the $\Delta\sigma'_N$ and $\Delta\sigma''_N$ values (equation 9), we see that the values $\Delta\sigma'_N$
 565 decrease with increasing salinities overall, agreeing with what we observe in Figure 5,
 566 for the normalized real conductivity. This behavior is not so clear or evident for the imag-
 567 inary part. We also observe that the $\Delta\sigma'_N$ and $\Delta\sigma''_N$ values are smaller between the mont-
 568 morillonite samples, as expected, that is the montmorillonite samples are electrically sim-
 569 ilar to each other. For the lowest salinity (initially de-ionized water) the biggest differ-
 570 ence in real conductivity is between the illite and the green montmorillonite samples (-116% ,
 571 the real conductivity of the illite sample is smaller than that of the montmorillonite sam-
 572 ple), and for the imaginary part it is between the kaolinite and the green montmorillonite
 573 samples (-149% , the imaginary conductivity of the kaolinite sample is smaller than that
 574 of the montmorillonite sample). For the initial 10^{-3} M salinity (NaCl) the biggest dif-
 575 ference in real conductivity is between the illite and the green montmorillonite samples

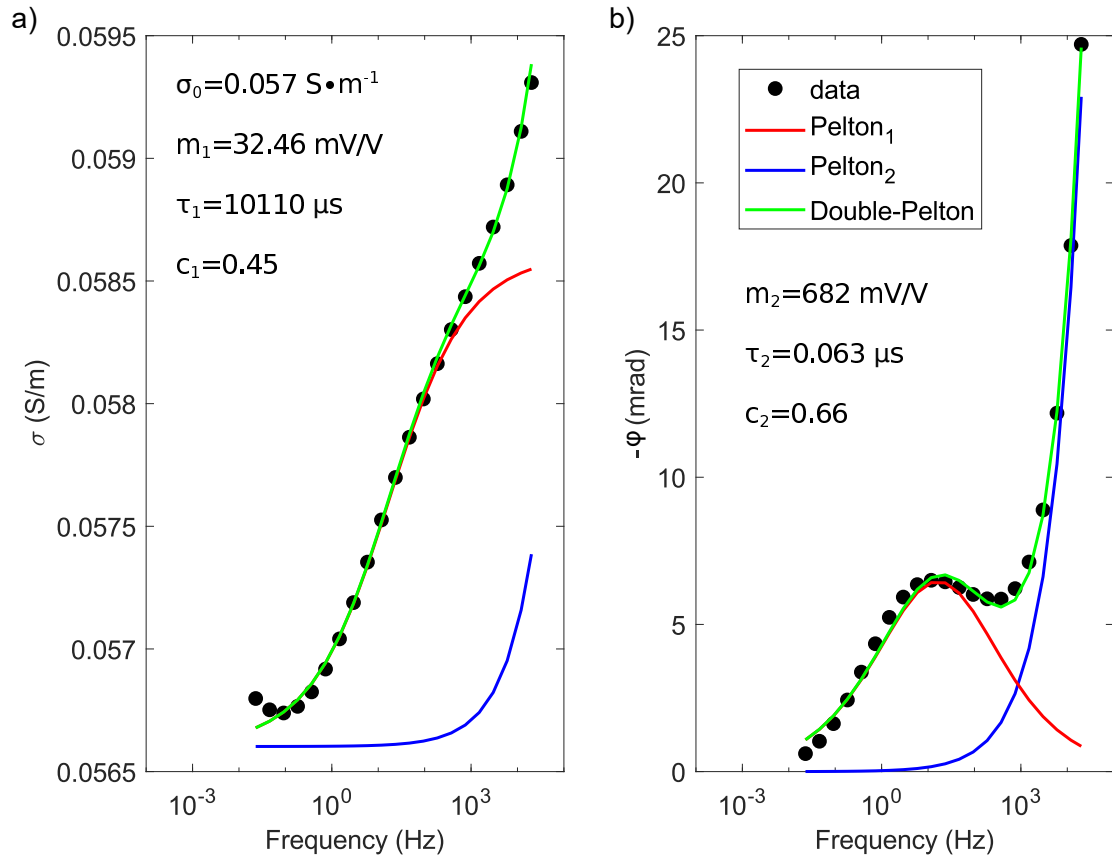


Figure 8. Fit of a double-Pelton model (equation 6) to our data, in both a) amplitude and b) phase. We present the illite sample dataset using initial de-ionized water (filled circles), and the corresponding double-Pelton model (green line), with two individual Pelton models (blue and red lines).

Table 5. $\Delta\sigma'_N$ and $\Delta\sigma''_N$ values (in %) for the initially 10^{-2} M of NaCl clay mixtures. These calculations are made using the complex conductivity at 1.46 Hz, the real part ($\Delta\sigma'_N$) is on the lower left triangle (in bold), and the imaginary part ($\Delta\sigma''_N$) is on the upper right triangle (in italics). MtG represents the green montmorillonite sample, MtR the red montmorillonite sample, Ka the kaolinite sample, and IL the illite sample.

