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1 **A mechanistic model for the complex conductivity of clay materials.**

2 **I. Theory**

3  
4 Philippe Leroy<sup>1,\*</sup>, Alexis Maineult<sup>2</sup>, Aida Mendieta<sup>3</sup>, Damien Jougnot<sup>4</sup>

5 <sup>1</sup> BRGM, French Geological Survey, 45060 Orléans, France.

6 <sup>2</sup> Laboratoire de Géologie, Ecole Normale Supérieure / CNRS UMR 8538, PSL Research  
7 University, 75005 Paris, France.

8 <sup>3</sup> Université de Paris, Institut de Physique du Globe de Paris, 75005 Paris, France.

9 <sup>4</sup> Sorbonne Université, CNRS, EPHE, UMR 7619 METIS, 75005 Paris, France.

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11 \*Corresponding author, p.leroy@brgm.fr

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26 **SUMMARY**

27 Clay materials are ubiquitous in the Earth's continental and oceanic crusts. They are  
28 characterized by a large specific surface area, and, in contact with water, they have  
29 remarkable adsorption, catalytic and containment properties. Clay materials also exhibit a  
30 high electrical conductivity response associated with their large surface. However,  
31 sedimentary clay minerals have a complex microstructure and electrochemistry that are not  
32 fully understood and make the quantitative petrophysical interpretation of geoelectrical  
33 measurements difficult. In this study, we have developed a new mechanistic model to better  
34 understand and predict the complex conductivity of clay materials from their microstructure  
35 and electrical double layer properties. For the conductive component, our model considers ion  
36 electromigration in bulk water, clay electrical diffuse layer, and interlayer space, if any.  
37 Concerning polarisation, it takes into account ion back-diffusion in the Stern layer and in the  
38 interlayer space, if any, and also Maxwell-Wagner effect. Water and clay surface  
39 conductivities, formation factor, cementation exponent and sample electrically connected  
40 porosity can be extracted from the comparison of the model to experimental data. This study  
41 is a step forward to better understand and quantify the complex conductivity of clays observed  
42 during electrical and electromagnetic measurements, from laboratory to geological formation  
43 scales.

44

45 **Keywords:** Electrical properties, Induced polarisation, Microstructure.

46

Symbol	Meaning	Unit
$a_i^b$	ion $i$ activity in bulk water	dimensionless
$\alpha$	empirical value to compute solid permittivity	$\text{m}^3 \text{kg}^{-1}$
$\beta_i^b$	ion mobility in bulk water due to electro-migration	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$\beta_{eo}^d$	mean ion electro-osmotic mobility in the diffuse layer	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$\beta_S$	mobility of the counter-ions in the Stern layer	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$\bar{\beta}_i^b$	ion mobility in bulk and distilled water due to electro-migration	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$B_i^d$	ion $i$ mobility in the diffuse layer with electro-osmosis	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$B_d$	mean ion mobility in the diffuse layer with electro-osmosis (thin diffuse layer assumption)	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$\widetilde{B}_d$	mean ion mobility in the diffuse layer with electro-osmosis around the aggregate (thin diffuse layer assumption)	$\text{m}^2 \text{s}^{-1} \text{V}^{-1}$
$c$	volume fraction of conductive water	dimensionless
CEC	cation exchange capacity	$\text{meq g}^{-1}$
$C_d$	differential capacitance of the diffuse layer	$\text{F m}^{-2}$
$C_i^b$	ion $i$ molar concentration	$\text{mol L}^{-1}$ (M)
$C_{salt}^b$	salt molar concentration	$\text{mol L}^{-1}$ (M)
$C_{\text{NaCl}}^0$	initial NaCl concentration in bulk water	$\text{mol L}^{-1}$ (M)
$C_{salt}^0$	initial salt concentration in bulk water	$\text{mol L}^{-1}$ (M)
$\overline{C}_i^d$	average ion concentration in the diffuse layer	$\text{mol L}^{-1}$ (M)
$\overline{C}_{i^{z_i^+}}^b$	cation concentration from dissolved minerals and montmorillonite interlayer space	$\text{mol L}^{-1}$ (M)
$\overline{C}_{j^{z_j^-}}^b$	anion concentration from dissolved minerals and montmorillonite interlayer space	$\text{mol L}^{-1}$ (M)
$\chi_d$	diffuse layer thickness	m
$\chi_D$	Debye length	m
$d$	diameter of the spherical particle	m
$d_k$	effective diameter of the $k^{\text{th}}$ aggregate	m
$d_S$	Stern layer thickness	m
$\delta_s$	clay powder mass	g
$\delta_{sc}$	main clay solid mass	g
$\delta_i^0$	sample mass before evaporation	g
$\delta_i^1$	sample mass after evaporation	g
$D_i^b$	ion $i$ self-diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
$\overline{D}_i^b$	ion $i$ self-diffusion coefficient in distilled (bulk) water	$\text{m}^2 \text{s}^{-1}$
$e$	elementary (or electron) charge	C
$e_c$	aggregate eccentricity	dimensionless
$\varepsilon$	medium permittivity	$\text{F m}^{-1}$
$\varepsilon_0$	vacuum permittivity	$\text{F m}^{-1}$
$\varepsilon_{in}$	interlayer space permittivity	$\text{F m}^{-1}$

$\varepsilon_s$	solid permittivity	F m <sup>-1</sup>
$\varepsilon_w$	liquid water permittivity	F m <sup>-1</sup>
$\frac{\varepsilon_w}{\varepsilon_w}$	average permittivity of the diffuse layer and interlayer space	F m <sup>-1</sup>
<b>E</b>	applied electrical field	V m <sup>-1</sup>
<b>E<sub>0</sub></b>	initial applied electrical field	V m <sup>-1</sup>
$f(d_k)$	aggregate size distribution of the $k^{\text{th}}$ aggregate	dimensionless
$f_Q$	fraction of the counter-charge in the Stern layer	dimensionless
$k_B$	Boltzmann's constant	J K <sup>-1</sup>
$K_w$	dissociation constant of water molecules	dimensionless
$\phi$	mud porosity	dimensionless
$\phi_a$	aggregate porosity	dimensionless
$\eta_w$	liquid water dynamic viscosity	Pa s
$h_k$	height of the $k^{\text{th}}$ aggregate	m
<b>H</b>	magnetic field strength	A m <sup>-1</sup>
$i$	imaginary number	dimensionless
$I$	ionic strength	mol L <sup>-1</sup> (M)
$\kappa$	inverse of the Debye length	m <sup>-1</sup>
$\varphi$	electrical potential in the diffuse layer	V
$\varphi_d$	electrical potential at the $d$ -plane	V
$\varphi_m$	average electrical potential in the diffuse layer	V
<b>J<sub>C</sub></b>	conduction current density	A m <sup>-2</sup>
<b>J<sub>D</sub></b>	displacement current density	A m <sup>-2</sup>
pH	potential of hydrogen ion in bulk water	dimensionless
$q$	mean charge of the counter-ions in the Stern layer	C
$q_i$	ion $i$ charge	C
$Q_0$	mineral surface charge density	C m <sup>-2</sup>
$Q_0^e$	edge surface mineral surface charge density	C m <sup>-2</sup>
$Q_0^b$	basal surface mineral surface charge density	C m <sup>-2</sup>
$Q_\beta$	Stern layer surface charge density	C m <sup>-2</sup>
$Q_d$	diffuse layer surface charge density	C m <sup>-2</sup>
$Q_{EDL}$	electrical double layer surface charge density	C m <sup>-2</sup>
$Q_V$	aggregate excess of charge per unit pore volume	C m <sup>-3</sup>
$Q_V^0$	excess of charge per unit Stern and diffuse layer volumes	C m <sup>-3</sup>
$Q_V^d$	excess of charge per unit diffuse layer volume	C m <sup>-3</sup>
$Q_V^{in}$	excess of charge per unit interlayer space volume	C m <sup>-3</sup>
$\Theta_w^d$	water volume fraction of the diffuse layer	dimensionless
$L$	depolarisation coefficient	dimensionless
$m$	cementation exponent of the clay aggregate	dimensionless
$m_i^d$	electro-osmotic effect on diffuse layer conductivity	dimensionless
$mr_s$	ion mobility ratio between in the Stern layer and distilled water	dimensionless

$M$	effect of the diffuse layer on Stern layer polarization	dimensionless
$n_c$	number of stacked sheets per particle	dimensionless
$N$	number of ion species in bulk and diffuse layer waters	dimensionless
$N_A$	Avogadro's number	mol <sup>-1</sup>
$N_{d_k}$	Number of different sized aggregates	dimensionless
$N_s$	number of solid inclusions in the modelling	dimensionless
$\nu$	empirical coefficient for temperature dependence of ion mobility	K <sup>-1</sup>
$pK_w$	minus log of dissociation constant of water molecules	dimensionless
$\rho_s$	solid volumetric mass density	kg m <sup>-3</sup>
$\sigma^{(1)}$	medium electrical conductivity	S m <sup>-1</sup>
$\sigma_0^{(1)}$	medium bulk conductivity (excluding polarisation effect)	S m <sup>-1</sup>
$\sigma_s^{(1)}$	"surface" conductivity due to Stern layer polarisation	S m <sup>-1</sup>
$\sigma_w^{(1)}$	water conductivity	S m <sup>-1</sup>
$\sigma_w^{b(1)}$	bulk water conductivity	S m <sup>-1</sup>
$\sigma_w^{d(1)}$	diffuse layer water conductivity	S m <sup>-1</sup>
$S_{in}$	surface area of the interlayer space	m <sup>2</sup>
$S_o$	outer surface area of the clay particle	m <sup>2</sup>
$SS$	total specific surface area of the clay particle	m <sup>2</sup> g <sup>-1</sup>
$SS_e$	specific surface area of the edge surface	m <sup>2</sup> g <sup>-1</sup>
$SS_b$	specific surface area of the basal surface	m <sup>2</sup> g <sup>-1</sup>
$SS_o$	total outer specific surface area of the clay particle	m <sup>2</sup> g <sup>-1</sup>
$\Sigma_s^d$	Surface conductivity of the diffuse layer	S
$\Sigma_S$	Surface conductivity of the Stern layer	S
$t$	time	s
$t_{in}$	interlayer thickness	m
$\tau$	relaxation time of the spherical particle	s
$\tau_k$	relaxation time of the $k^{\text{th}}$ sized aggregate	s
$T$	absolute temperature	K
$T_C$	temperature in degree Celsius	°C
$g$	surface area weighting coefficient	dimensionless
$V_{in}$	interlayer space volume	m <sup>3</sup>
$V_s$	solid volume	m <sup>3</sup>
$V_{sc}$	solid clay layer volume	m <sup>3</sup>
$V_{so}$	weakly conductive other solid volume	m <sup>3</sup>
$V_S$	Stern layer volume	m <sup>3</sup>
$V_t$	sample volume	cm <sup>3</sup>
$V_w^d$	volume of diffuse layer water	m <sup>3</sup>
$V_w^b$	volume of bulk water	m <sup>3</sup>
$\omega$	angular frequency of the applied electrical current	rad s <sup>-1</sup>

$\Omega_s$	solid content in the sample	dimensionless
$x$	distance from the $d$ -plane	m
$\xi_c$	solid volume fraction of the main clay mineral	dimensionless
$z$	mean valence of the counter-ions	dimensionless
$z_i$	ion $i$ valence	dimensionless

48 <sup>(1)</sup> Followed by “\*” means including displacement current.

49

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## 50 1 INTRODUCTION

51 Clay minerals or clays are fine-grained materials (particle size below 2  $\mu\text{m}$ ) that are very  
52 common in geologic deposits, terrestrial weathering environments (e.g., regolith), and marine  
53 sediments (Sposito 1989). They have a high specific surface area (SSA), the highest known  
54 among major natural minerals (Leroy & Revil 2009). For instance, one gram of  
55 montmorillonite (Mt), which belongs to the smectite group, can cover a surface of roughly  
56 800  $\text{m}^2$  (Tournassat & Appelo 2011). Unlike other high-SSA natural minerals such as zeolites  
57 and manganese and iron (hydr)oxides, clay minerals are frequently the main components of  
58 soils and extended sedimentary stratigraphic layers, making around 40% of the minerals in  
59 sedimentary rocks (Schroeder 2018).

60 Unique properties of clays are due to their microstructure – among them high adsorption  
61 capability, swelling, catalysis, plasticity when wet, and very low permeability (Grim 1962).  
62 These minerals are hydrous layer aluminosilicates, which form a diverse group constituting  
63 the greater part of the phyllosilicate family of minerals. Clays are mostly made of aluminum,  
64 silicon, and oxygen atoms interacting with water molecules on the mineral surface, sometimes  
65 with variable amounts of iron, alkali metals (e.g.,  $\text{Na}^+$  or  $\text{K}^+$ ), and alkaline earth metals (e.g.,  
66  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ) (Tournassat *et al.* 2015). They have a layered structure containing an  
67 octahedral (O) alumina sheet sandwiched between two tetrahedral (T) silica sheets (case of Mt  
68 and illite) or a tetrahedral silica and octahedral alumina sheet (case of kaolinite) that are  
69 stacked to form a particle (Leroy & Revil 2004).

70 Clay minerals have remarkable adsorption properties reflected by their high cation exchange  
71 capacities (CEC), typically between 0.1 and 1.5  $\text{meq g}^{-1}$  for, in ascending order, chlorite,  
72 kaolinite, illite and Mt (Revil & Leroy 2004). Isomorphic substitutions in the crystal are, e.g.,  
73 the replacement of  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  ions in octahedral sheets or  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  ions



74 in tetrahedral sheets with most of the substitutions occurring in the octahedral sheets for illite  
75 and Mt (Leroy *et al.* 2017b). Isomorphic substitutions are responsible for a high permanent  
76 negative surface charge mostly expressed on the basal clay surfaces (Bourg & Sposito 2011).  
77 This surface charge, conjointly with the high specific surface area of illite (typically 100-200  
78  $\text{m}^2 \text{g}^{-1}$  compared to a kaolinite SSA of typically 10-20  $\text{m}^2 \text{g}^{-1}$ ) and Mt (typically 700-800  $\text{m}^2 \text{g}^{-1}$ )  
79 <sup>1</sup>) (Revil & Leroy 2004), are at the origin of the high measured CEC of illite (~0.2-0.3 meq  $\text{g}^{-1}$ )  
80 <sup>1</sup>) and Mt (~0.7-1.5 meq  $\text{g}^{-1}$ ) (Revil & Leroy 2004; Tournassat *et al.* 2015). Clays such as Mt  
81 also have swelling properties due to the presence of hydrated cations such as  $\text{Na}^+$  ions  
82 adsorbed in the interlayer space between TOT layers (Massat *et al.* 2016) and catalytic  
83 properties because of their high reactive specific surface area (Ismadji *et al.* 2015). Clay  
84 minerals also have rheological properties and develop plasticity when wet because of a  
85 molecular film of water surrounding clay particles, but become hard, brittle and non-plastic  
86 upon drying or firing (Guggenheim & Martin 1995).

87 Clays play a major role in the terrestrial biogeochemical cycling of metal cations (e.g.,  $\text{K}^+$  or  
88  $\text{Ca}^{2+}$ ) and in the chemical homeostasis of the oceans (Sposito *et al.* 1999) because they are  
89 abundant in Earth's soil and subsurface and of their high chemical reactivity (regarding, e.g.,  
90 adsorption and catalysis) (Sposito *et al.* 1999). These minerals also provide an efficient  
91 confinement environment for biomolecules and might have enhanced biochemical reactions to  
92 develop life during early life evolution on Earth (Yang *et al.* 2013) and possibly on Mars  
93 (Azua-Bustos *et al.* 2020). Due to clay rheological properties, shale beds (sedimentary rocks  
94 composed of very fine clay particles) have preserved a remarkable range of fossils, e.g., hard  
95 body parts, soft tissues, feathers, prints, and burrows (Petraglia *et al.* 2014). Therefore these  
96 clayey rocks provide records of Earth's evolutionary history and inspired Charles Darwin for  
97 his theory of evolution (Charlet *et al.* 2017). Clay minerals also provide indicators of the

98 evolution of aqueous conditions and possible habitats for life on ancient Mars (Bristow *et al.*  
99 2018).

100 In addition, clays are used in a broad range of engineering processes, for instance as  
101 lubricants in oil industry (Udonne 2011), industrial catalysts for the synthesis of organic  
102 compounds (Nagendrappa 2011), and for pharmaceutical drug delivery (Viseras *et al.* 2010).  
103 Since the Neolithic period, clay minerals have also been employed for pottery (Vandiver *et al.*  
104 1989). Special attention is currently devoted to the pharmacological functions of clays and  
105 their biomedical applications in pelotherapy, wound healing, regenerative medicine,  
106 antimicrobial, and dermocosmetics (Viseras *et al.* 2019). Natural and synthetic clays are also  
107 used as semi-permeable membrane barriers adsorbing metallic pollutants (Gehin *et al.* 2007),  
108 salt ions (water desalinisation (Ali *et al.* 2021)) and organic pollutants (Kausar *et al.* 2018) to  
109 improve the quality of water resources. They are also used as containers in landfills because  
110 of their confining properties towards industrial and domestic wastes (Malusis *et al.* 2003).

111 Clay-rich (argillaceous) rocks, including marls, shale, mudstone, argillite and claystone  
112 (herein referred to as clay rocks), are sedimentary formations with a very low permeability  
113 (typically between  $10^{-23}$  and  $10^{-17}$  m<sup>2</sup>, see Neuzil 1994). The low permeability of clay rocks is  
114 a consequence of consolidated fine-grained sediments containing a large fraction of nanopores  
115 (Yven *et al.* 2007) with a loss of pore connectivity during diagenetic or metamorphic rock  
116 reactions (Charlet *et al.* 2017). Because of their confining properties, clay geological  
117 formations act as cap rocks above oil and gas (“carbonated” energies) (Li *et al.* 2006) and  
118 geothermal energy (“decarbonated” energy) (Guisseau *et al.* 2007) reservoirs. They are also  
119 frequently used for the geological storage of H<sub>2</sub> (energy “vector”) (Liu *et al.* 2022), CO<sub>2</sub>  
120 (Busch *et al.* 2016) and high-level nuclear waste (Sellin & Leupin 2013). Smectite minerals  
121 can adsorb and store CO<sub>2</sub> in their interlayer space to mitigate greenhouse gas emissions (Bø  
122 Hunvik *et al.* 2021). The swelling of smectite minerals in contact with an aqueous solution

123 can also produce strong adverse effects in the extraction of oil and gas (Karaborni *et al.* 1996)  
124 and of “green” geothermal energy (Xu *et al.* 2006), and is of major concern in civil  
125 engineering due to quick clay landslides (Khalidoun *et al.* 2009).