	MtG	MtR	Ka	IL
MtG	0	<i>2.56</i>	<i>129.84</i>	<i>81.20</i>
MtR	10.85	0	<i>128.34</i>	<i>79.06</i>
Ka	-82.00	-90.83	0	<i>-66.04</i>
IL	-74.37	-85.53	9.01	0

576 (-105%), and for the imaginary part it is between the kaolinite and the green montmo-
577 rillonite samples (-143%). For the initial 10^{-2} M salinity, the biggest difference in real
578 conductivity is between the kaolinite and the red montmorillonite samples (-91%), and
579 for the imaginary part it is between the kaolinite and the green montmorillonite sam-
580 ples (-130%). For the initial 10^{-1} M salinity, the biggest difference in real conductiv-
581 ity is between the illite and the green montmorillonite samples (-45%), and for the imag-
582 inary part it is between the kaolinite and the green montmorillonite samples (-162%).
583 For the highest salinity, the biggest difference in real conductivity is between the kaoli-
584 nite and the green montmorillonite samples (20%), and for the imaginary part it is be-
585 tween the kaolinite and the red montmorillonite samples (-169%). Table 5 presents the
586 $\Delta\sigma'_N$ and $\Delta\sigma''_N$ values for the initial salinity of 10^{-2} M of NaCl. We use x_1 (see equa-
587 tion 9) as the value of the column, and x_2 of the row. For example, in Table 5, we ob-
588 tained 10.85, using the σ' of the red montmorillonite sample as σ'_1 , and of the green mont-
589 morillonite sample as σ'_2 (see equation 9). The lower left triangle corresponds to calcu-
590 lation for the real part ($\Delta\sigma'_N$) of the complex conductivity (in bold), and the upper right
591 triangle corresponds to the imaginary part ($\Delta\sigma''_N$, in italics). The tables for the rest of
592 the salinities are presented in the supplementary information part of this paper.

5 Discussion

In this study we propose a new experimental protocol with verified repeatability to characterize the complex electrical conductivity spectra of non-consolidated clay samples. We obtain a unique SIP dataset composed of four types of clay samples and saturated by a NaCl solution at five different salinities. We first interpreted the dataset at 1.46 Hz for the real and imaginary parts of the electrical conductivity before studying the entire spectra and fitting them with a double-Pelton phenomenological model, and presenting a schematic figure on how we interpret the polarization phenomena of our results.

Our measurements, at 1.46 Hz (Figure 4b), show that the quadrature conductivity (imaginary part of the complex conductivity) hits a maximum at a certain salinity and then decreases. The salinity at which this maximum exists depends on the type of clay. For the kaolinite and the illite samples, we have the maximum at the mid-salinity (around 10^{-2} M of NaCl salinity range), while it is a higher salinity for the montmorillonite samples (around 10^{-1} M of NaCl). It should be noted that we do not have the exact salinity at which the maximum quadrature conductivity happens because we investigated 5 finite salinities, that is, perhaps the maximum of the quadrature happens between two of our measured salinities. Among the published SIP datasets on clay samples, Vinegar & Waxman (1984) present an extensive dataset of the complex electrical conductivity from 21 shaly sands, measured at 4, 5 or 7 different salinities (0.01, 0.05, 0.1, 0.25, 0.5, 1.0, and 2.0 M NaCl); see Tables 1 and 2 of Vinegar & Waxman (1984). Some of their samples also exhibit the behavior with a maximum quadrature conductivity at a particular salinity, notably the samples with more shale content. They propose that the decrease of the quadrature conductivity happens due to a decrease of the membrane effect. Weller et al. (2010) proposed that the relationship between the imaginary conductivity and the water conductivity is guided by the specific surface area per unit pore volume. For this, they analyzed IP or SIP data from 114 samples, including sandstones, and sand and clay mixtures. Revil & Skold (2011) also present a dataset composed of 7 samples of sandstones and unconsolidated sand from the literature where most of the datasets present the same trend where a maximum in quadrature conductivity appears at a particular salinity. The behavior shown in Figure 4b is also consistent with the one reported by Weller & Slater (2012), both share the same water conductivity range. They measured SIP on 67 samples of sandstones and unconsolidated sediments. Okay et al. (2014)