126 When clay mineral is in contact with water, an electrical double layer (EDL) lies on the  
127 mineral outer surface to compensate the usual negative surface charge not compensated by  
128 interlayer cations (Bourg *et al.* 2007). Some clays like kaolinite can have a positive surface  
129 charge in acidic conditions because of the adsorption of protons on surface oxygen (Tombacz  
130 & Szekeres 2006). The clay EDL is made of a “compact” Stern layer with a solid-like  
131 viscosity and containing mostly counter-ions and of a diffuse layer with a liquid-like viscosity  
132 and containing an excess of counter-ions and a deficiency of co-ions (Leroy & Revil 2004).  
133 The EDL controls the distribution and displacement of electrical charges on the surface of  
134 clays because of the high surface charge magnitude and specific surface area of clays  
135 (Tournassat & Steefel 2019). Therefore, clay EDL has a strong influence on clay electrical  
136 conductivity (Waxman & Smits 1968).

137 In geophysics, electrical and electromagnetic methods are very sensitive to electrical charge  
138 transport in clay materials, especially in the EDL at the interface between solid clay and bulk  
139 pore water (e.g., Revil & Leroy 2001; Jougnot *et al.* 2010a; Qi & Wu 2022). Any perturbation  
140 of chemical, electrical, hydrostatic and thermal nature in a geological system containing a  
141 significant fraction of clays should be theoretically captured by these methods (Revil & Leroy  
142 2004; Revil *et al.* 2005; Revil & Linde 2006). Notably, the electrical current injected into the  
143 ground containing clay materials moves the electrical charges in the pore water, especially  
144 those in the diffuse part of the clay EDL and in the stagnant part of the clay EDL (Stern  
145 layer), which in turn influence ground electrical conductivity (ability of the medium to carry  
146 electric current) (e.g., Revil 2012; Okay *et al.* 2014; Qi & Wu 2024). In the laboratory, a  
147 tension typically  $\pm 5V$  and a resulting weak electrical current typically in the mA range is

148 injected when investigating pluricentimetric samples (Zimmermann *et al.* 2008). In the field,  
149 considerably higher voltages and currents are typically injected into the ground depending on  
150 the depth of the investigation (Kemna *et al.* 2012). The measured electrical and magnetic  
151 fields and related conductivities and susceptibilities can thus be used to estimate the  
152 petrophysical, state and transport properties of clay materials in geological formations  
153 (Triantafilis & Lesch 2005; Glaser *et al.* 2023; Porté *et al.* 2023).

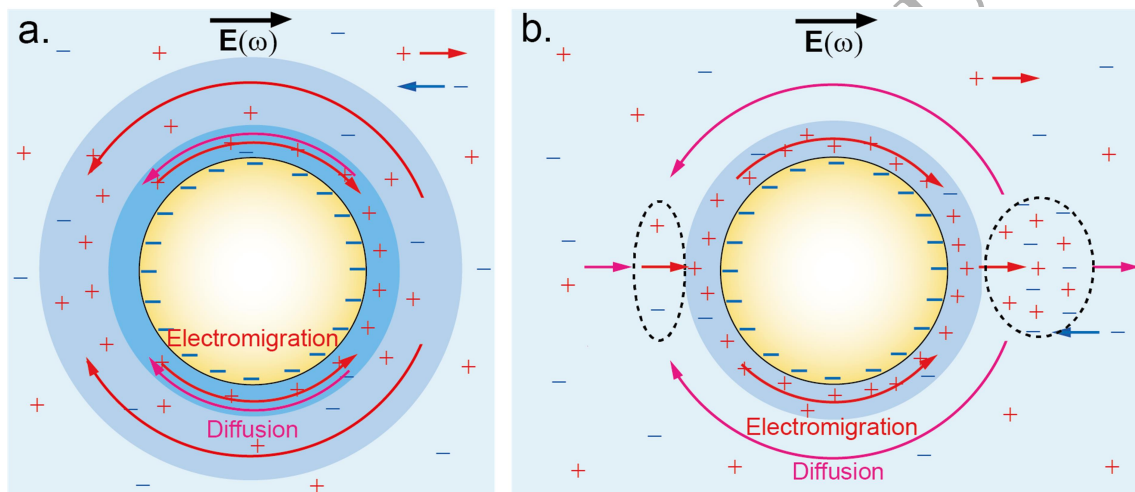
154 A main inherent drawback of the conventional direct current (DC) resistivity survey is its  
155 ambiguity in distinguishing between the effects of groundwater salinity, clay content, and  
156 pore space geometry (Binley & Kemna 2005; Binley & Slater 2020). Among the electrical  
157 and electromagnetic methods, one named “induced polarisation” (IP) is of particular interest  
158 for geophysicists due to its increasing sensitivity to subsurface processes over the last 20  
159 years (Kemna *et al.* 2012; Binley *et al.* 2015). The induced polarisation method is related to  
160 the reversible “storage” of electrical charges in porous media (Revil & Skold 2011). It was  
161 discovered more than 100 years ago by Conrad Schlumberger (as far as we know). After  
162 cutting the electrical current injected into the ground containing sulphide ores, Schlumberger  
163 observed that the related voltage did not disappear immediately and instead decreased slowly  
164 with time (Schlumberger 1920). Integrating the measured voltage in excess over the time after  
165 switching off the current allows estimating the chargeability of the investigated porous  
166 medium (Pelton *et al.* 1978). In the case of clay materials, the chargeability is sensitive to the  
167 excess of electrical conductivity in the clay EDL compared to in bulk water, which is  
168 responsible for clay “surface” conductivity controlled by clay microstructural and  
169 electrochemical properties (Leroy & Revil 2009; Leroy *et al.* 2017b; Revil *et al.* 2023). The  
170 IP method gives therefore access not only to the DC (“zero frequency”) conductivity or  
171 resistivity but it also gives access to the chargeability of the investigated clayey medium  
172 (Revil & Florsch 2010; Revil 2012; Qi & Wu 2024). These physical quantities, due to their

173 dependence on clay pore water and surface conductivity, can deliver important information on  
174 the petrophysical properties of clay materials. These properties are, for instance, mineralogy,  
175 pore structure, water and clay contents, and transport properties including ion diffusivity and  
176 rock permeability (Jougnot et al. 2009, 2010b; Revil & Florsch 2010; El Alam et al. 2023;  
177 Revil et al. 2023).

178 The spectral induced polarisation (SIP) method belongs to the broader family of IP methods.  
179 Rather than switching off and on the injected current, a sinusoidal, low-frequency (typically  
180 in the mHz to kHz frequency range) electrical current is injected into the ground and the  
181 resulting voltage is measured (Marshall & Madden 1959). There are different ways of doing  
182 TDIP and SIP measurements in the laboratory and in the field. In the case of the Wenner  
183 alpha configuration, two current electrodes are used to inject the current and two potential  
184 electrodes located between the current electrodes and at equal separation distance are used to  
185 measure the resulting voltage in the investigated porous medium (e.g., Martin *et al.* 2020).  
186 Other frequently employed configurations are dipole-dipole, pole-dipole or Wenner-  
187 Schlumberger ones (Aizebeokhai & Oyeyemi, 2014).

188 During SIP measurements on clay materials, the magnitude of the measured voltage depends  
189 on ion fluxes induced by the imposed electrical field in the pore water especially on those in  
190 the clay diffuse layer and in the clay Stern layer (ion electromigration processes) (e.g., Leroy  
191 & Revil 2009; Okay *et al.* 2014). The measured phase-shift between injected current and  
192 measured voltage depends on ion counteracting diffusion fluxes to reestablish their  
193 distribution at thermodynamic equilibrium (Fig. 1) (e.g., Lyklema *et al.* 1983; Grosse &  
194 Delgado 2010). Indeed, when the frequency of the injected sinusoidal current is sufficiently  
195 low (typically below 1 kHz), the EDL polarizes (i.e. counter-ions in the EDL have time to  
196 electromigrate tangentially to the particle surface) to accumulate on one side of the particle,  
197 and to diffuse back to their initial position (Fig. 1a, Schwarz 1962). These ion movements,

198 which can be characterized by a relaxation time, thus create a complex surface conductivity  
 199 increasing the electrical conductivity of the medium (e.g., Leroy *et al.* 2008; Leroy *et al.*  
 200 2017a). When the frequency of the injected sinusoidal current is higher (typically above 1  
 201 kHz), there is a charge build-up at the boundary between two phases presenting different  
 202 conductivities and permittivities, like solid clay and water, responsible for another  
 203 polarisation mechanism, Maxwell-Wagner polarisation, and increasing the electrical  
 204 conductivity of the medium (de Lima & Sharma 1992). Nanoporous clay materials are  
 205 characterized by a broad distribution of relaxation times due to Stern layer polarisation  
 206 influencing in particular medium and high-frequency SIP measurements (Leroy & Revil  
 207 2009).



208

209 **Figure 1.** Sketch of EDL polarisation at low frequencies of the injected current for a  
 210 negatively charged particle. Model of Lyklema *et al.* (1983) (generalized Schwarz model)  
 211 showing the capacitive effect of the polarized thin layer usually assumed to be the Stern layer  
 212 (surface diffusion processes) (a., modified from Leroy *et al.* 2017b). Model of Grosse &  
 213 Delgado (2010) showing the formation of ion clouds in excess and deficiency outside the  
 214 EDL compared to in the surrounding electrolyte due to EDL (here diffuse layer) polarisation  
 215 (concentration polarisation, volume diffusion processes) (b., modified from Grosse &  
 216 Delgado 2010).

217 Petrophysical models have been developed to understand quantitatively SIP laboratory and  
 218 field IP measurements on clayey media. For instance, Vinegar & Waxman (1984) developed a

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219 petrophysical SIP model for shaly sands based on an equivalent circuit model. Following  
220 Waxman & Smits (1968), their model assumes that the measured real part of the complex  
221 conductivity, the measured in-phase conductivity, can be understood quantitatively  
222 considering two conductances in parallel, one associated with electromigrating ions in the  
223 bulk pore water and one associated with electromigrating cation counter-ions on the clay  
224 surface. Following the membrane polarisation model of Marshall & Madden (1959), they  
225 considered in addition two conductances in series, one related to clay counter-ion  
226 displacement in clay-free zones and one related to electrolyte blockage by the clay-site  
227 membranes, to explain imaginary, quadrature conductivity measurements on shaly sands  
228 between 1 Hz and 1 kHz. In the model of Vinegar & Waxman 1984, the in-phase and  
229 quadrature (or out-of-phase) conductivities depend on  $Q_v$ , which is the excess of counter-  
230 charge (canceling clay surface charge) per unit pore volume and is calculated from the  
231 measured porosity and clay cation exchange capacity. The SIP model of Vinegar & Waxman  
232 (1984) is elegant and easy to use but its main drawback is, in our opinion, its establishment at  
233 the macroscale of the centimetric sample that does not allow it to explicitly consider clay  
234 microstructure and EDL properties. de Lima & Sharma (1992) developed mechanistic SIP  
235 models for clay materials considering explicitly Stern layer (Schwarz 1962) or diffuse layer  
236 (Fixman 1980) polarisation and Maxwell-Wagner polarisation (Sen *et al.* 1981). The SIP  
237 model of de Lima & Sharma 1992 is more physical and more difficult to handle than the SIP  
238 model of Vinegar & Waxman (1984). In our opinion its main drawback is its inability to  
239 capture clay microstructure with very elongated interacting clay particles on the contrary to  
240 the spherical clay particle considered in the model of de Lima & Sharma (1992). Most of the  
241 following SIP models for clay materials were inspired by the works of Vinegar & Waxman  
242 (1984) and de Lima & Sharma (1992) (e.g., Leroy & Revil 2009; Jougnot *et al.* 2010a; Revil  
243 2012; Okay *et al.* 2014; Weller *et al.* 2015; Leroy *et al.* 2017b; Revil *et al.* 2023; Qi & Wu

244 2024). For instance, Leroy *et al.* (2017b) considered a Stern layer polarisation model for  
245 dispersed clay particles interacting with each other and forming aggregate. However, they did  
246 not consider Maxwell-Wagner polarisation. In addition, the role of the interlayer space of Na-  
247 montmorillonite (Na-Mt) containing hydrated and mobile Na<sup>+</sup> cations (Bourg *et al.* 2003) on  
248 clay conduction and polarisation during SIP measurement was not investigated in the  
249 previously reported works. In our knowledge, most of the current SIP models are not  
250 considering explicitly clay microstructure and EDL properties. The microstructural and  
251 electrical properties of the different components of the clay material, e.g., bulk pore water,  
252 diffuse layer, Stern layer, and interlayer space, are not clearly described.

253 In this study, we propose a new mechanistic model to interpret SIP measurements on  
254 unconsolidated clay materials (e.g., muds) as a function of salinity and temperature from clay  
255 microstructural and EDL properties. Our model is an extension of the SIP model of Leroy *et al.*  
256 *et al.* (2017b). It considers bulk pore water and diffuse layer conductivities as well as Stern layer  
257 and Maxwell-Wagner polarisations including the contribution of the interlayer space of Na-  
258 Mt, which both were neglected in Leroy *et al.* (2017b) due to the low concentration of clay  
259 particles in the suspension (less than 60 g of clay powder per liter of electrolyte). Porosity,  
260 cementation exponent, electrical formation factor, surface conductivity and water conductivity  
261 can be extracted from our model compared to experimental data in order to better understand  
262 the electrical properties of clay materials and to test the assumptions of SIP petrophysical  
263 models developed at larger scale (e.g., Weller *et al.* 2013). Section 2 of our manuscript  
264 explains the microstructural and electrochemical properties of the main clay minerals, i.e.  
265 kaolinite, illite and montmorillonite clays. Section 3 presents the theory of our mechanistic  
266 SIP model that is compared to the experimental data of Mendieta *et al.* (2021) in the  
267 companion paper by Mainault *et al.* (2024).

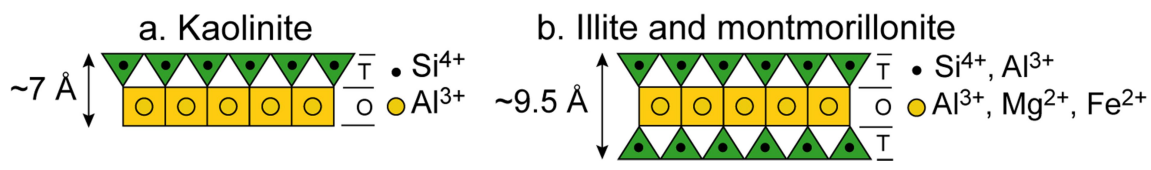


## 269 2 CHARACTERISTICS OF KAOLINITE, ILLITE AND MT PARTICLES

### 270 2.1. Microstructural properties

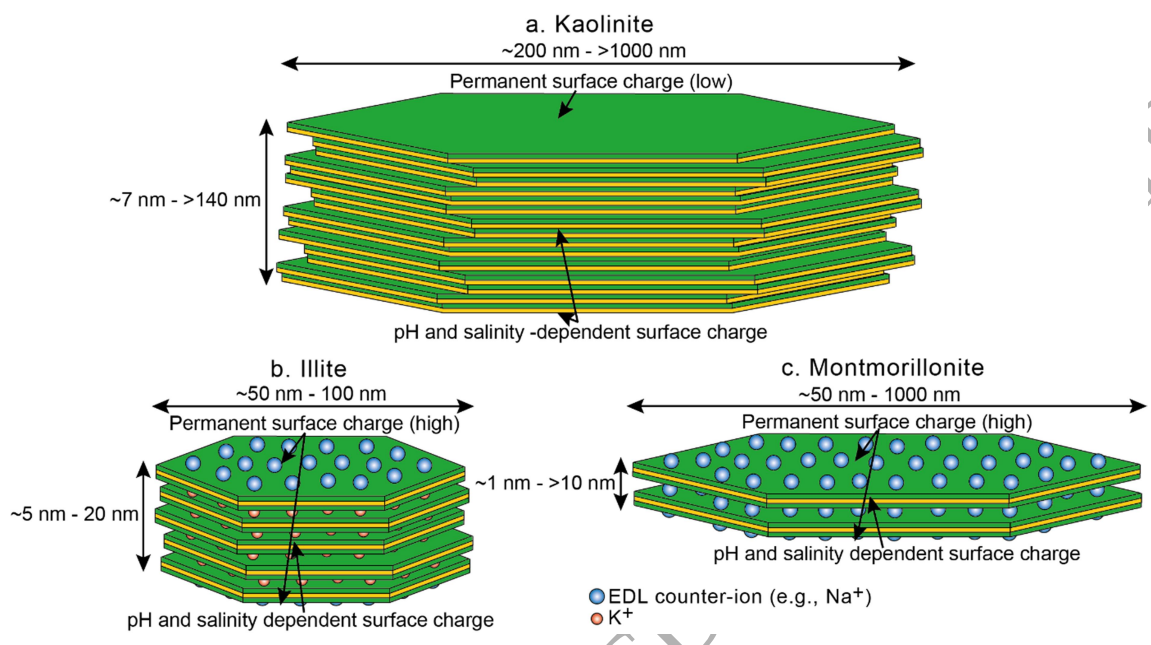
271 Clay minerals are characterized by a wide variety of mineralogies, sizes and shapes, and  
272 heterogeneities in their surface properties (the edge surfaces behave differently than the basal  
273 surfaces) (Tombacz & Szekeres 2006; Brigatti *et al.* 2013). Clay particles (or tactoids) are a  
274 stack of platelets that are very elongated (Tournassat *et al.* 2015). These particles have  
275 therefore a high aspect ratio with a thickness considerably smaller than length for illite and Mt  
276 particles. Typical dimensions of clay platelets and particles are indicated in the following text.