626 measured SIP on bentonite and kaolinite quartz sand mixtures, at different clay contents
627 100%, 20%, 5%, and 1%. They present the behavior of the quadrature conductivity with
628 respect to water conductivity at only three NaCl salinities. Their bentonite samples (95%
629 smectite content) and kaolinite samples (15% smectite content) present an increase in
630 the quadrature conductivity with salinity; the maximum water conductivity presented
631 is around 1.5 S/m. Finally, Lévy et al. (2019b) measured the SIP response of a set of
632 88 volcanic altered rocks with varying amounts of smectite. They present the SIP spec-
633 tra from four of their samples (Figure 1 in Lévy et al., 2019b), using four different fluid
634 conductivities, 0.04, 0.1, 0.5, and 1.5 S m⁻¹ (from four different NaCl concentrations).
635 They show an overall increase in polarization (quadrature conductivity) with salinity for
636 these four samples. If we only analyze the smectite samples of our dataset, we see a pro-
637 gressive increase in the quadrature conductivity with increase of fluid conductivity, un-
638 til we reach the highest salinity, where we see a decrease (see Figure 4b). Only one of
639 the samples presented with the full conductivity spectra (Figure 1 in Lévy et al., 2019b)
640 has more than 20 % smectite. If we only take a look at this sample, it doesn't show a
641 decrease in quadrature conductivity with the highest salinity, although, their highest pre-
642 sented pore water conductivity for this data subset is 1.5 S m⁻¹. For the smectite sam-
643 ples of our dataset, we see a decrease on the quadrature conductivity just at the high-
644 est pore water conductivity, around 10 S m⁻¹. According to these studies, it is interest-
645 ing to notice that the increase of the quadrature conductivity with salinity is larger for
646 sandstones and quartz sand than for smectite minerals. This observation confirms the
647 assumption that the quadrature conductivity of these materials is directly sensitive to
648 their surface charge controlling EDL polarization (Okay et al., 2014; Leroy et al., 2017a).
649 Indeed, the surface charge of quartz strongly increases with pH and salinity due to the
650 deprotonated silanol surface sites whereas the smectite minerals carry a permanent neg-
651 ative surface charge less sensitive to pH and salinity on their basal surface due to iso-
652 morphic substitutions in the crystal lattice. Weller & Slater (2012) suggest further in-
653 vestigation at even higher salinities, this could be important for high salinity environ-
654 ments, such as oceanic shale reservoirs (Morsy & Sheng, 2014). Due to such a high elec-
655 trical conductivity of such sample, the SIP measurement logistics could be complex, and
656 better protocols and measuring equipment with low uncertainty at high conductivities
657 are needed.

658 Furthermore, Weller et al. (2013), Woodruff et al. (2014), and Lévy et al. (2019b) ob-
 659 served a linear relation between σ''_{surf} and σ'_{surf} . Weller et al. (2013) used a database
 660 composed of 63 sandstones and unconsolidated sediment samples. They overall found
 661 the linear parameter (l) of equation 5 to be 0.042. Woodruff et al. (2014) worked on a
 662 variety of shales, and found $l = 0.022$ for their dataset, they call it parameter R in their
 663 work. In addition, Lévy et al. (2019b) studied a variety of volcanic rocks, with different
 664 smectite contents, and they found that the linear relation between σ''_{surf} and σ'_{surf} de-
 665 creases in magnitude with smectite content. They calculate $l = 0.002$ for a data sub-
 666 set with more than 20% smectite content. According to Revil (2012), this very low l value
 667 of samples with high smectite content compared to the l value of sandstones and uncon-
 668 solidated sediment samples may be due to the restricted cation mobility in the Stern layer
 669 of clays. Also, it is not sure that it is possible to correctly capture the surface conduc-
 670 tivity of clays with such linear model (de Lima & Sharma, 1990).

671 We used σ' values at 1.46 Hz for the four highest salinities (10^{-3} -1 M of NaCl) to ad-
 672 just one formation factor and one surface conductivity per clay type using equation 2.
 673 Then, we recalculated σ'_{surf} values for each salinity (using equation 3) and considered
 674 equation 4 to associate the measured values of σ'' to σ''_{surf} . Figure 9b shows the rela-
 675 tion between σ'_{surf} and σ'' . We obtained the best fit for equation 5 for $l = 0.0039$, that
 676 is, almost an order of magnitude smaller than the value of Weller et al. (2013) ($l = 0.042$)
 677 from samples containing no clay. Our data agree more with the value of l proposed by
 678 Lévy et al. (2019b) ($l = 0.002$, when samples had more than 20% smectite), than the
 679 one of Weller et al. (2013). As we only consider clay samples, this difference could be
 680 attributed to the difference in mineralogical composition. Perhaps sandstones and sed-
 681 iments behave more like what Weller et al. (2013) present, but as clay materials have a
 682 significant σ'_{surf} , they present a different, but also seemingly linear behavior.