277 The chemical formula of kaolinite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  (Grim 1962). A kaolinite particle is a  
278 stack of several silica tetrahedral (T) and alumina octahedral (O) sheets linked by hydrogen  
279 bonds (1:1 clay). The thickness of a TO sheet is  $\sim 7 \text{ \AA}$  (Fig. 2a) and its length is typically  
280 between 200 and more than 1000 nm (Fig. 3a) (Tournassat *et al.* 2015). The specific surface  
281 areas (SSA) of the TO platelets (or layers) can be estimated from crystallography (Leroy &  
282 Revil 2004). Indeed, a square TO platelet with a thickness of  $7.2 \text{ \AA}$ , a length of 500 nm and a  
283 solid volumetric density of  $2.62 \text{ g cm}^{-3}$  (Hassan *et al.* 2006) has a total specific surface area of  
284 about  $1063 \text{ m}^2 \text{ g}^{-1}$  from which the edge surface share is about  $3 \text{ m}^2 \text{ g}^{-1}$  and the basal surface  
285 share is about  $1060 \text{ m}^2 \text{ g}^{-1}$ . According to the previous calculation and Hassan *et al.* 2006 and  
286 Tournassat *et al.* 2015, the edge specific surface area of a TO platelet is about  $2\text{-}7 \text{ m}^2 \text{ g}^{-1}$  and  
287 the basal specific surface area of a TO platelet is about  $1060\text{-}1070 \text{ m}^2 \text{ g}^{-1}$ . The edge SSA of  
288 individual TO layers is therefore roughly 150 to 500 times lower than their basal SSA. In  
289 addition, a kaolinite particle is considerably thicker and larger in average than an illite and Mt  
290 particle (Fig. 3). Kaolinite particle thickness is typically from less than 7 nm to more than 140  
291 nm (Tournassat *et al.* 2015). The number of stacked TO layers of a kaolinite particle can  
292 therefore range from 10 to more than 200.



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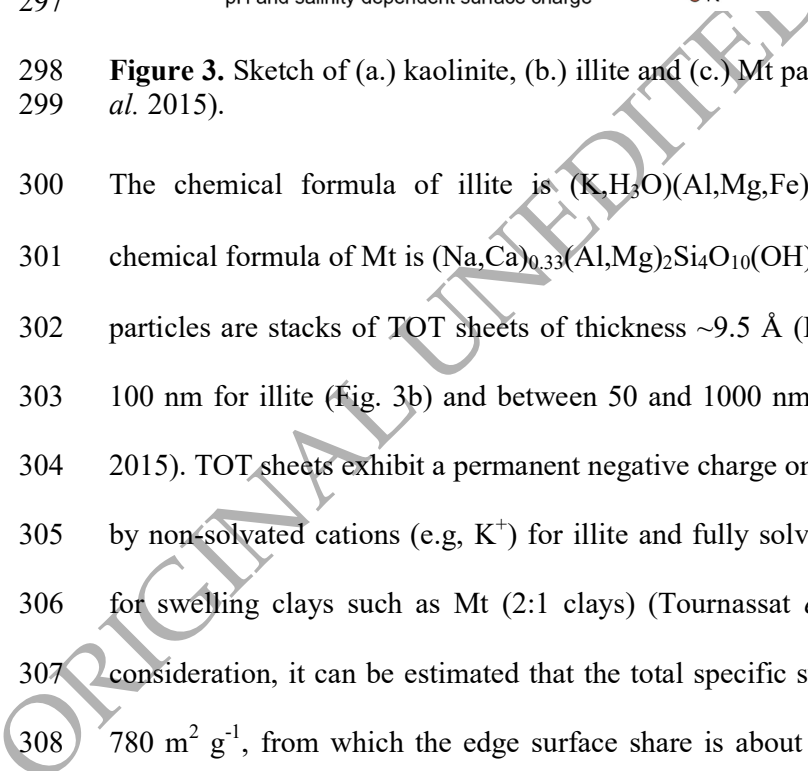
**Figure 2.** Sketch of (a.) kaolinite, and (b.) illite and Mt platelets (modified from Leroy & Revil 2009).



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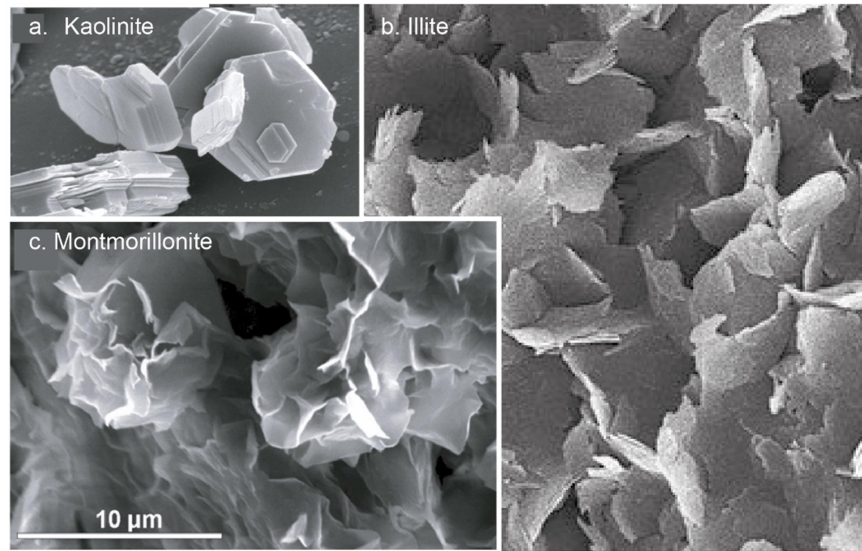
**Figure 3.** Sketch of (a.) kaolinite, (b.) illite and (c.) Mt particles (modified from Tournassat *et al.* 2015).

300 The chemical formula of illite is  $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$  and the  
 301 chemical formula of Mt is  $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$  (Grim 1962). Illite and Mt  
 302 particles are stacks of TOT sheets of thickness  $\sim 9.5 \text{ \AA}$  (Fig. 2b) and length between 50 and  
 303 100 nm for illite (Fig. 3b) and between 50 and 1000 nm for Mt (Fig. 3c) (Tournassat *et al.*  
 304 2015). TOT sheets exhibit a permanent negative charge on their basal surfaces and are bonded  
 305 by non-solvated cations (e.g.  $K^+$ ) for illite and fully solvated cations (e.g.,  $Na^+$  and/or  $Ca^{2+}$ )  
 306 for swelling clays such as Mt (2:1 clays) (Tournassat *et al.* 2015). From crystallographic  
 307 consideration, it can be estimated that the total specific surface area of a TOT layer is about  
 308  $780 \text{ m}^2 \text{ g}^{-1}$ , from which the edge surface share is about  $10\text{-}30 \text{ m}^2 \text{ g}^{-1}$  and the basal surface



309 share is about  $750\text{-}770\text{ m}^2\text{ g}^{-1}$  (Leroy *et al.* 2015). The edge SSA of individual TOT layers is  
310 therefore roughly 20 to 80 times lower than their basal SSA. The SSA of clay layers are thus  
311 dominated by the contribution of the basal surfaces, as the edge SSA represents only a minor  
312 part of the total SSA. Furthermore, illite particle thicknesses are typically from 5 nm to 20 nm  
313 and Mt particle thicknesses are typically from 1 nm to above 10 nm (Tournassat *et al.* 2015).  
314 Therefore, Mt particles are more elongated than illite particles. Illite particles typically consist  
315 of 5 to 20 stacked TOT layers. The TOT layers of Mt particles can become completely  
316 delaminated. The number of TOT layers per Mt particle rarely exceeds 10 in water  
317 (Tournassat & Appelo 2011). The number of TOT layers per Mt particle increases with  
318 decreasing water chemical potential and also tends to increase with the valence of the counter-  
319 ion in the interlayer space (Tournassat *et al.* 2015). According to viscosity and light-  
320 transmission experiments, Na-Mt dispersions in pure water contain particles made up of 1-2  
321 TOT layers, whereas Ca-Mt or Mg-Mt dispersions in pure water contain particles made up of  
322 6-10 TOT layers (Schramm & Kwak 1982).

323 The total SSA of a kaolinite particle, typically  $10\text{-}20\text{ m}^2\text{ g}^{-1}$  (where the edge surface shares  
324 around 15% of it, around  $1.5\text{-}3\text{ m}^2\text{ g}^{-1}$  (Hassan *et al.* 2006)), is considerably smaller than the  
325 total SSA of an illite or Mt particle, which is typically between 100 and  $200\text{ m}^2\text{ g}^{-1}$  for illite  
326 and between  $750\text{ and }800\text{ m}^2\text{ g}^{-1}$  for Na-Mt (Revil & Leroy 2004; Hassan *et al.* 2006;  
327 Tournassat & Appelo 2011; Tournassat *et al.* 2015). Due to the irregular morphology of clay  
328 mineral layers, the edge surfaces of different layers in a single particle may be misaligned.  
329 Moreover, translational and rotational disorder between adjacent layers makes the structure  
330 turbostratic at the scale of individual clay mineral particles. Clay minerals have different  
331 morphologies: kaolinite and well-crystallized illite have a tendency toward hexagonal and  
332 elongated hexagonal morphologies, respectively, whereas Mt and less well-crystallized illite  
333 have mostly irregular platy or lath-shaped morphologies (Fig. 4).



334

335 **Figure 4.** Scanning electron microscopy (SEM) images of dried kaolinite (a., modified from  
 336 Christidis 2010), illite (b., modified from Mc Bride 2012), and Mt (c., modified from  
 337 Christidis 2010) particles. All images are at the same scale.

338

## 339 2.2. Electrochemical properties

340 The different faces of clay particles exhibit different electrochemical properties (Tombacz &  
 341 Szekeres 2006; Bourg *et al.* 2007; Tournassat *et al.* 2016a). The electrochemical properties of  
 342 kaolinite particles are mainly controlled by the edge surfaces and the alumina basal surfaces  
 343 due to the weak negative structural charge on the silica basal surfaces (Tombacz & Szekeres  
 344 2006) (Fig. 3a). The electrochemical properties of Mt particles and in lesser extent of illite  
 345 particles are mainly controlled by the basal surfaces due to their larger specific surface area  
 346 than the edge surfaces and to the structural charge (Tombacz & Szekeres 2004; Leroy & Revil  
 347 2009; Tournassat *et al.* 2011; Tournassat *et al.* 2013) (Figs 3b and 3c). In the following, we  
 348 define  $Q_0$  as the surface charge density of the clay mineral (in  $C m^{-2}$ ),  $Q_0^b$  as the basal surface  
 349 charge density,  $Q_0^e$  as the edge surface charge density,  $Q_i$  as the negative and permanent  
 350 structural surface charge density due to isomorphic substitutions, and  $Q_{EDL}$  as the surface  
 351 charge density of the EDL.

352 The quantity  $Q_0$  is an accurate indicator of the EDL properties controlling the IP response  
 353 because of the electroneutrality condition (Hunter 1981) implying

$$Q_0 + Q_{EDL} = 0, \quad (1)$$

354 and then

$$Q_{EDL} = -Q_0. \quad (2)$$

355 Therefore, according to Eq. 2, a high clay surface charge density magnitude implies a high  
 356 EDL surface charge density magnitude and potentially a high IP real conductivity response  
 357 (due to EDL conduction) and a high IP imaginary conductivity response (due to EDL  
 358 polarisation) (Leroy & Revil 2009). The quantity  $Q_0$  depends on the contributions of the edge  
 359 and basal surfaces considering

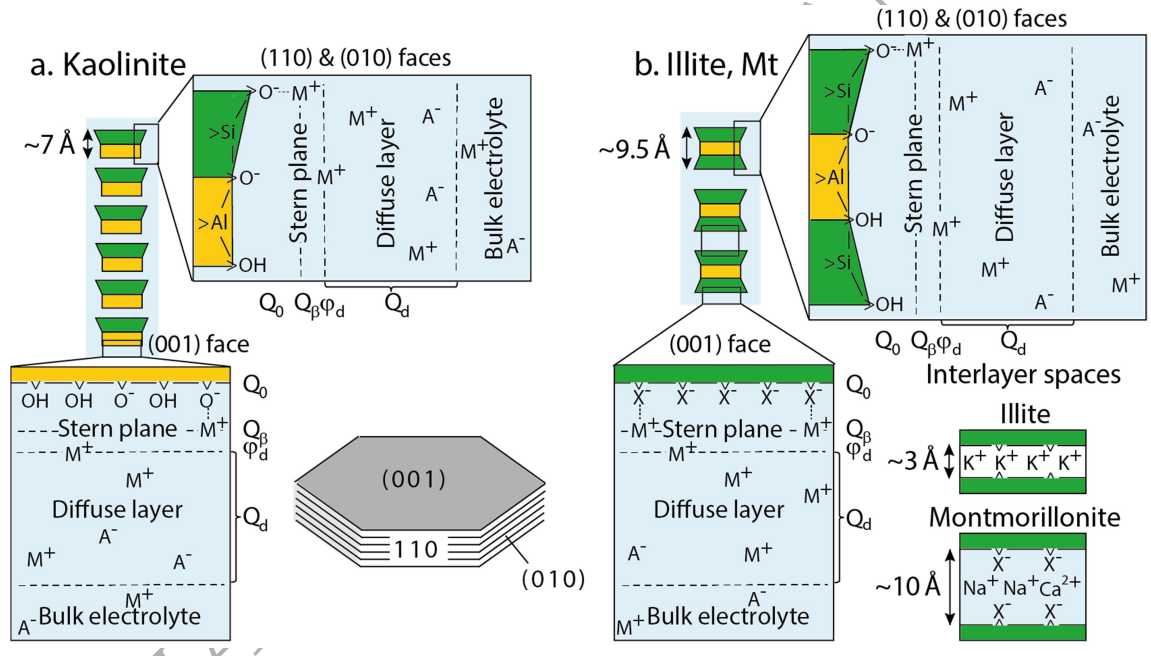
$$Q_0 = \frac{Q_0^e SS_e + Q_0^b SS_b}{SS}, \quad (3)$$

360 where  $SS_e$  is the edge specific surface area (in  $m^2 g^{-1}$ ),  $SS_b$  is the basal specific surface area,  
 361 and  $SS$  is the total specific surface area,  $SS = SS_e + SS_b$ .

362 The surface charge density  $Q_0^e$  is controlled by the amphoteric aluminol,  $>Al-OH$ , and silanol,  
 363  $>Si-OH$ , hydroxyl surface sites that are sensitive to pH and salinity of the surrounding  
 364 electrolyte due to proton desorption and adsorption on mineral surface (e.g.,  $>S-OH \leftrightarrow >S-$   
 365  $O^- + H^+$  where  $>S = >Al$  or  $>Si$ ) and salt counter-ion adsorption and desorption in the Stern  
 366 layer (e.g.,  $>S-O^- + M^+ \leftrightarrow >S-O^- - M^+$  where  $M^+ = Na^+$ ) (Leroy & Revil 2004; Tombacz &  
 367 Szekeres 2004; Tombacz & Szekeres 2006; Tournassat *et al.* 2016a). The alumina basal  
 368 surface of kaolinite particle is also sensitive to pH and salinity (Tombacz & Szekeres 2006).

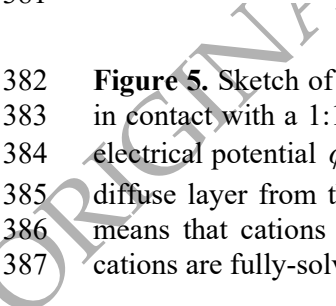
369 In absence of strong  $Q_i$  influence and dissolution/precipitation reactions,  $Q_0^e$  magnitude

370 should increase when pH moves from the point of zero charge (PZC, pH value where the  
 371 surface charge involving only amphoteric sites is zero). Indeed, in these conditions, when pH  
 372 decreases from PZC, mineral edge surface charge should become more positive because of  
 373 the increasing adsorption of protons  $H^+$ , and when pH increases from PZC, mineral edge  
 374 surface charge should become more negative because of the increasing desorption of protons  
 375  $H^+$  (Leroy *et al.* 2011). In these conditions also,  $|Q_0^e|$  should increase when salinity increases  
 376 because of the adsorption of salt counter-ions in the Stern layer (Leroy *et al.* 2013). The  
 377 replacement of chemically adsorbed protons by salt cations mostly adsorbed further away  
 378 from the mineral surface in the Stern layer increases the magnitude of the negative surface  
 379 charge (the surface charge due to negative oxygen atoms is not compensated by  $H^+$  anymore,  
 380 see Fig. 5).



381

382 **Figure 5.** Sketch of the electrochemical properties of (a.) kaolinite, (b.) illite and Mt particles  
 383 in contact with a 1:1 electrolyte like NaCl or KCl (modified from Leroy & Revil 2009). The  
 384 electrical potential  $\phi_d$  is assumed to be located at the  $d$ -plane delimiting the beginning of the  
 385 diffuse layer from the mineral surface. In Figure 5b, the white color in the interlayer space  
 386 means that cations are non-solvated and the blue color in the interlayer space means that  
 387 cations are fully-solvated.