683 In order to test the hypothesis that l decreases with clay content, in Figure 9a we eval-
 684 uated the combined dataset of Woodruff et al. (2014), Lévy et al. (2019b), and ours. For
 685 Lévy et al. (2019b) we selected the data that contained more than 20% smectite, from
 686 their Table 1. As mentioned previously, using only our dataset we obtain $l = 0.0039$.
 687 From Figure 9a we can see that none of the proposed values for l fit perfectly this com-
 688 bined dataset. The results are in agreement with Lévy et al. (2019b) on the idea that
 689 l seems to decrease with increasing smectite content. Further than that, these data would
 690 seem to suggest that the relation between σ'' and σ'_{surf} is a non-linear one over multi-

691 ple types of minerals. A more thorough analysis over multiple types of minerals needs
 692 to be performed in order to determine if there is a larger obtainable linear or non-linear
 693 relation between σ'' and σ'_{surf} . Another interesting relationship that is studied between
 694 two SIP parameters is the relationship between σ'' and the surface area per unit volume
 695 (S_{por}), see Weller et al. (2015a) and Revil (2012). In the supplementary information, we
 696 present a comparison of our data and that presented in Weller et al. (2015a) and Börner
 697 (1992). It should be noted that we use clay samples and not a mix of sand and clay, and
 698 thus the results between the data presented in Weller et al. (2015a), Börner (1992), and
 699 our data do not align perfectly. As a whole, we observe that the imaginary conductiv-
 700 ity increases with the surface area per unit volume, as previously observed by Börner (1992),
 701 Revil (2012), and Weller et al. (2015a).

702 Among the various existing phenomenological models, we used a double-Pelton model
 703 to fit our data. We noticed that a double-Warburg model ($c=0.5$) was suitable for three
 704 of our datasets (kaolinite, red, and green montmorillonite samples). Revil et al. (2014)
 705 have proposed rather the use of a Warburg model over a Debye or Pelton model, after
 706 analyzing SIP datasets of metal-free and clayey materials. This holds true for three of
 707 the measured types of clay, that is the kaolinite, red and green montmorillonite samples.
 708 Only the illite sample cannot be fitted by a double-Warburg and presents the most no-
 709 ticeable mid-frequency (around 10 Hz) peak of all the measured types of clay. We present
 710 in Figure 10, trends we found among all double-Pelton parameters. To further interpret
 711 the results of the double-Pelton model, one can consider the classic formula of charge-
 712 ability (m):

$$m = \frac{\sigma_{\infty} - \sigma_0}{\sigma_{\infty}}, \quad (10)$$

713 where σ_{∞} can be thought of as the conductivity at high frequency or the AC conduc-
 714 tivity due to polarization plus the DC conductivity, and σ_0 can be thought of as the con-
 715 ductivity at low frequency or only the DC conductivity. In this way, if we notice an in-
 716 crease of m_1 or m_2 , we could interpret this as that possibly AC conductivity increases
 717 faster with respect to DC conductivity. Similarly, if we notice a decrease of m_1 or m_2 ,
 718 we could interpret this as DC conductivity increasing faster than the AC conductivity.
 719 We see an overall decrease of m_1 with an increase of σ_0 , and we observe a decrease of
 720 τ_2 with an increase of m_2 . We could interpret the first as a direct result of our data pro-