388

389 Illite and Mt particles exhibit a permanent and negative structural charge on their basal  
390 surface ( $Q_0^b$  value typically between  $-0.20 \text{ C m}^{-2}$  and  $-0.10 \text{ C m}^{-2}$ ) due to isomorphic  
391 substitutions within the mineral crystal (Grim 1962; Bourg *et al.* 2007; Leroy *et al.* 2007;  
392 Leroy *et al.* 2017b). This structural surface charge is partly compensated by non-solvated  
393 cations (e.g.,  $\text{K}^+$  or  $\text{NH}_4^+$  ions with low hydration energy) and hydrated cations (e.g.,  $\text{Na}^+$   
394 and/or  $\text{Ca}^{2+}$  ions) in the interlayer space of illite and Mt (dioctahedral smectite), respectively  
395 (Melkior *et al.* 2009; Tournassat *et al.* 2015). In most of natural Mts,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions  
396 commonly coexist in the interlayer space (Tournassat *et al.* 2011). Hydrated cations such as  
397  $\text{Na}^+$  ions have a significant mobility in the interlayer space of Mt (for instance, around 20% of  
398 their mobility in bulk water according to the molecular dynamic simulations of Tournassat *et*  
399 *al.* 2009) whereas non-solvated cations such as  $\text{K}^+$  ions have a negligible mobility in the  
400 interlayer space of illite (Ruiz Pestana *et al.* 2016). Therefore, in the following, we consider  
401 that the interlayer space of Mts such as Na-Mt is conductive and polarizable in the mHz to  
402 kHz frequency range on the contrary to the illite interlayer space.

403 The behavior of the clay surface charge is therefore more complicated than for oxides such as  
404  $\text{SiO}_2$  (Leroy *et al.* 2013) or  $\text{TiO}_2$  (Leroy *et al.* 2011) or carbonates (Li *et al.* 2016) because, as  
405 written previously, the different faces have not the same electrochemical properties  
406 (Tournassat *et al.* 2013). For instance, the PZC of the edge face of Na-Mt is around 6.5  
407 whereas its basal faces do not exhibit a PZC value because of the strong influence of the  
408 negative structural surface charge (Tombacz & Szekeres 2004). The basal faces (or surfaces)  
409 of illite and Mt are less sensitive to pH and salinity than their edge face because the hydroxyl  
410 sites are less abundant and of the strong influence of the structural surface charge (Tournassat  
411 *et al.* 2015). In a system where protons and hydroxide ions are the only aqueous species, the  
412 point of zero net proton charge (PZNPC) of a mineral defines the pH at which the positively

413 and negatively charged functional groups on its surface are equal (Hao *et al.* 2018). For clay  
414 minerals presenting both pH-dependent surface charge and a permanent structural surface  
415 charge, the PZNPC is a better indicator of the state of the surface charge than the PZC  
416 (Tombacz & Szekeres 2004). The PZNPC of clays decreases to lower pH with increasing,  
417 e.g., NaCl concentration in bulk water (not influenced by the electrically charged surface)  
418 because of the structural charge influence, which is stronger for, e.g., Na-Mt or illite than for  
419 kaolinite (Avena & De Pauli 1998; Tombacz & Szekeres 2006). Tombacz & Szekeres (2006)  
420 reported that the PZNPC of Na-Mt ranges from around 8.75 at a salinity of 0.01 M NaCl to  
421 around 6.75 at a salinity of 1 M NaCl and that the PZNPC of kaolinite ranges from around  
422 6.75 at a salinity of 0.01 M NaCl to around 5.25 at a salinity of 1 M NaCl (see their Fig. 6).  
423 This confirms that the structural charge influence on clay surface charge is stronger for Na-Mt  
424 than for kaolinite and hence that the surface charge of kaolinite is more sensitive to pH and  
425 salinity compared to the surface charge of Na-Mt. Using measured PZNPC values, Hao *et al.*  
426 (2018) showed that the surface charge of kaolinite is more sensitive to pH and salinity  
427 compared to the surface charge of Mt and also illite in a lesser extent (a significant part of the  
428 structural surface charge of illite is compensated by non-solvated  $K^+$  counter-ions).

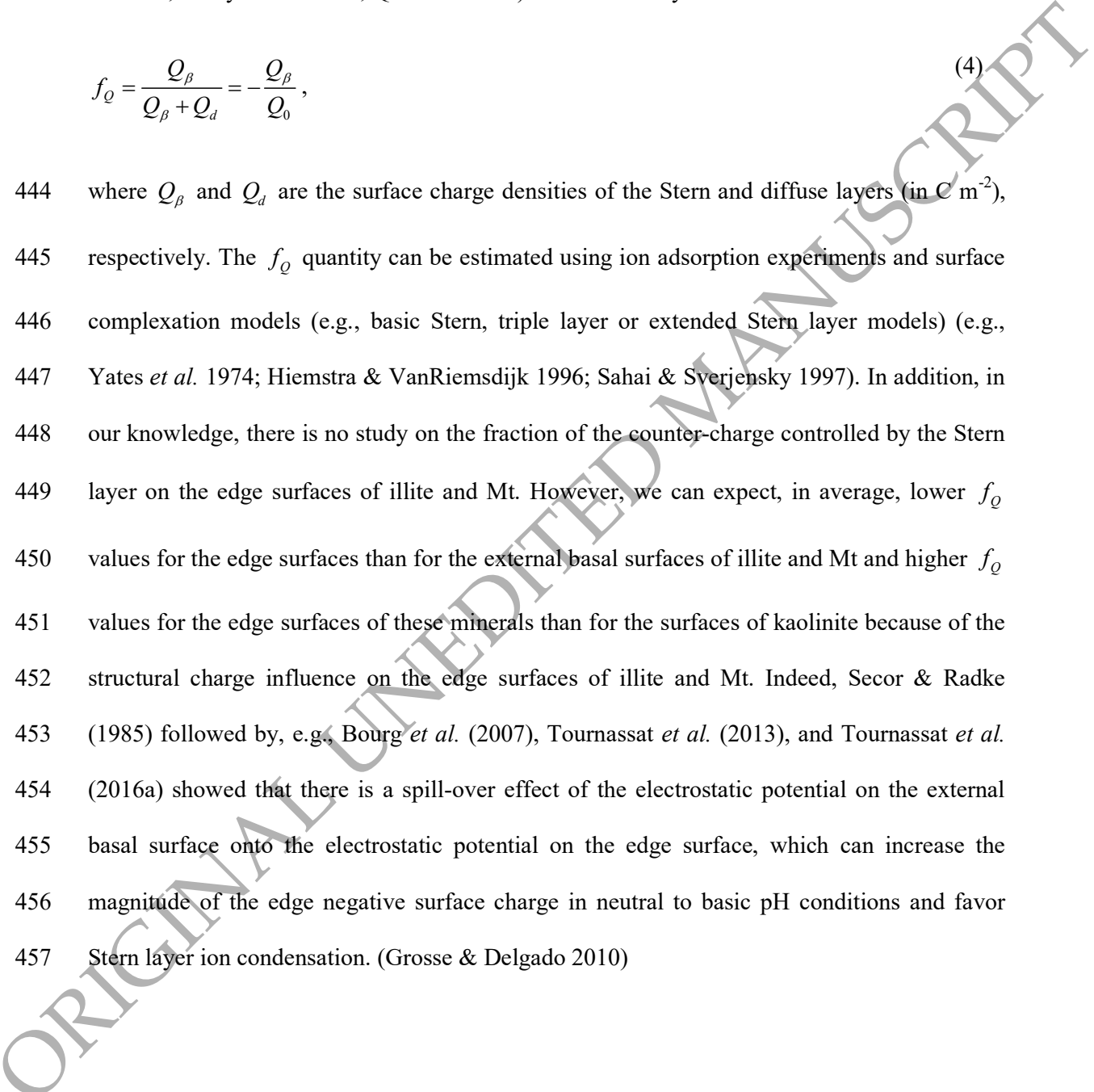
429 The outer mineral surface charge, i.e., the mineral surface charge not compensated by the  
430 interlayer counter-ions, is compensated by counter-ions adsorbed in the “compact” Stern layer  
431 that has a solid-like water viscosity and is located between the mineral surface and the shear  
432 (or slipping) plane when water flow occurs on the mineral surface (Revil & Leroy 2001). The  
433 remaining outer mineral surface charge is compensated by counter-ions in excess and co-ions  
434 in deficiency compared to their concentration in bulk water that follow a Boltzmann type  
435 distribution in the diffuse part of the EDL (Leroy & Revil 2004) (Fig. 5). The high negative  
436 surface charge on the basal faces of Mt and illite favors counter-ion condensation within the  
437 Stern layer (Leroy & Revil 2009). This is the reason why the fraction of the surface charge



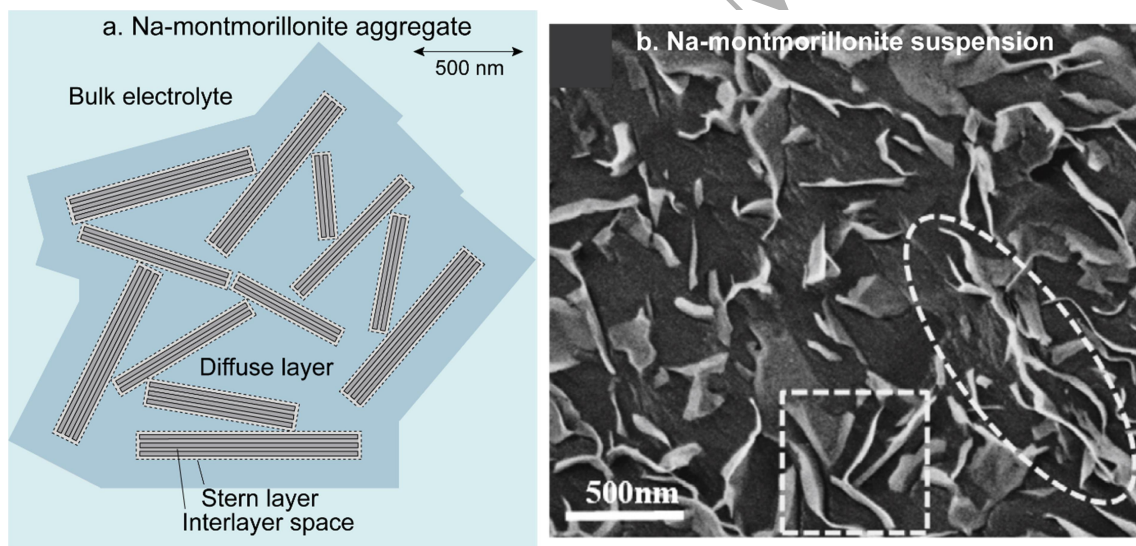
438 compensated by the Stern layer on the external basal surface of such clay minerals ( $f_Q$ ) is  
 439 typically above 50% (Leroy & Revil 2004; Tombacz & Szekeres 2004; Leroy *et al.* 2007;  
 440 Leroy & Revil 2009; Leroy *et al.* 2015). The  $f_Q$  quantity is of paramount importance for SIP  
 441 models because they consider that the Stern and diffuse layers have different contributions to  
 442 measured SIP data (e.g., de Lima & Sharma 1992; Leroy & Revil 2009; Revil 2012; Okay *et*  
 443 *al.* 2014; Leroy *et al.* 2017b; Qi & Wu 2024). It is defined by:

$$f_Q = \frac{Q_\beta}{Q_\beta + Q_d} = -\frac{Q_\beta}{Q_0}, \quad (4)$$

444 where  $Q_\beta$  and  $Q_d$  are the surface charge densities of the Stern and diffuse layers (in  $C\ m^{-2}$ ),  
 445 respectively. The  $f_Q$  quantity can be estimated using ion adsorption experiments and surface  
 446 complexation models (e.g., basic Stern, triple layer or extended Stern layer models) (e.g.,  
 447 Yates *et al.* 1974; Hiemstra & VanRiemsdijk 1996; Sahai & Sverjensky 1997). In addition, in  
 448 our knowledge, there is no study on the fraction of the counter-charge controlled by the Stern  
 449 layer on the edge surfaces of illite and Mt. However, we can expect, in average, lower  $f_Q$   
 450 values for the edge surfaces than for the external basal surfaces of illite and Mt and higher  $f_Q$   
 451 values for the edge surfaces of these minerals than for the surfaces of kaolinite because of the  
 452 structural charge influence on the edge surfaces of illite and Mt. Indeed, Secor & Radke  
 453 (1985) followed by, e.g., Bourg *et al.* (2007), Tournassat *et al.* (2013), and Tournassat *et al.*  
 454 (2016a) showed that there is a spill-over effect of the electrostatic potential on the external  
 455 basal surface onto the electrostatic potential on the edge surface, which can increase the  
 456 magnitude of the edge negative surface charge in neutral to basic pH conditions and favor  
 457 Stern layer ion condensation. (Grosse & Delgado 2010)



458 In water, clay particles in contact with each other form aggregates in particular because of  
 459 EDL interactions between particles (Fig. 6) (Mc Bride & Baveye 2002). Attractive edge-to-  
 460 face interactions (when  $\text{pH} < \text{PZC}$  of the edge faces) and repulsive face-to-face interactions as  
 461 well as edge-to-edge interactions regulate the size and shape of the clay aggregate and its  
 462 internal porosity, which are strongly depend on pH and salinity (e.g., Leroy *et al.* 2015, Leroy  
 463 *et al.* 2017b, Rasmusson *et al.* 1997, Sondi *et al.* 1996, Tombacz & Szekeres 2006). The  
 464 critical coagulation concentration (CCC) is defined as the minimum concentration of salt  
 465 counter-ions to induce coagulation of colloidal particles. Above the CCC, which is typically  
 466 between 0.01 and 0.1 mol L<sup>-1</sup> (M) for dispersed clays in NaCl electrolyte, clay particles  
 467 coagulate due to diffuse layer compression and form larger particles with more interlayer  
 468 space for illite and Mt than at lower salinities (e.g., Sondi *et al.* 1996, Rasmusson *et al.* 1997,  
 469 Tombacz & Szekeres 2004, Tombacz & Szekeres 2006, Leroy *et al.* 2015, Leroy *et al.* 2017b,  
 470 Mendieta *et al.* 2021).



471  
 472 **Figure 6.** Sketch of a Na-Mt aggregate containing interacting clay particles (a., modified from  
 473 Leroy *et al.* 2015, in reality particles are thinner than those represented here) and Cryo-SEM  
 474 images of high-pressure frozen and freeze-fractured SWy-2 bentonite in distilled water with  
 475 5% (wt/wt) solid content (b., Na-ion exchanged gel, modified from Mouzon *et al.* 2016).

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476 The surface conductivity influencing IP measurements is defined as the excess of electrical  
477 conductivity in the EDL compared to in bulk water integrated over the thickness of the EDL  
478 (Revil & Glover 1997; Lyklema & Minor 1998). According to O'Konski 1960, surface  
479 conductivity contributes to particle conductivity when the thickness (or radius) of the particle  
480 is larger than the thickness of the EDL. However, the EDL can be thicker than clay such as  
481 illite or Na-Mt particle (section 2.1.), meaning that in that case it can contribute to water  
482 conductivity (Dufreche *et al.* 2001; Leroy & Revil 2009). In addition, the electrochemical  
483 properties and surface conductivity of kaolinite are more sensitive to pH and salinity than the  
484 electrochemical properties and surface conductivity of Mt and illite in a lesser extent (Leroy  
485 & Revil 2004). Furthermore, because a kaolinite TO sheet has a weaker structural surface  
486 charge and a kaolinite particle has a smaller specific surface area than an illite or a Mt  
487 particle, kaolinite has weaker electrochemical and adsorption properties, and hence surface  
488 conductivity than illite and Mt (Leroy & Revil 2004; Tombacz & Szekeres 2006; Okay *et al.*  
489 2014). Mt surface conductivity should be higher than illite surface conductivity because Mt  
490 has a larger reactive specific surface area than illite (Leroy & Revil 2009). This should be  
491 particularly true for Na-Mt containing hydrated and mobile  $\text{Na}^+$  cations in its interlayer space.  
492 This conclusion also means that the laboratory CEC measurement, which depends on the  
493 product of the surface charge density ( $Q_0$ ) with the reactive specific surface area (Leroy *et al.*  
494 2007; Okay *et al.* 2014), cannot be used to characterize the electrochemical and IP properties  
495 of clays such as kaolinite because of the strong dependence of  $Q_0$  on the bulk pore water  
496 composition (pH, salinity). Indeed, CEC laboratory measurements are done using a particular  
497 bulk water composition (Khaled & Stucki 1991) that does not correspond necessarily to the  
498 bulk pore water composition in the laboratory samples during SIP measurements and in-situ  
499 during field geophysical measurements. However, the laboratory CEC measurement could be  
500 safely employed to characterize the electrochemical and IP properties of Mt and in a lesser

501 extent of illite and soils, sediments and rocks containing a significant fraction of these  
502 minerals because of the strong influence of the permanent and negative structural charge  
503 (Vinegar & Waxman 1984; Revil 2012; Weller *et al.* 2013; Okay *et al.* 2014; Leroy *et al.*  
504 2017b).