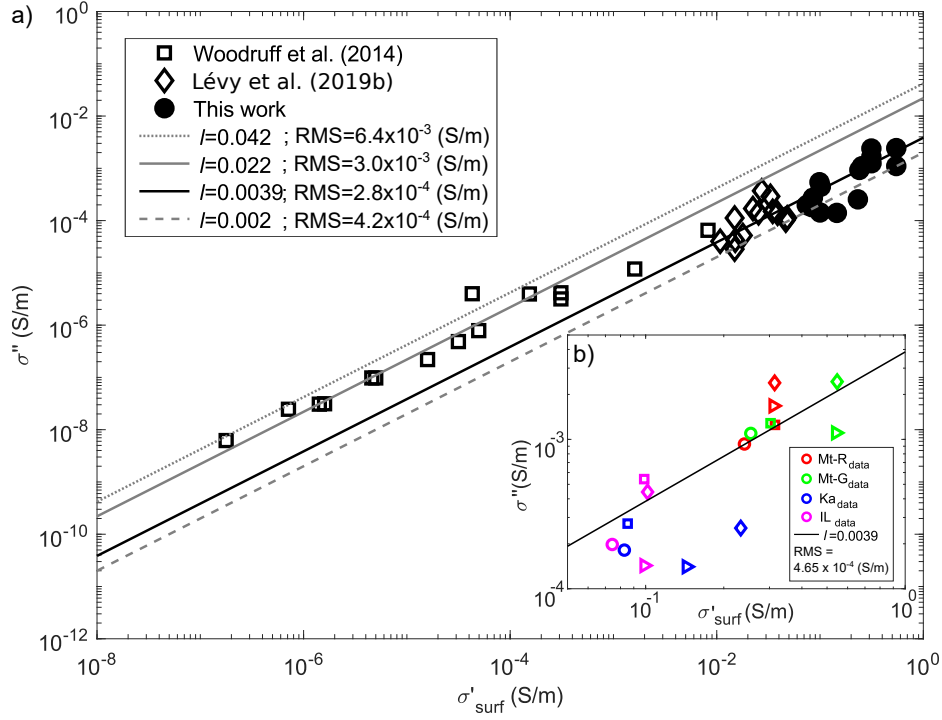


Figure 9. Relationship between σ'' and σ'_{surf} . a) Comparison of different linear parameters presented in the literature and the datasets from Woodruff et al. (2014) and Lévy et al. (2019b). b) Linear fit ($l = 0.0039$) between σ'' and σ'_{surf} , with our data at 1.46 Hz and with the four highest salinities. The red symbols represent the red montmorillonite sample, the green represent the green montmorillonite sample, the blue symbols the kaolinite sample, and the magenta represent the illite sample. The symbols (in b) representing data from the lower to higher salinity are: circle, square, diamond, and triangle.

721 cessing protocol. By optimizing the Pelton parameters from the curves of amplitude and
 722 phase, we see an overall decrease of the mid-frequency peak (red peak in Figure 8b) with
 723 an increase in salinity of the clay sample. We attribute the decrease of m_1 with salin-
 724 ity to maybe the cease of a polarization mechanism at a particular salinity. The fact that
 725 we don't necessarily see a decrease of m_2 with salinity means that perhaps, at a certain
 726 salinity some other polarization mechanisms are still active. Which polarization mech-
 727 anism acts at which salinity is still an open question. Further investigation needs to be
 728 done, specifically on the modeling side, to better understand the SIP response of clay
 729 samples for varying salinities, with individual polarization mechanisms in mind. The cor-
 730 relation of τ_2 and m_2 could be an artifact present in our optimization process. However,
 731 we do not see such a behavior between τ_1 and m_1 . Schwartz & Furman (2015) adjust
 732 a single Pelton on their SIP data on soil organic matter, and they also see a decrease of
 733 τ with an increase of m . They attribute this phenomenon to the fact that an ion mo-
 734 bility reduction causes an increase in the relaxation time and a decrease in polarization.
 735 Indeed, as presented in Table 4 and Figure 10b, we see that for m_2 and τ_2 of our dataset
 736 this holds truth as well. An explanation of the observed inverse correlation between m_2
 737 and τ_2 could be also due to the EDL polarization of the smallest clay particles at high
 738 frequency. Large clay particles tend to polarize less than smaller clay particles due to
 739 their lower total specific surface area, and thus lower surface conductivity. However, the
 740 relaxation time of the EDL polarization increases when the size of the particle increases.
 741 Therefore, the chargeability due to these small clay particles may decrease when the re-
 742 laxation time increases. More modeling work is necessary on the polarization of the EDL
 743 of clay particles to better interpret our results with respect to individual polarization mech-
 744 anisms, in particular the EDL polarization.

745 Our $\Delta\sigma'_N$ and $\Delta\sigma''_N$ calculations agree with the fact that the highest conduction and po-
 746 larization values come from the smectite samples. We could interpret this as a result of
 747 the fact that the smectite samples have a higher specific surface area than illite sample,
 748 which has a higher specific surface area than the kaolinite sample. The surface charge
 749 of montmorillonite and illite may also be higher in magnitude than the surface charge
 750 of kaolinite. The imaginary conductivity amplitude is roughly one order of magnitude
 751 higher for the montmorillonite samples than for other clay samples. Due to their higher
 752 specific surface area and stronger EDL (reflected in the CEC measurements, see Table
 753 3), the montmorillonite samples may polarize more than the kaolinite and illite samples,

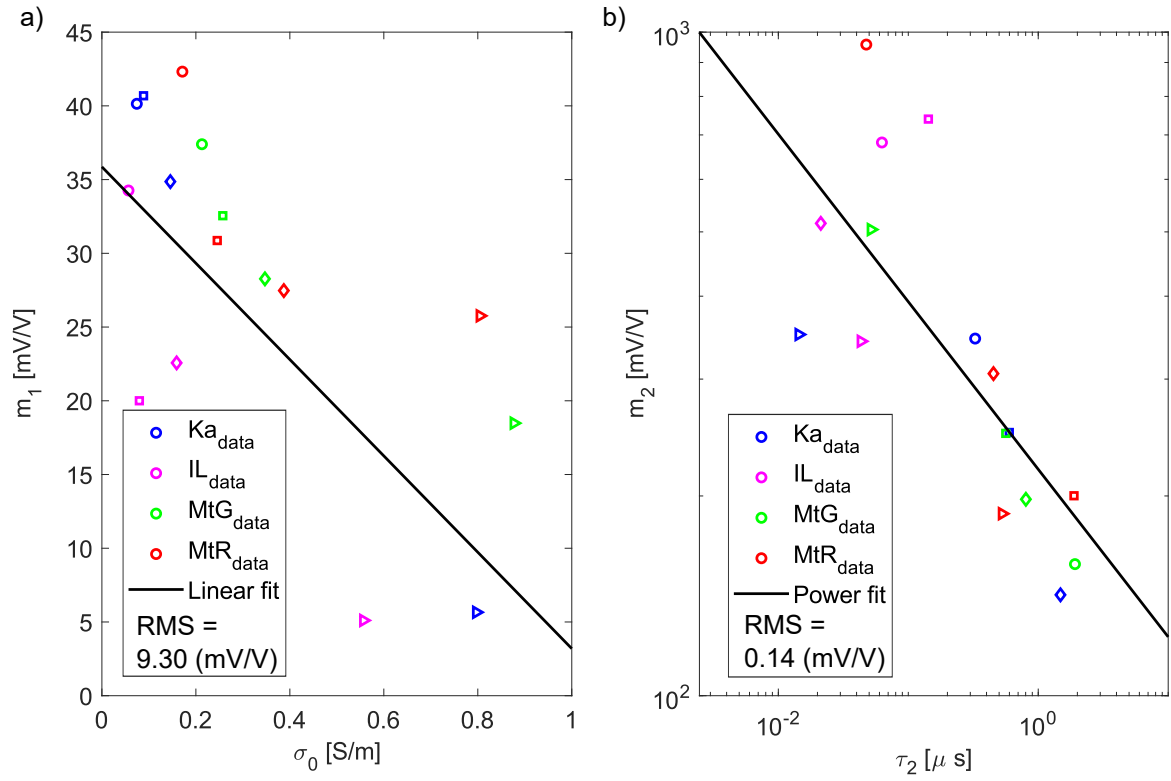


Figure 10. From the double-Pelton optimization parameters: a) dependence of m_1 and σ_0 , and b) dependence of τ_2 and m_2 . The red symbols represent the red montmorillonite sample, the green represent green montmorillonite sample, the blue the kaolinite sample, and the magenta represent the illite sample. The symbols representing data from lower to higher salinity are: circle, square, diamond, and triangle.

754 and this may also explain why more salt is necessary to "saturate" the EDL polariza-
755 tion controlling imaginary conductivity. For the red and green montmorillonite samples,
756 we interpret the fact that the peak of polarization (see Figure 4) happens around a 10^{-1}
757 M NaCl salinity due to the high electrical charge (see the CEC values in Table 3) on the
758 basal surfaces of all smectites. Diffuse layers around montmorillonite particles are strongly
759 repulsive, meaning that a high ion concentration in the pore water is necessary to com-
760 press the diffuse layers which decreases membrane polarization effects and favour coag-
761 ulation of the particles (Tombácz & Szekeres, 2006). Coagulated particles exhibit a smaller
762 external surface area available for polarization. Illite and kaolinite have a smaller spe-
763 cific surface area, therefore, the peak in their imaginary conductivity may happen at a
764 smaller ion concentration in the pore water.

765 If we take a look at Figures 6 and 7, we see that for both conductivities (real and imag-
766 inary), the montmorillonite samples are less dispersed than the kaolinite and illite sam-
767 ples. Meaning, the maximum and minimum values are closer together for the montmo-
768 rillonite samples than for the illite and kaolinite samples. This could be due to the fact
769 that montmorillonites have a far more important specific surface area than illite and kaoli-
770 nite, therefore a change in salinity effects more the conductivities (real and imaginary)
771 of kaolinite and illite. Furthermore, we can observe in Figure 6 that the surface conduc-
772 tivity of the montmorillonite samples is higher than the surface conductivity of the kaoli-
773 nite and illite samples. We can see this as in the lowest salinity, we have higher values
774 for the real conductivity of the montmorillonite samples in comparison to the kaolinite
775 and illite samples. At the lowest salinity, we can assume that the surface conductivity
776 is the most important between pore water conductivity and surface conductivity (see equa-
777 tion 2). The high surface conductivity of the montmorillonite samples could also explain
778 the fact that the difference between maximum and minimum conductivities is bigger for
779 the kaolinite and illite samples, than for the montmorillonite samples (see Figure 6). Again,
780 as the salinity increases (more available ions), it can significantly effect the pore water
781 conductivity and thus the total measured conductivity of the kaolinite and illite sam-
782 ples. As for the montmorillonite samples, this is less clear because of the high surface
783 conductivity. For the montmorillonites and kaolinite samples, the imaginary conductiv-
784 ity spectra are less sensitive to salinity than for the illite sample. This may be due to
785 the permanent negative surface charge of the basal surface of montmorillonite (see Fig-
786 ure 1) which may control polarization of montmorillonites and kaolinite (to a lesser ex-

787 tent due to a significant content of smectite). In addition, the illite sample exhibits a po-
788 larization peak at a frequency of around 10 Hz, which is not seen for the other clay types
789 (flatter signals). Following Schwarz (1962), we could attribute this 10 Hz peak of polar-
790 ization in the illite sample to a possible presence of bigger clay aggregates compared to
791 the rest of the clay samples. The illite sample used for our measurements (see Table 1)
792 has 12% calcite that could perhaps correspond to polarization around large calcite grains,
793 or a smaller polarization of grains themselves, as shown by Leroy et al. (2017b).