505

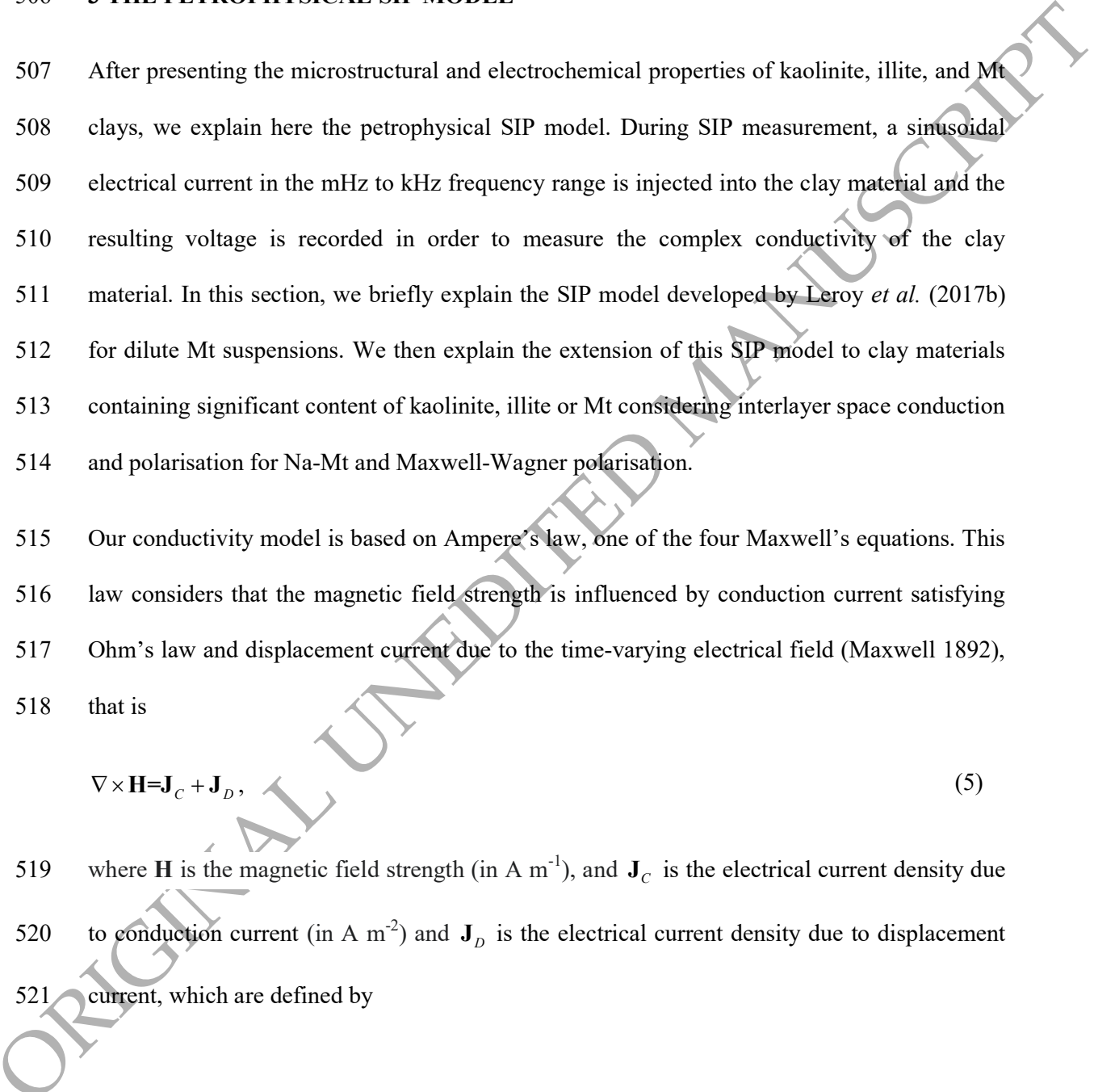
### 506 **3 THE PETROPHYSICAL SIP MODEL**

507 After presenting the microstructural and electrochemical properties of kaolinite, illite, and Mt  
508 clays, we explain here the petrophysical SIP model. During SIP measurement, a sinusoidal  
509 electrical current in the mHz to kHz frequency range is injected into the clay material and the  
510 resulting voltage is recorded in order to measure the complex conductivity of the clay  
511 material. In this section, we briefly explain the SIP model developed by Leroy *et al.* (2017b)  
512 for dilute Mt suspensions. We then explain the extension of this SIP model to clay materials  
513 containing significant content of kaolinite, illite or Mt considering interlayer space conduction  
514 and polarisation for Na-Mt and Maxwell-Wagner polarisation.

515 Our conductivity model is based on Ampere's law, one of the four Maxwell's equations. This  
516 law considers that the magnetic field strength is influenced by conduction current satisfying  
517 Ohm's law and displacement current due to the time-varying electrical field (Maxwell 1892),  
518 that is

$$\nabla \times \mathbf{H} = \mathbf{J}_C + \mathbf{J}_D, \tag{5}$$

519 where  $\mathbf{H}$  is the magnetic field strength (in  $\text{A m}^{-1}$ ), and  $\mathbf{J}_C$  is the electrical current density due  
520 to conduction current (in  $\text{A m}^{-2}$ ) and  $\mathbf{J}_D$  is the electrical current density due to displacement  
521 current, which are defined by



$$\mathbf{J}_C = \sigma \mathbf{E}, \quad (6)$$

522 and

$$\mathbf{J}_D = \frac{\partial \mathbf{D}}{\partial t}, \quad (7)$$

523 where  $\sigma$  is the electrical conductivity of the investigated medium (in  $\text{S m}^{-1}$ ),  $\mathbf{E}$  is the applied

524 electrical field (in  $\text{V m}^{-1}$ ),  $\mathbf{D}$  is the dielectric displacement (in  $\text{C m}^{-2}$ ), and  $t$  is the time (in s).

525 The applied sinusoidal electrical field and the dielectric displacement are respectively defined

526 by

$$\mathbf{E} = \mathbf{E}_0 \exp(i\omega t), \quad (8)$$

527 and

$$\mathbf{D} = \varepsilon \mathbf{E}, \quad (9)$$

528 where  $i$  is the imaginary number ( $i^2 = -1$ ),  $\omega$  is the angular frequency of the applied electrical

529 current (in  $\text{rad s}^{-1}$ ;  $\omega = 2\pi f$  with  $f$  being the frequency in Hz), and  $\varepsilon$  is the permittivity of the

530 investigated medium (in  $\text{F m}^{-1}$ ). By using Eqs 6 to 9, we finally obtain for the total current

531 density

$$\mathbf{J}_t = (\sigma + i\omega\varepsilon) \mathbf{E}, \quad (10)$$

532 and then for the medium conductivity

$$\sigma^* = \sigma + i\omega\varepsilon, \quad (11)$$

533

534

535

536 **3.1. Model assumptions**

537 A clay aggregate can be decomposed into different compartments: bulk (electroneutral) water,  
538 diffuse layer water, Stern layers and interlayer spaces of particles, which exhibit different  
539 electrical conductivities (Leroy & Revil 2009; Okay *et al.* 2014; Leroy *et al.* 2017b) (Fig. 6).

540 Following the works of Revil and co-workers (e.g., Leroy & Revil 2009; Jougnot *et al.* 2010a;  
541 Revil 2012; Okay *et al.* 2014), the SIP model of Leroy *et al.* (2017b) assumes that the bulk  
542 water and the diffuse layer water surrounding clay particles are continuous at the scale of the  
543 laboratory centimetric measurement and hence do not contribute to the polarisation of the  
544 particles. According to Leroy *et al.* (2017b), the bulk and diffuse layer waters only contribute  
545 to conductivity at zero frequency (direct current, DC conductivity) influencing clay material  
546 in-phase conductivity (real component of clay material complex conductivity). Similarly to  
547 the SIP models of Revil and co-workers, the model of Leroy *et al.* (2017b) considers that the  
548 Stern layers around clay particles are discontinuous at the scale of the centimetric laboratory  
549 measurement and polarize, influencing clay material in-phase conductivity and quadrature  
550 conductivity (imaginary component of clay material complex conductivity). Leroy *et al.*  
551 2017b) assumed that the clay material polarizes at the scale of the clay aggregate, meaning  
552 that they considered the polarisation of the Stern layers on the clay particles in contact with  
553 each other. Similarly to the works of Revil and co-workers, Leroy *et al.* (2017b) did not  
554 consider the adsorption/desorption kinetics of the ions in the Stern layer as well as their  
555 exchange with the ions in the diffuse layer and bulk water because they assumed that these  
556 processes are instantaneous compared to the movements of the ions in the EDL and bulk  
557 water.

558 Following the works of, e.g., Dufreche *et al.* (2001), Bourg *et al.* (2003), Rotenberg *et al.*  
559 (2005), and Cadene *et al.* (2006), we consider that some fully hydrated ions (such as Na<sup>+</sup> ions

560 and/or  $\text{Ca}^{2+}$  ions in a lesser extent (Tournassat *et al.* 2009; Bourg & Sposito 2011; Greathouse  
561 *et al.* 2016)) are mobile in the interlayer space of Mt particle and hence contribute to low-  
562 frequency conduction and polarisation in clay particles in contact with each other.

563 Our model has been developed to extract porosity, electrical formation factor, clay aggregate  
564 size distribution, and water and surface conductivities from complex conductivity  
565 measurements. It was used to interpret SIP measurements reported in Mendieta *et al.* (2021)  
566 from the measured experimental conditions (Maineult *et al.* 2024). For instance, prior to the  
567 SIP measurements, Mendieta *et al.* (2021) measured the mass of the dry clay powder, i.e. the  
568 solid mass ( $\delta_s$ ) (in g), before mixing it with a NaCl electrolyte of known salt concentration ( $C_{\text{NaCl}}^0$ ) (in mol L<sup>-1</sup>, M). It should be noted that the SIP model presented here can be  
569 generalized to any type of electrolyte but the case of a NaCl electrolyte is considered here in  
570 order to compare in Maineult *et al.* (2024) the model to the experimental data reported in  
571 Mendieta *et al.* 2021 on kaolinite, illite and Mt muds. In these experiments, the (total) volume  
572 of the sample ( $V_t$ ) (in m<sup>3</sup>), the temperature ( $T_c$ ) (in °C) ( $T_c = T - 273.15$  where  $T$  is the  
573 absolute temperature in K), and the (total) masses of the sample before and after water  
574 evaporation ( $\delta_t^0$  and  $\delta_t^1$ , respectively) (in g), were also recorded. In our model, measured  $\delta_s$ ,  
575 and  $V_t$  values as well as the measured volume fraction of the main clay mineral in the solid  
576 phase ( $\xi_c$ ) (by X-ray diffraction, XRD) are used to compute the volumes of the different  
577 components of the clay material intervening in the SIP model (Appendix A). Measured  $T_c$   
578 values are used to compute the model parameter values as a function of temperature  
579 (Appendix B), and measured  $C_{\text{NaCl}}^0$ ,  $\delta_t^0$  and  $\delta_t^1$  values are used to calculate NaCl  
580 concentration in bulk water after evaporation and bulk water chemical composition  
581 (Appendix C).  $\text{Na}^+$  and  $\text{Cl}^-$  ion mobilities in bulk water intervening in the SIP model are also  
582 computed as a function of NaCl concentration (Appendix B) because of the mutual influence  
583

584 of cations and anions decreasing their mobility and hence the related electrical conductivity  
585 (Leroy *et al.* 2015).

586

### 587 **3.2. Calculation of the EDL properties**

588 We have developed here a new approach to directly compute the electrical potential at the  $d$ -  
589 plane (delimiting the beginning of the diffuse layer from the mineral surface) ( $\varphi_d$ ) (in V, Fig.

590 4), from the fraction of the counter-charge in the Stern layer ( $f_Q$ ) and the mineral surface

591 charge density ( $Q_0$ ) (in C m<sup>-2</sup>). The mineral surface charge density is computed from ratio of

592 the measured cation exchange capacity (CEC) (in meq g<sup>-1</sup>) to the specific surface area where

593 cation exchange reactions occur on clay mineral surface ( $SS$ ) (in m<sup>2</sup> g<sup>-1</sup>) (Okay *et al.* 2014).

594 The  $SS$  quantity can be estimated using crystallography (Leroy & Revil 2004). In the case of

595 Na-Mt, it can be approximated by the total specific surface area of the basal surfaces ( $SS_b$ )

596 (Leroy *et al.* 2015; Leroy *et al.* 2017b). Clay particles exhibit different electrical potentials on

597 their surfaces (Bourg *et al.* 2007; Tournassat *et al.* 2013). Our approach considers a

598 dominating electrical potential at the  $d$ -plane on the clay surface ( $\varphi_d$ ) and not a distribution of

599  $\varphi_d$  potentials on the clay surface, which will make the modeling considerably more complex.

600 The advantage of our approach is also that it does not need an electrostatic surface

601 complexation model, that can be very complicated, to estimate  $\varphi_d$  from bulk water chemical

602 composition (see for example Tournassat *et al.* 2013).

603 The  $\varphi_d$  potential is a physical quantity of paramount importance in the colloidal and interface

604 science and geophysical communities focusing on understanding electrochemical properties.

605 Indeed, it regulates electrostatic attraction/repulsion on charged surfaces and electrostatic

606 interaction between charged surfaces when in contact with a polar solvent like water (Gouy



607 1910; Chapman 1913; Grahame 1947). This electrical potential is commonly assumed to be  
608 equal to the zeta potential inferred from electrokinetic measurements when a shear or slipping  
609 plane involving polar solvent flow occurs on the surfaces (von Smoluchowski 1905; von  
610 Smoluchowski 1921). Knowing the  $\varphi_d$  potential value is useful here to compute two  
611 processes considered in the SIP model: (i) the effect of the diffuse layer on Stern layer  
612 polarisation through the  $M$  parameter value ( $M \geq 1$ ) and (ii) the electrical conductivity of the  
613 diffuse layer (that will be fully explained in Sections 3.3 and 3.4). According to Lyklema *et al.*  
614 (1983), ions in the diffuse layer counterbalance locally ions in the polarized Stern layer to  
615 ensure local electroneutrality. This effect decreases the length of the pathway of the migrating  
616 ions in the Stern layer and hence it decreases the relaxation time of the polarized Stern layer  
617 (Fig. 1, Fig. 7b and Eq. 15).

618 Ions in the diffuse layer counteracting ions in the Stern layer contributing to polarisation  
619 could in principle not contribute also to conduction via electromigration. However, on the  
620 contrary to what is shown by Lyklema *et al.* (1983) about the EDL of a single particle, the  
621 diffuse layers around clay particles are probably connected and may fill a significant part of  
622 the pore space in clay materials when the clay concentration in the sample is large. For  
623 instance, clay muds can contain a large mass of dry clay powder per liter of sample. In the SIP  
624 experiments of Mendieta *et al.* (2021), clay muds contain about one thousand grams of dry  
625 clay powder per liter of sample. This means that the diffuse layers are not necessarily  
626 disconnected and hence solely counteracting Stern layer polarisation. For this reason, we  
627 consider in the following that the diffuse layer contributes to DC conductivity implying that  
628  $M = 1$  theoretically (no effect of diffuse layer on Stern layer polarisation). However, we also  
629 consider here a hybrid approach assuming that the diffuse layer can locally (at the particle  
630 scale) counter-balance Stern layer polarisation through the computation of  $M \geq 1$  and  
631 contribute also to conduction via electromigration (at the sample scale).

632 The following function is minimized to estimate  $\varphi_d$  from  $f_Q$  and  $Q_0$  (Appendix D) (knowing  
633 the bulk water chemical composition):

$$\left| \sqrt{2\overline{\varepsilon_w}k_B T 10^3 N_A \sum_{i=1}^N C_i^b \left[ \exp\left(-\frac{q_i \varphi_d}{k_B T}\right) - 1 \right]} - Q_0 (1 - f_Q) \right| = 0, \quad (12)$$

634 where  $\overline{\varepsilon_w}$  represents the mean water permittivity (in F m<sup>-1</sup>) including in the interlayer space  
635 of Na-Mt (we consider that  $\varepsilon_w$  has the same value in the diffuse layer and bulk water, see  
636 Appendix B for  $\varepsilon_w$  values), and  $k_B$  is the Boltzmann's constant ( $\sim 1.381 \times 10^{-23}$  J K<sup>-1</sup>). In Eq.  
637 12,  $N$  represents the number of different ion species  $i$  in bulk water with ion concentration  $C_i^b$   
638 (in mol L<sup>-1</sup>, M) and charge  $q_i = \pm e z_i$  (in C) where “+” and “-” stand for cations and anions,  
639 respectively,  $e$  is the elementary (or electron) charge ( $\sim 1.602 \times 10^{-19}$  C),  $z_i$  is the ion valence  
640 (e.g.,  $z_i = 1$  for sodium or chloride ion and  $z_i = 2$  for calcium, magnesium or sulfate ion), and  
641  $N_A$  is the Avogadro's number ( $\sim 6.022 \times 10^{23}$  mol<sup>-1</sup>).

642 In the case of Na-Mt, we assume in Eq. 12 the same electrical potential  $\varphi_d$  in the interlayer  
643 space and diffuse layer on the external clay surface (Dufreche *et al.* 2001). However, for Na-  
644 Mt, the water permittivity value intervening in the calculation of  $\varphi_d$  (Eqs 12 or 15) and of the  
645 differential capacitance of the diffuse layer  $C_d$  (in F m<sup>-2</sup>) (Hunter 1981) to compute  $M$  (Eq.  
646 16) could be significantly smaller in the interlayer space than in the diffuse layer on the  
647 external clay surface due to the stronger electrical field (Hiemstra & Van Riemsdijk 2006)  
648 and the weaker level of hydration (Wander & Clark 2008) in the interlayer space. In our  
649 knowledge, the water permittivity value is not accurately known in the interlayer space of Na-  
650 Mt and should be between clay solid permittivity value ( $\varepsilon_s \cong 5\varepsilon_0$  where  $\varepsilon_0$  is vacuum  
651 permittivity, see Section 3.3) and bulk water permittivity value ( $\varepsilon_w \cong 78.3\varepsilon_0$  for distilled

652 water at a temperature of 298.15 K, see Appendix B). For that reason, we consider in the  
 653 following that the water permittivity value in the interlayer space of Na-Mt is half the value in  
 654 bulk water, i.e.  $\varepsilon_{in} = \varepsilon_w / 2$ . In Eqs 12 or 15 and 16, water permittivity is therefore computed  
 655 using

$$\frac{\varepsilon_w}{\varepsilon_w} = \frac{\varepsilon_w V_w^d + \varepsilon_{in} V_{in}}{V_w^d + V_{in}} = \frac{\varepsilon_w}{V_w^d + V_{in}} \left( V_w^d + \frac{V_{in}}{2} \right), \quad (13)$$

656 where  $V_w^d$  is the calculated diffuse layer volume (in  $\text{m}^3$ ) and  $V_{in}$  is the calculated interlayer  
 657 space volume when it contains mobile ions such as  $\text{Na}^+$  ions (see Appendix A).

658 If  $Q_0$  is considered homogeneous on the mineral surface, it can be computed as a function of  
 659 the measured CEC and  $SS$  (Okay *et al.* 2014) using

$$Q_0 = -\frac{eN_A \text{CEC}}{10^3 SS}, \quad (14)$$

660 then when using Eq. 14, Eq. 12 becomes

$$\left| \sqrt{2\varepsilon_w k_B T 10^3 N_A \sum_{i=1}^N C_i^b \left[ \exp\left(-\frac{q_i \varphi_d}{k_B T}\right) - 1 \right]} - \frac{eN_A \text{CEC}}{10^3 SS} (1 - f_Q) \right| = 0. \quad (15)$$

661 The  $M$  parameter value (Lyklema *et al.* 1983) is computed from  $f_Q$  and  $\varphi_d$  according to

$$M = 1 + \frac{qQ_\beta}{k_B TC_d}, \quad (16)$$

662 where  $q$  is the mean charge of the counter-ions in the Stern layer (in C;  $q = \pm ez$  with  $z$  is the  
 663 mean valence of the counter-ions). The  $Q_\beta$  quantity in Eq. 16 is determined as a function of  
 664  $f_Q$  and the surface charge density on the mineral surface ( $Q_0$ ) using (Appendix D)

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$$Q_\beta = -f_Q Q_0, \quad (17)$$

665 where  $Q_0$  can be computed as a function of the measured CEC and  $SS$  using Eq. 7. The  
 666 differential capacitance of the diffuse layer (Eq. 16) is determined from  $\varphi_d$  (Leroy *et al.*  
 667 2017a) according to

$$C_d = -\frac{\partial Q_d}{\partial \varphi_d} = \sqrt{\frac{\varepsilon_w}{2k_B T}} \frac{10^3 N_A \sum_{i=1}^N q_i C_i^b \exp\left(-\frac{q_i \varphi_d}{k_B T}\right)}{\sqrt{10^3 N_A \sum_{i=1}^N C_i^b \left[\exp\left(-\frac{q_i \varphi_d}{k_B T}\right) - 1\right]}}, \quad (18)$$

668 and for a symmetric electrolyte of valence  $z$ , Eq. 18 reduces to

$$C_d = \varepsilon_w \kappa \cosh\left(\frac{ze\varphi_d}{2k_B T}\right), \quad (19)$$

669 where  $\kappa = \chi_D^{-1}$  is the inverse of the Debye length (in  $\text{m}^{-1}$ ) (see Eq. A5 (Lyklema *et al.* 1983)),  
 670 and then the  $M$  parameter value is computed from  $f_Q$  and  $Q_0$  or CEC and  $SS$  according to  
 671 Eqs 12 to 18 or 19. The case  $M = 1$  corresponds to the Schwarz's model (Schwarz 1962) with  
 672 no effect of the diffuse layer on Stern layer polarisation. Leroy *et al.* (2017b) found that  
 673  $M \cong 4$  for the basal surface of Na-Mt, meaning that, in this case, ions in the diffuse layer  
 674 significantly decrease the length of the pathways and then the relaxation time of ions in the  
 675 polarized Stern layer according to the generalized Schwarz model of Lyklema *et al.* (1983).

676

### 677 3.3. Aggregate conductivity due to surface conductivity

678 A mineral surface in contact with a polar solvent like water and submitted to a low-frequency  
 679 electrical field expresses a surface conductivity response due to migrating ions in the EDL  
 680 (O'Konski 1960). Surface conductivity (or surface conductance) is defined as a surface

681 quantity in Siemens and not as a volume quantity in Siemens per meter. However, we will  
 682 define it in the following as a volume quantity because of its widespread use as a volume  
 683 quantity like water conductivity in the geophysical community. Like our water conductivity  
 684 model, our “surface” conductivity model is based on Ampere’s law (Eq. 5) (e.g., Schwarz  
 685 1962; de Lima & Sharma 1992; Chelidze & Gueguen 1999; Leroy *et al.* 2008). The resulting  
 686 surface conductivity is written as (Eq. 11)

$$\sigma_s^*(\omega) = \sigma_s(\omega) + i\omega\varepsilon_s, \tag{20}$$

687 where the first term (a complex quantity when considering EDL polarisation) arises from  
 688 conduction current and the second term arises from displacement current in the presence of an  
 689 applied sinusoidal electrical field with  $\varepsilon_s$  being the solid dielectric constant (in  $F\ m^{-1}$ ). In our  
 690 model, we assume that clay aggregates control the surface conductivity and induced  
 691 polarisation response of the material. Therefore, the symbol  $\sigma_s^*$  reported in Eq. 20 for the  
 692 clay aggregate conductivity corresponds to the symbol used by most IP practitioners for the  
 693 surface conductivity of the whole material. In addition, in Eq. 20, we do not consider  
 694 anisotropy in the calculation of the surface conductivity. Therefore, our model is particularly  
 695 adapted to unconsolidated clay materials like uncompacted clay muds.

696 Clay particles assemble themselves to make clay aggregate, which can be considered a  
 697 spherical object with a surface area made of the surface area of the particles constituting the  
 698 aggregate at first approximation. Leroy *et al.* (2017b) developed petrophysical relationships to  
 699 compute  $\sigma_s$  in Eq. 20 from the Mt aggregate microstructural and electrochemical properties.  
 700 They considered that the surface conductivity of a Mt aggregate is similar to the surface  
 701 conductivity of an equivalent spherical particle with an amplified surface area  $S$  (in  $m^2$ )  
 702 compared to its surface area if it is considered perfectly smooth and non-porous. In the model  
 703 of Leroy *et al.* (2017b),  $S$  is related to the specific surface area of all the polarising clay

704 platelets inside the aggregate (Fig. 6a). In addition, the SIP model of Leroy *et al.* (2017b) uses  
705 the generalized Schwarz model developed by Lyklema *et al.* (1983) to simulate the effect of  
706 the diffuse layer on the polarisation of the Stern layer surrounding clay particle (Fig. 1a).

707 It is actually very difficult and time-consuming to numerically compute the induced  
708 polarisation response of interacting clay particles because of (i) their high aspect ratio, (ii)  
709 heterogeneities in their surface electrical properties, and (iii) the physical-chemical  
710 mechanisms involved in the interaction (interacting diffuse and Stern layers) (Tournassat *et*  
711 *al.* 2013; Tournassat *et al.* 2015; Bucker *et al.* 2019). For this reason, we have to make the  
712 assumption that the polarisation of the Stern layers surrounding interacting clay particles is  
713 equivalent to the polarisation of a porous clay aggregate with an effective diameter  
714 surrounded by a Stern layer (for more information read Leroy *et al.* 2017b). In other words, in  
715 our model, the Stern layers of the interacting clay particles are assumed continuous at the  
716 scale of the aggregate (see also discussion in Jougnot *et al.* 2010a).

717 It should be noted that, according to some molecular dynamic (MD) simulations, most  $\text{Na}^+$   
718 and  $\text{Ca}^{2+}$  counter-ions in the Stern layer on the Mt basal surface may be adsorbed beyond the  
719 first hydration layer plane as outer-sphere surface complexes, keeping their hydration shell  
720 (e.g., Tournassat *et al.* 2009; Bourg & Sposito 2011). These MD simulations show that these  
721 counter-ions may behave in terms of ion diffusivity like ions in the diffuse layer. Therefore,  
722 according to these MD simulations, we can expect that, for a single clay particle, Stern layer  
723 polarisation is not necessarily different from diffuse layer polarisation on the basal surface of  
724 Mt.

725 We can attribute diffuse layer polarisation to a volume diffusion mechanism involving  
726 migrating ions in the diffuse layer and ions clouds in bulk water (Fig. 1b) and Stern layer  
727 polarisation to a surface diffusion mechanism associated with migrating ions on particle

728 surface (Fig. 1a) (Grosse & Delgado 2010). Delgado *et al.* (1998) showed that the  
 729 contribution of the volume diffusion mechanism to the measured dielectric dispersion of  
 730 polymer latex particles in the kHz to MHz frequency range decreases compared to the  
 731 contribution of the surface diffusion mechanism because the space available for volume  
 732 diffusion in bulk water decreases faster than the space available for surface diffusion when the  
 733 particle concentration in solution increases (here particle volume fraction ranges from 3 to  
 734 16%). Concentrated colloidal suspensions like clay muds have solid volume fractions  
 735 typically above 10% (Richter & Sevick-Muraca 2000). Our model is adapted to saturated clay  
 736 materials presenting typically a high concentration of clay particles with a high fraction of  
 737 counter-charge in the Stern layer ( $f_Q$ ). For this reason, we believe that the polarisation  
 738 models of Schwarz (1962) and Lyklema *et al.* (1983) considering surface diffusion is suitable  
 739 to simulate EDL polarisation of clay materials.

740 According to Leroy *et al.* (2017b), the low-frequency surface conductivity of clay aggregates  
 741 is written as

$$\sigma_s^* = \frac{2}{3} \phi_a \beta_s f_Q Q_V \sum_{k=1}^L f(d_k) \frac{i\omega\tau_k}{1+i\omega\tau_k} + i\omega\alpha\rho_s\varepsilon_0, \quad (21)$$

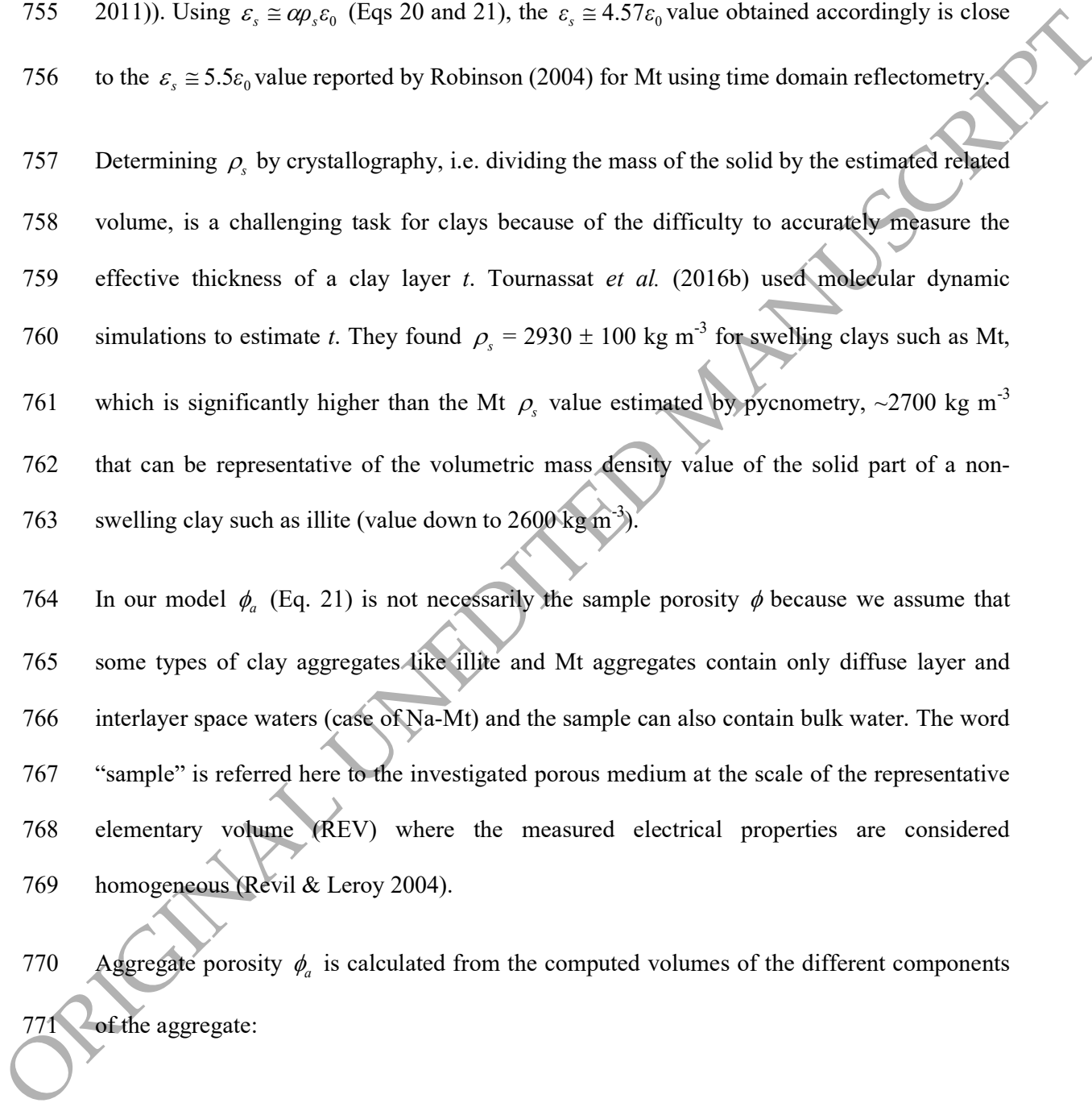
742 where  $\phi_a$  is the porosity of the aggregate (dimensionless, between 0 and 1),  $\beta_s$  is the mean  
 743 ion mobility of the counter-ions moving along the particle surface contributing to low-  
 744 frequency polarisation (in  $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$ ), and  $Q_V$  is the excess of counter-charge of the EDL per  
 745 unit pore volume of the aggregate (in  $\text{C m}^{-3}$ ). In Eq. 21,  $f(d_k)$ ,  $k=1\dots L$ , is the discretized  
 746 distribution of the effective sizes of the aggregates with  $d_k$  being the effective diameter of the  
 747  $k^{\text{th}}$  aggregate (in m) and  $L$  being the number of different effective diameters of the aggregates  
 748 in the model. In Eq. 21 also,  $\tau_k$  is the relaxation time of the polarized Stern layers within the  
 749  $k^{\text{th}}$  aggregate (in s),  $\alpha = 0.00191 \text{ m}^3 \text{ kg}^{-1}$  is an empirical value that was used by Olhoeft

750 (1981) to adjust solid permittivity spectra,  $\rho_s$  is the solid volumetric mass density (in  $\text{kg m}^{-3}$ ),  
751 and  $\varepsilon_0 \cong 8.854 \times 10^{-12} \text{ F m}^{-1}$  is the vacuum permittivity. According to the crystallographic unit  
752 cell,  $\rho_s \cong 2700 \text{ kg m}^{-3}$  for clays ( $\sim 2600$ ,  $2700$ , and  $2800 \text{ kg m}^{-3}$  for kaolinite, smectite and  
753 illite, respectively (Leroy & Revil 2009);  $\sim 2710$  and  $2840 \text{ kg m}^{-3}$  for Kunipia-G Na-Mt  
754 (Massat *et al.* 2016) and MX80 bentonite – mostly made of Na-Mt (Tournassat & Appelo  
755 2011)). Using  $\varepsilon_s \cong \alpha \rho_s \varepsilon_0$  (Eqs 20 and 21), the  $\varepsilon_s \cong 4.57 \varepsilon_0$  value obtained accordingly is close  
756 to the  $\varepsilon_s \cong 5.5 \varepsilon_0$  value reported by Robinson (2004) for Mt using time domain reflectometry.

757 Determining  $\rho_s$  by crystallography, i.e. dividing the mass of the solid by the estimated related  
758 volume, is a challenging task for clays because of the difficulty to accurately measure the  
759 effective thickness of a clay layer  $t$ . Tournassat *et al.* (2016b) used molecular dynamic  
760 simulations to estimate  $t$ . They found  $\rho_s = 2930 \pm 100 \text{ kg m}^{-3}$  for swelling clays such as Mt,  
761 which is significantly higher than the Mt  $\rho_s$  value estimated by pycnometry,  $\sim 2700 \text{ kg m}^{-3}$   
762 that can be representative of the volumetric mass density value of the solid part of a non-  
763 swelling clay such as illite (value down to  $2600 \text{ kg m}^{-3}$ ).

764 In our model  $\phi_a$  (Eq. 21) is not necessarily the sample porosity  $\phi$  because we assume that  
765 some types of clay aggregates like illite and Mt aggregates contain only diffuse layer and  
766 interlayer space waters (case of Na-Mt) and the sample can also contain bulk water. The word  
767 “sample” is referred here to the investigated porous medium at the scale of the representative  
768 elementary volume (REV) where the measured electrical properties are considered  
769 homogeneous (Revil & Leroy 2004).

770 Aggregate porosity  $\phi_a$  is calculated from the computed volumes of the different components  
771 of the aggregate:





$$\phi_a = \frac{V_S + V_w^d + V_w^b}{V_{sc} + V_S + V_w^d + V_w^b}, \quad (22)$$

772 for kaolinite, and

$$\phi_a = \frac{V_S + V_w^d}{V_{sc} + V_{in} + V_S + V_w^d}, \quad (23)$$

773 for illite, and

$$\phi_a = \frac{V_{in} + V_S + V_w^d}{V_{sc} + V_{in} + V_S + V_w^d}, \quad (24)$$

774 for Mt such as Na-Mt, where  $V_w^b$ ,  $V_S$ , and  $V_{sc}$  are the computed volumes of the bulk water (in  
 775  $\text{m}^3$ ), Stern layer, and solid clay layers, respectively (Appendix A). Kaolinite aggregates are  
 776 assumed to contain bulk and diffuse layer waters (Eq. 22). Illite and Mt aggregates are  
 777 assumed to contain only diffuse layer and interlayer space waters (case of Na-Mt) because of  
 778 their higher specific surface areas and surface charges and smaller pores than kaolinite  
 779 aggregates (Leroy & Revil 2009; Okay *et al.* 2014; Leroy *et al.* 2015) (Eqs 23 and 24). In Eq.  
 780 23, we assume that  $\text{K}^+$  ions migrate and diffuse very slowly along the surface of the interlayer  
 781 space of illite compared to in bulk water (Ruiz Pestana *et al.* 2016) and hence that they do not  
 782 contribute to low-frequency polarisation. We also assume that they do not contribute to low-  
 783 frequency conduction. In Eq. 24, we assume that  $\text{Na}^+$  ions migrate and diffuse significantly  
 784 along the surface of the interlayer space of Na-Mt compared to in bulk water (Bourg *et al.*  
 785 2003; Zhang *et al.* 2014) and hence that they contribute to low-frequency polarisation  
 786 (Rotenberg *et al.* 2005; Cadene *et al.* 2006). We also assume that the part of  $\text{Na}^+$  ions in the  
 787 interlayer space not contributing to low-frequency polarisation contributes to low-frequency  
 788 conduction. Mt particles containing immobile or very slow ions in the interlayer space can be  
 789 considered similar to illite particles.