794 In Figure 11 we present a conceptual sketch of what we interpret occurs to clay parti-
795 cles with increasing salinity. As the salinity increases, it seems plausible that clay parti-
796 cles coagulate; and thus the distance between clay particles decreases with increasing
797 salinity, up until a point of coagulation where two clay particles can be thought of as a
798 thicker clay particle. As a result, initially at the lowest salinity (Figure 11a), we have
799 two clay particles with a negative surface charge, and an overlapping diffuse layer, with
800 a membrane effect polarization. At the mid-salinity (Figure 11b), we have a larger ionic
801 concentration (NaCl), thus more available ions to polarize, and so we see an increase in
802 polarization from Figure 11a to Figure 11b. However, we see an overlap in the diffuse
803 layer, with a possible reduced membrane effect polarization. Therefore the overall to-
804 tal polarization increases from Figure 11a to Figure 11b (even if individual polarization
805 mechanisms such as the membrane polarization decreases from Figure 11a to Figure 11b).
806 On the contrary, at the highest salinity (Figure 11c), where clay particles have coagu-
807 lated and thus we have a smaller external specific surface charge; a smaller area for ions
808 to polarize. In addition, we have a null membrane polarization effect at the highest salin-
809 ity. To make the link with Figure 4b, for the montmorillonite samples, the two lowest
810 salinities (10^{-2} - 10^{-1} S/m range) would correspond to the state presented in Figure 11a,
811 the 10^0 S/m salinity would correspond to in Figure 11b, and the 10^1 S/m would cor-
812 respond to Figure 11c. For the kaolinite and illite samples, we would rather couple the
813 10^{-2} S/m (presented in Figure 4b) to Figure 11a, the 10^{-1} S/m to Figure 11b, and fi-
814 nally the two highest salinities (10^0 - 10^1 S/m range) to 11c. This is consistent with, Vine-
815 gar & Waxman (1984), who proposed that the decrease of the quadrature conductivity
816 with salinity in shaly sands happens due to a decrease of the membrane effect. Revil (2012)
817 mentions that there is a relative change on the effect of polarization mechanisms with
818 salinity. Furthermore, Hördt et al. (2016) made a numerical membrane polarization study
819 of wide and narrow pores of different sizes and varying salinity and pH. They find that

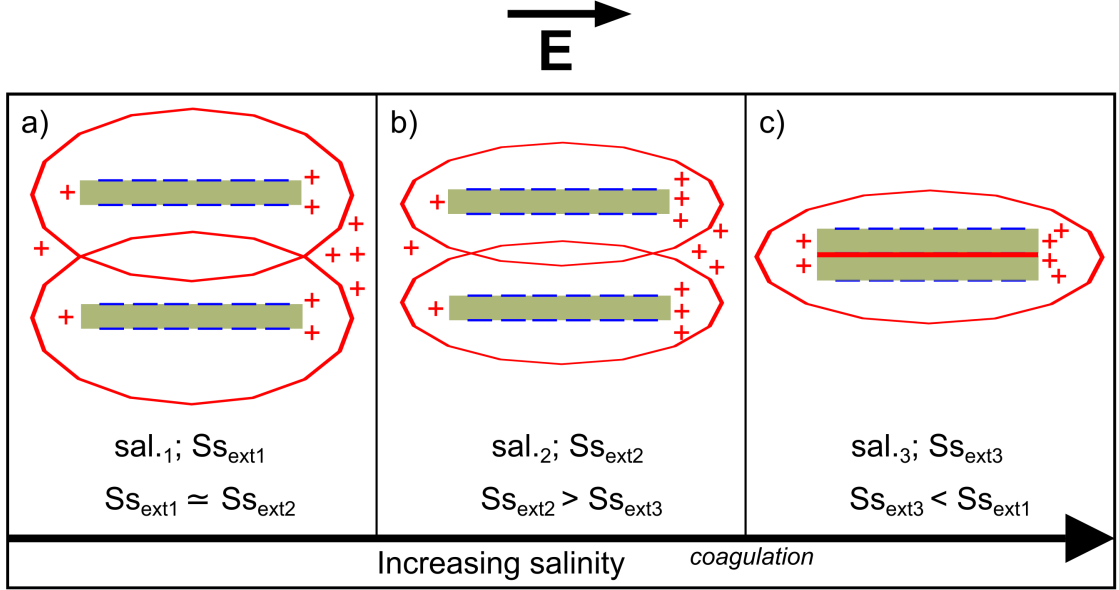


Figure 11. An interpreted process of how clay particles behave with increasing salinity. The state of two clay particles at a) the lowest salinity, b) mid-salinity and c) highest salinity. In green we present individual clay particles. In blue the negative surface charge of the clay particle, and in red the EDL (Stern and diffuse layer). In this figure, we refer as *sal.* to salinity, and $S_{s_{ext}}$ to the specific surface area of the clay particle. Numbers 1, 2, and 3 represent different stages of increasing salinity and therefore coagulation.