790 Sample porosity can be computed using

$$\phi = \frac{V_{in} + V_w^d + V_w^b}{V_t}, \quad (25)$$

791 where  $V_t$  is the measured total volume of the sample during laboratory SIP measurements.

792 In Eq. 21, the  $Q_V$  quantity is given by

$$Q_V = \rho_s \left( \frac{1 - \phi_a}{\phi_a} \right) e N_A \text{CEC}. \quad (26)$$

793 Eq. 21 uses a parallel mixing formula for the modelling of the surface conductivity ( $\sigma_s$ ) of  
 794 the clay aggregates with different sizes, i.e., to compute  $\sigma_s$ , the surface conductivity response  
 795 of each aggregate of diameter  $d_k$  is weighted by its volume relative to the total volume of the  
 796 aggregates (Lesmes & Morgan 2001). As stated by, e.g., Lesmes & Morgan (2001), the  
 797 parallel mixing formula gives an upper bound for the computed complex surface conductivity  
 798 of different sized particles. The geometric mean mixing formula, which arises from random  
 799 networks consisting of both parallel and serial connections (Madden 1976), would have been  
 800 more realistic to compute  $\sigma_s$  in our model because it gives an average value for the computed  
 801 complex surface conductivity of different sized particles. However, the parameter  
 802 optimization procedure to obtain the relaxation time distribution intervening in the SIP model  
 803 from the SIP measurement is the Debye decomposition approach here (for more details on the  
 804 optimization procedure, see Mainault *et al.* 2024). The parallel mixing formula gives for  $\sigma_s$   
 805 an Eq. equivalent to the Eq. inferred from the Debye decomposition approach (Lesmes &  
 806 Morgan 2001). This is the reason why our model uses the parallel mixing formula for  $\sigma_s$   
 807 similarly to Lesmes & Morgan (2001).

808 The relaxation time  $\tau_k$  (Eq. 21) is the time necessary for the counter-ions in the Stern layers  
 809 within the  $k^{\text{th}}$  aggregate to diffuse back to their equilibrium position once the Stern layers are  
 810 polarized due to ion electromigration (Lyklema *et al.* 1983; de Lima & Sharma 1992;  
 811 Chelidze & Gueguen 1999) (see Fig. 1a). It is related to the effective diameter and surface ion  
 812 mobility using

$$\tau_k = \frac{d_k^2 |q|}{8k_B T \beta_S M}, \quad (27)$$

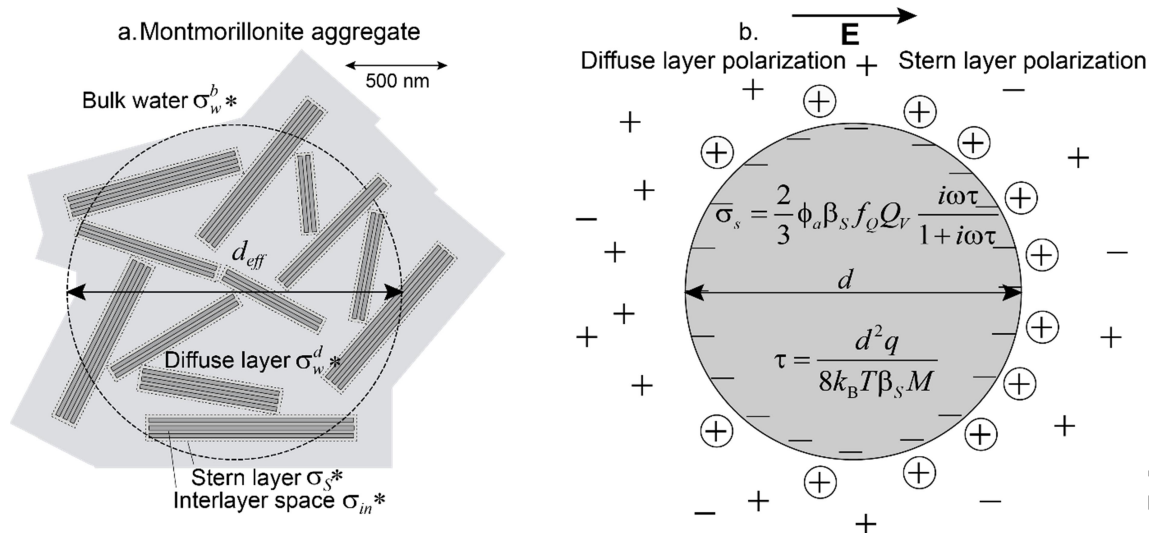
813 Eq. 27 shows that, for each aggregate of effective size  $d_k$ , the generalized Schwarz model of  
 814 Lyklema *et al.* (1983) considers one relaxation time  $\tau_k$  (see Fig. 7). Therefore, our model  
 815 simulates a Debye type response for the increase of the real and imaginary conductivity  
 816 response due to the low-frequency polarisation of the aggregate. Our modelling approach is  
 817 based on (i) fitting the complex conductivity spectra to obtain the relaxation time distribution  
 818  $f(\tau_k)$ ,  $k=1\dots L$  and the aggregate size distribution  $f(d_k)$ ,  $k=1\dots L$  (for more details on the  
 819 optimization procedure see Leroy *et al.* 2017b and Mainault *et al.* 2024) and (ii) computing  
 820 the aggregate effective size  $d_k$  from the obtained relaxation time  $\tau_k$  and the optimized  $\beta_S$   
 821 value obtained by successfully comparing measured to predicted complex conductivity  
 822 spectra using

$$d_k = \sqrt{8 \frac{k_B T}{|q|} \beta_S M \tau_k}, \quad (28)$$

823 meaning that for given values of  $\beta_S$  and  $\tau_k$ , increasing  $M$  increases the calculated effective  
 824 diameter of the  $k^{\text{th}}$  aggregate.

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827 **Fig. 7.** Sketch of a Mt aggregate with an effective diameter  $d_{eff}$  showing the clay particles  
 828 interacting with each other and the electrical conductivities of the different components (not  
 829 in scale) (a.). Sketch of the equivalent Stern layer polarisation model of Leroy *et al.* (2017b)  
 830 around a negatively charged spherical particle in contact with a monovalent electrolyte (not in  
 831 scale) (b.) (modified from Leroy *et al.* 2017b).

832 In Section 3.4, we will explain that the diffuse layer of clay particles, especially illite and Na-  
 833 Mt particles, contributes to the volume conductivity of the clay material and not to its surface  
 834 conductivity because the diffuse layer thickness can be larger than the clay particle thickness  
 835 (see Section 2.1) (O'Konski 1960; Dufreche *et al.*, 2001). However, at high ionic strength  $I$   
 836 (typically  $\geq 1$  M), the diffuse layer is highly compressed. For instance, the Debye length  
 837 characterizing the diffuse layer thickness is  $\sim 3$  Å at  $T = 298.15$  K and ionic strength  $I = 1$  M  
 838 (see Eqs A5 and B16). In that case, the diffuse layer thickness can be smaller than the  
 839 thickness of the clay layer and the assumption of the diffuse layer contributing to the volume  
 840 conductivity of the clay material does not necessarily hold because the diffuse layer can  
 841 contribute to the surface conductivity of the particle (O'Konski 1960). For larger clay particles  
 842 such as kaolinite particles, the diffuse layer can be thinner than the particle thickness for  
 843 smaller ionic strengths compared to illite and Mt particles and hence contribute to surface  
 844 conductivity according to O'Konski (1960). For this reason, in this condition, Eq. 21 becomes  
 845 (Leroy *et al.* 2008; Leroy *et al.* 2017b) (Appendix D):

$$\sigma_s^* = \frac{2}{3} \phi_a \sum_{k=1}^{N_{dk}} f(d_k) \left[ \beta_s f_Q \frac{i\omega\tau_k}{1+i\omega\tau_k} + \widetilde{B}_d (1-f_Q) \right] Q_V + i\omega\alpha\rho_s\varepsilon_0, \quad (29)$$

846 where  $\widetilde{B}_d$  is the ion mobility in the diffuse layer including electro-osmosis (in  $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$ )  
 847 (Revil & Glover 1997), which can be calculated according to

$$\widetilde{B}_d = \frac{1}{\mathcal{G}} \left( \beta_i^b + \frac{2\overline{\varepsilon_w} k_B T}{\eta_w |q_i|} \right), \quad (30)$$

848 where  $\mathcal{G}$  ( $\mathcal{G} \geq 1$ ) is a weighting coefficient that can be considered equal to the ratio of the  
 849 surface area of the clay particles within the clay aggregate to the surface area of the equivalent  
 850 non-porous spherical particle (Appendix D),  $\beta_i^b$  is the ion mobility in the diffuse layer due to  
 851 electro-migration (in  $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$ ) (we assume  $\beta_i^d = \beta_i^b$ ) and  $q_i$  is the charge of the dominating  
 852 ion in the diffuse layer (in C). For a 1:1 electrolyte such as NaCl electrolyte at a temperature  
 853 of 298.15 K, the second term of Eq. 30 describing electro-osmotic effect yields  
 854  $m_i^d \cong 3.78 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{V}^{-1}$  using  $\overline{\varepsilon_w} = 78.3\varepsilon_0$ , which is in the same order of magnitude than  
 855 the ion mobility values in bulk and distilled water due to electro-migration ( $\beta_{\text{Na}^+}^b = 5.17 \times 10^{-8}$   
 856  $\text{m}^2 \text{ s}^{-1} \text{V}^{-1}$  and  $\beta_{\text{Cl}^-}^b = 7.89 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{V}^{-1}$ ), meaning that electro-osmosis cannot be neglected  
 857 for the computation of the surface conductivity of the diffuse layer. It should be noted that it  
 858 may be complicated to distinguish between Stern and diffuse layer contributions to surface  
 859 conductivity especially at high ionic strengths due to diffuse layer compression and to the fact  
 860 that most counter-ions adsorbed in the Stern layer on the basal clay surface may be adsorbed  
 861 as outer-sphere surface complexes.

862

863

864 **3.4. Water conductivity**

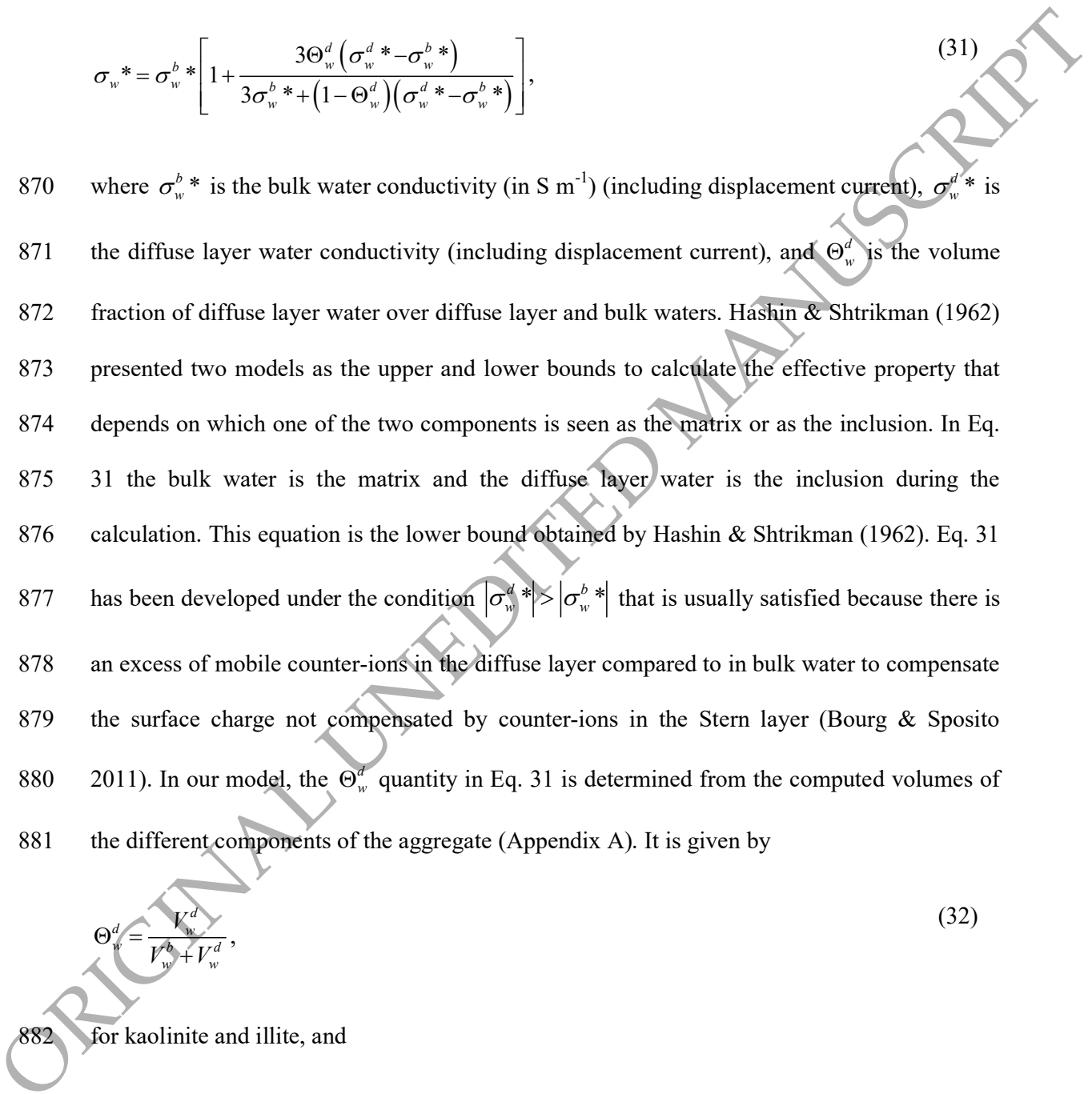
865 We consider that the bulk water and the diffuse layer water are continuous at the scale of the  
 866 SIP laboratory measurement and hence that they only contribute to the in-phase conductivity  
 867 of the clay material (see Section 3.1). The self-consistent model developed by Hashin &  
 868 Shtrikman (1962) is used here to compute clay water conductivity including the diffuse layer  
 869 contribution in the case of the thick diffuse layer assumption. It is written as

$$\sigma_w^* = \sigma_w^{b*} \left[ 1 + \frac{3\Theta_w^d (\sigma_w^{d*} - \sigma_w^{b*})}{3\sigma_w^{b*} + (1 - \Theta_w^d)(\sigma_w^{d*} - \sigma_w^{b*})} \right], \quad (31)$$

870 where  $\sigma_w^{b*}$  is the bulk water conductivity (in  $\text{S m}^{-1}$ ) (including displacement current),  $\sigma_w^{d*}$  is  
 871 the diffuse layer water conductivity (including displacement current), and  $\Theta_w^d$  is the volume  
 872 fraction of diffuse layer water over diffuse layer and bulk waters. Hashin & Shtrikman (1962)  
 873 presented two models as the upper and lower bounds to calculate the effective property that  
 874 depends on which one of the two components is seen as the matrix or as the inclusion. In Eq.  
 875 31 the bulk water is the matrix and the diffuse layer water is the inclusion during the  
 876 calculation. This equation is the lower bound obtained by Hashin & Shtrikman (1962). Eq. 31  
 877 has been developed under the condition  $|\sigma_w^{d*}| > |\sigma_w^{b*}|$  that is usually satisfied because there is  
 878 an excess of mobile counter-ions in the diffuse layer compared to in bulk water to compensate  
 879 the surface charge not compensated by counter-ions in the Stern layer (Bourg & Sposito  
 880 2011). In our model, the  $\Theta_w^d$  quantity in Eq. 31 is determined from the computed volumes of  
 881 the different components of the aggregate (Appendix A). It is given by

$$\Theta_w^d = \frac{V_w^d}{V_w^b + V_w^d}, \quad (32)$$

882 for kaolinite and illite, and



$$\Theta_w^d = \frac{V_w^d + V_{in}}{V_w^b + V_w^d + V_{in}}, \quad (33)$$

883 for Mt such as Na-Mt, where the interlayer space of Na-Mt is considered contributing of the  
 884 volume conductivity of the clay material similarly to the diffuse layer. Despite the fact that  
 885 the thickness of the interlayer space of Na-Mt is on the same order of magnitude than the  
 886 thickness of a TOT layer ( $\sim 1$  nm), we do not consider here that the part of the interlayer  
 887 space of Na-Mt that is not polarizing contributes to the surface conductivity of Na-Mt. Indeed,  
 888 it would be too complicated to consider at this stage of our model that the interlayer space  
 889 would contribute to the surface conductivity of the clay particles while the diffuse layer would  
 890 contribute to the water conductivity. In addition, our diffuse layer surface conductivity model  
 891 is more accurate for low  $\varphi_d$  potentials (see Appendix D) whereas our diffuse layer volume  
 892 conductivity model is adapted to any  $\varphi_d$  potentials when the electrolyte is symmetric (Leroy  
 893 *et al.* 2015) (see discussion related to Eq. 38).

894 In Eq. 31, the conductivity of the bulk water is calculated from ion concentration in bulk  
 895 water ( $C_i^b$ ) considering conduction current from ion electro-migration and displacement  
 896 current (Leroy *et al.* 2008)

$$\sigma_w^{b*} = e10^3 N_A \sum_{i=1}^N z_i \beta_i^b C_i^b + i\omega \epsilon_w. \quad (34)$$

897 In our model, simulated bulk water conductivity depends on temperature and salinity. Indeed,  
 898 in Eq. 34, computed ion mobilities in bulk water ( $\beta_i^b$ ) consider temperature and salinity (here  
 899 NaCl concentration) effects, and bulk water permittivity ( $\epsilon_w$ ) considers temperature effect  
 900 (Appendix B). Computed ion concentration in bulk water ( $C_i^b$ ) also considers temperature  
 901 effect via the simulation of the temperature dependence of the dissociation constant of water

902 molecules  $K_w$  (Eq. B2). For other types of ions than  $\text{Na}^+$  and  $\text{Cl}^-$  ions (here  $\text{H}^+$ ,  $\text{OH}^-$ , and  
 903  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions),  $\beta_i^b$  (298) is also computed as a function of the measured ion self-  
 904 diffusion coefficient in distilled water at a temperature of 298.15 K  $\overline{D}_i^b$  (298) (in  $\text{m}^2 \text{s}^{-1}$ )  
 905 reported in the phreeqc.dat database of the geochemical software Phreeqc (Parkhurst &  
 906 Appelo 2013).