820 specially for narrow pores, the imaginary conductivity increases with salinity until a maximum
 821 value, and then decreases. Additionally, Weller et al. (2015b) and Lesmes & Frye
 822 (2001) have interpreted the decrease of the polarization of sandstones at high salinities
 823 by a decrease of the ionic mobility at high salinities in the EDL. Although according to
 824 molecular dynamics (MD) predictions (Bourg & Sposito, 2011), the mobility of counter-
 825 ions (Na^+) in the Stern layer does not decrease when salinity increases. More physical
 826 or numerical modeling of clays needs to be done to better understand exactly how each
 827 phenomenon (clay coagulation and decrease of ionic mobility) effects the polarization of
 828 clay samples at varying salinities.

829 On the differentiation of clay types by using SIP, we can think of two things. If we take
 830 a look at the parameters of Table 4, we could say these parameters are very close to each
 831 other, and on a field scale experiment, realistically differentiating two types of clay seems
 832 very ambitious. The success of such a task would depend on the fieldwork planning, so

833 a correct resolution is used, but with single parameters such as σ_0 , the task would seem
834 complicated. However, if we take a look at figures 6 and 7, differentiating types of clay
835 using multiple frequencies seems easier of a task. Therefore, if a fieldwork campaign is
836 carried out with the objective of differentiating two or more types of clay in a formation,
837 we recommend using multi-frequency electrical methods. Moreover, differentiating two
838 types of montmorillonites in the field and laboratory scale seems impossible if only us-
839 ing geo-electrical methods. However, differentiating between a montmorillonite and il-
840 lite or kaolinite seems more achievable of a task in both the field and laboratory scales.
841 If in the laboratory we run experiments in a controlled environment using relatively pure
842 clays, the application of our findings in the field will be more challenging due to a com-
843 bination of subsurface heterogeneity and greater measurement noise due to larger cou-
844 pling effects.

845 Zonge et al. (2005) mention that the differentiation of clay types in IP is possible at fre-
846 quencies above 1000 Hz. Our dataset could help establishing a basis to differentiate types
847 of clay at lower frequencies (<1000 Hz) using the widely used low frequency geo-electrical
848 methods. We understand that, just because we can see a clear difference in the resistiv-
849 ity values of our clay samples (see Table 5), this does not necessarily mean that, this dif-
850 ferentiation could be done for all field conditions. Differentiating types of clay would de-
851 pend on the clay samples themselves and the resolution of method used for the data col-
852 lection in the field. As future work, we could use our dataset as a basis for forward-modeling
853 to better understand if the differentiation of types of clay would be possible at the field
854 scale. Also more experiments at a larger laboratory scale (pluri-decimetric) to test if we
855 are able to differentiate types of clay using geo-electrical methods in a controlled envi-
856 ronment.

857 6 Conclusions

858 We present a new laboratory protocol to characterize clay samples with good re-
859 peatability, and a new SIP dataset consisting of four different types of clay (red and green
860 montmorillonite samples, an illite sample, and a kaolinite sample) at five different NaCl
861 salinities (from initially de-ionized water to 1 M NaCl). Our data shows an increase of
862 the real part of the conductivity with salinity, while there is a non-monotonous behav-
863 ior with the imaginary conductivity. A possible interpretation of this behavior could be
864 that as salinity increases, coagulation happens. At a particular salinity threshold some

865 polarization mechanisms cease to act, possibly membrane polarization effects, thus de-
866 creasing at a particular salinity the imaginary conductivity of the clay sample. There
867 is a difference in the peak of polarization between clay types, varying both with salin-
868 ity and in amplitude. Montmorillonite samples may present this polarizability peak at
869 a higher salinity than the kaolinite and illite samples. This agrees with the fact that smec-
870 tites need a higher ion concentration in the pore water to diminish membrane polariza-
871 tion effects and favour particle coagulation. We calculate the surface conductivities of
872 the clay samples for the four highest salinities and we confirm that both montmorillonite
873 samples have higher surface conductivities with respect to the kaolinite and illite sam-
874 ples and correlate well with the measured CEC. We found the linear parameter (l) be-
875 tween both surface conductivities to be 0.0039 for our dataset. A wider dataset of clayey
876 materials would seem to suggest that l decreases with clay content.

877 More work on the side of the physical modeling needs to be done in order to be able to
878 interpret our dataset by polarization mechanisms. Additionally more laboratory work,
879 at a slightly bigger scale (pluri-decimetric) or directly field scale using multi-frequency
880 geo-electrical methods could be used to validate the differentiation of clay types at big-
881 ger scales.

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