907 Similarly to bulk water conductivity, the volume conductivity of the diffuse layer water is  
 908 determined from

$$\sigma_w^{d*} = \frac{e10^3 N_A}{\chi_d} \int_{x=0}^{x=\chi_d} \sum_{i=1}^N z_i B_i^d(x) C_i^b \exp\left[-\frac{q_i \varphi(x)}{k_B T}\right] dx + i\omega \overline{\varepsilon}_w, \quad (35)$$

$$B_i^d(x) = \beta_i^b \pm \beta_{eo}^d(x), \quad (36)$$

$$\beta_{eo}^d(x) = \frac{\varepsilon_w}{\eta_w} [\varphi(x) - \varphi_d], \quad (37)$$

$$\varphi(x) = \frac{4k_B T}{ez} \tanh^{-1} \left[ \tanh \left( \frac{ez\varphi_d}{4k_B T} \right) \exp(-\kappa x) \right], \quad (38)$$

909 where  $x$  is the distance from the beginning of the diffuse layer on the mineral side (in m),  
 910  $\chi_d = 2\chi_D$  (Leroy *et al.* 2015) is the diffuse layer thickness (with  $\chi_D$  being the Debye length,  
 911 Eq. A5) (in m),  $B_i^d$  is the ion mobility in the diffuse layer considering electro-osmosis (in  $\text{m}^2$   
 912  $\text{s}^{-1} \text{V}^{-1}$ ), and  $\kappa = \chi_D^{-1}$  (Leroy *et al.* 2015; Leroy *et al.* 2017b). Liquid water dynamic viscosity  
 913  $\eta_w$  (in  $\text{Pa s}^{-1}$ ) intervening in the calculation of the effect of electro-osmosis on surface  
 914 conductivity (Eqs 36 and 37) is calculated as a function of temperature (Appendix B). In Eq.  
 915 36, “+” and “-” stand for cations and anions, respectively. Eqs 35-38 show interesting  
 916 features for the conductivity calculations compared to the surface conductivity model based



917 on Bikerman's equation (Eqs D12-D14). Eq. 36 shows that electro-osmosis associated with  
 918 cations increases conductivity whereas it shows that electro-osmosis associated with anions  
 919 decreases conductivity because the solvent flow due to the excess of cationic charge is in the  
 920 direction of the electrical field and the solvent flow due to the excess of anionic charge is in  
 921 the direction opposed to the electrical field (Leroy *et al.* 2015). Eqs 37-38 also show that  
 922 electro-osmotic effect on conductivity is larger when the  $\varphi_d$  potential is larger hence when  
 923 ionic strength decreases at fixed pH or when pH is further away from IEP (pH value where  
 924 the zeta potential is zero) at fixed ionic strength. Bikerman's Eq. considers that both cations  
 925 and anions increase conductivity due to electro-osmosis with a value independent on the  $\varphi_d$   
 926 potential (Eqs D12 to D14).

927 When the electrolyte is not symmetric, the following equation, based on the Debye-Hückel  
 928 approximation (Appendix D), is used to calculate the electrical potential distribution in the  
 929 diffuse layer instead of Eq. 38:

$$\varphi(x) = \varphi_d \exp(-\kappa x). \quad (39)$$

930 Leroy *et al.* (2017b) computed the diffuse layer volume conductivity by calculating an  
 931 average (or mean) electrical potential in the diffuse layer  $\varphi_m$  (see Appendix E). In that case,  
 932 Eqs 35-38 become

$$\sigma_w^{d*} = e10^3 N_A \sum_{i=1}^N z_i B_i^d C_i^b \exp\left(-\frac{q_i \varphi_m}{k_B T}\right) + i\omega \varepsilon_w, \quad (40)$$

$$B_i^d = \beta_i^b \pm \beta_{eo}^d, \quad (41)$$

$$\beta_{eo}^d = \frac{\varepsilon_w}{\eta_w} (\varphi_m - \varphi_d), \quad (42)$$

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933 where  $\varphi_m$  is computed according to Eq. E8 for kaolinite and illite and Eq. E7 for Mt with  
 934 mobile ions in the interlayer space such as Na-Mt. Compared to Eqs 35-38, Eqs 40-42 and E8  
 935 or E7 have the advantage of not needing to know the electrical potential distribution in the  
 936 diffuse layer. But, these Eqs can be more approximate because they do not consider the  
 937 dependence on the distance from the beginning of the diffuse layer, which can lead to less  
 938 accurate results for the electrical potential distribution, especially at high ionic strengths when  
 939 the diffuse layer is highly compressed.

940

941 **3.5. Clay material conductivity**

942 In our model, minerals other than the main clay mineral are not considered conductive  
 943 compared to water and the main clay mineral. The effect of weakly conductive minerals on  
 944 the modeled background conductivity ( $\sigma_0^*$ ), which does not consider surface conductivity of  
 945 the particles, is considered here using the self-consistent model developed by Hashin &  
 946 Shtrikman (1962)

$$\sigma_0^* = \sigma_w^* \left[ 1 - \frac{3(1-c)}{(3-c)} \right], \quad (43)$$

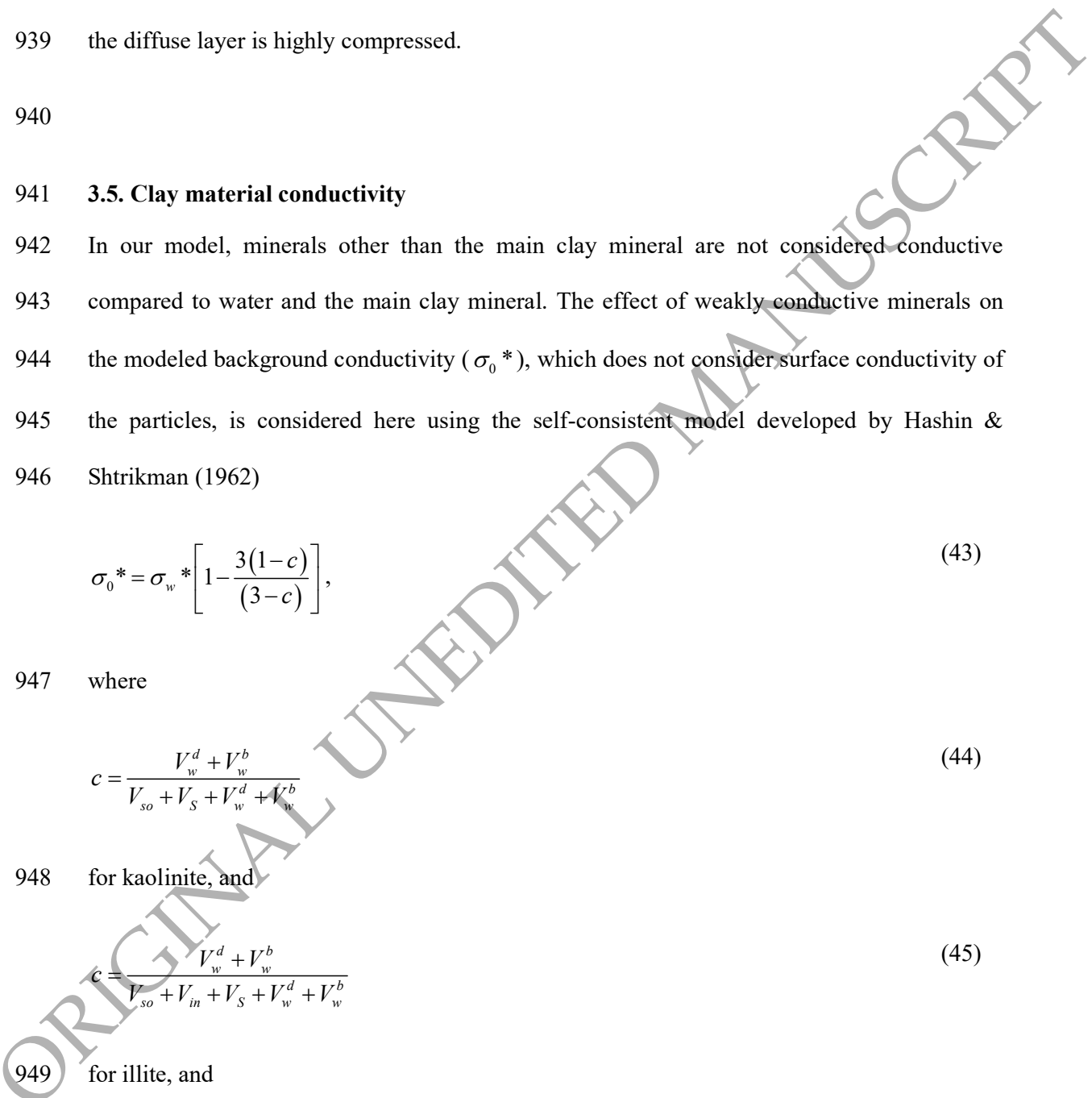
947 where

$$c = \frac{V_w^d + V_w^b}{V_{so} + V_S + V_w^d + V_w^b} \quad (44)$$

948 for kaolinite, and

$$c = \frac{V_w^d + V_w^b}{V_{so} + V_{in} + V_S + V_w^d + V_w^b} \quad (45)$$

949 for illite, and



$$c = \frac{V_{in} + V_w^d + V_w^b}{V_{so} + V_{in} + V_S + V_w^d + V_w^b}, \quad (46)$$

950 for Mt such as Na-Mt, where  $c$  is the volume fraction of conductive water and  $V_{so}$  (in  $m^3$ ) is  
 951 the volume of weakly conductive minerals (compared to water and the main clay mineral; the  
 952 subscript “so” means “solid other”) that are not considered conductive. The Stern layer is  
 953 considered not conductive too here.

954 The differential effective medium (DEM) theory (Bruggeman 1935; Hanai 1968; Sen 1984) is  
 955 used to compute the complex conductivity of the clay material after calculating the complex  
 956 conductivity of the clay particles and of the background medium. In the DEM theory, clay  
 957 particles are embedded in a self-similar way in the background medium (Sen *et al.* 1981).  
 958 First, a particle is added to the background medium and the influence of the particle upon the  
 959 conductivity of the medium is calculated. Then, the particle/background medium mixture is  
 960 added to another particle in the background medium and the conductivity of the new  
 961 particle/background medium mixture is calculated, and so on following an iterative procedure  
 962 until the desired porosity is reached (see Fig. 1 of Sen *et al.* 1981). The DEM theory assumes  
 963 that the current crosses all the pores in the investigated sample, i.e. that they are all  
 964 interconnected electrically speaking. It works well to describe the electrical properties  
 965 (conductivity and permittivity) of porous media with small and isolated contact regions  
 966 between the particles. It also simulates Maxwell-Wagner polarisation effect (Leroy & Revil  
 967 2009).

968 The DEM model uses the computed background conductivity ( $\sigma_0^*$ ), aggregate surface  
 969 conductivity ( $\sigma_s^*$ ) and volume fraction of the solid part of the main clay mineral in the  
 970 investigated sample ( $\Omega_s = V_{sc} / V_t$ ) ( $V_{sc}$  in  $m^3$  is the volume of the solid part of the main clay  
 971 mineral and  $V_t$  in  $m^3$  is the sample volume, see Appendix A) to compute clay material

972 complex conductivity. The cementation exponent  $m$  characterizing the shape of the aggregates  
 973 should also be considered in the DEM model. For a sphere,  $m = 1.5$  (Sen *et al.* 1981), and the  
 974  $m$  value increases when the aspect ratio (width to height ratio) of the particles or grains of the  
 975 material with a  $\sigma_s^*$  conductivity increases. For unconsolidated sands packed in the  
 976 laboratory,  $m = 1.3$ , consolidated sandstones,  $1.8 \leq m \leq 2$ , and  $1.2 \leq m \leq 4$  for most minerals  
 977 with goethite and clay particles exhibiting the highest  $m$  values (Mendelson & Cohen 1982).

978 In our model, DEM computations are presented as follows. The initial electrical conductivity  
 979 of the clay material is the background conductivity, i.e.  $\sigma^* = \sigma_0^*$  initially. Inclusions are clay  
 980 aggregates with a given shape that have a surface conductivity  $\sigma_s^*$  and volume fraction  $d\Omega_s$ ,  
 981 and that are randomly oriented in the medium. The depolarisation factor of inclusions,  $L$  (  
 982  $0 \leq L \leq 1$ ), which is necessary for the calculation of  $\sigma^*$  according to the DEM theory  
 983 (Mendelson & Cohen 1982), is calculated from

$$L = \frac{3 + \sqrt{9 + 36m^2 - 60m}}{6m}, \quad (47)$$

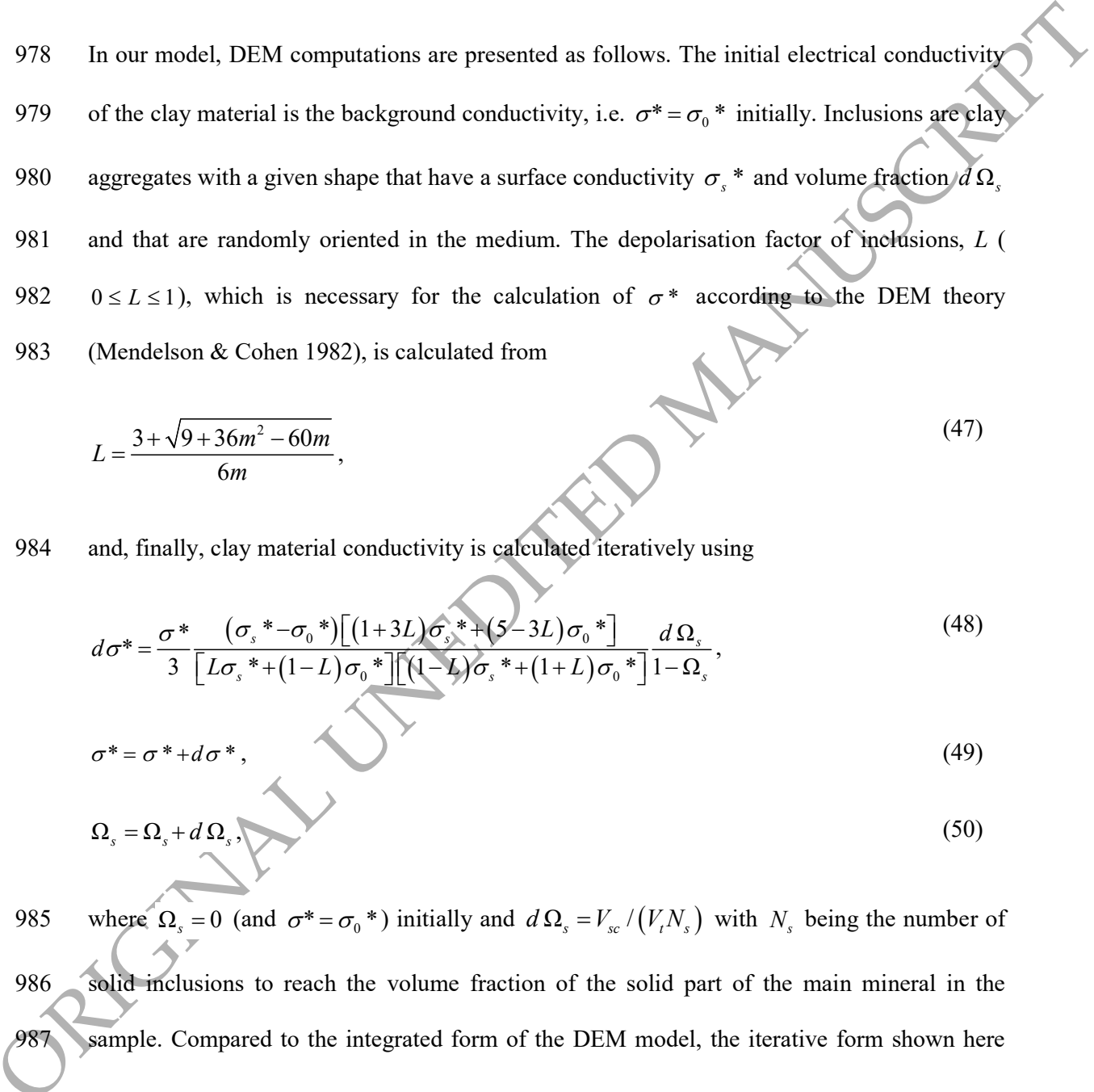
984 and, finally, clay material conductivity is calculated iteratively using

$$d\sigma^* = \frac{\sigma_s^* (\sigma_s^* - \sigma_0^*) [(1 + 3L)\sigma_s^* + (5 - 3L)\sigma_0^*]}{3 [L\sigma_s^* + (1 - L)\sigma_0^*] [(1 - L)\sigma_s^* + (1 + L)\sigma_0^*]} \frac{d\Omega_s}{1 - \Omega_s}, \quad (48)$$

$$\sigma^* = \sigma^* + d\sigma^*, \quad (49)$$

$$\Omega_s = \Omega_s + d\Omega_s, \quad (50)$$

985 where  $\Omega_s = 0$  (and  $\sigma^* = \sigma_0^*$ ) initially and  $d\Omega_s = V_{sc} / (V_t N_s)$  with  $N_s$  being the number of  
 986 solid inclusions to reach the volume fraction of the solid part of the main mineral in the  
 987 sample. Compared to the integrated form of the DEM model, the iterative form shown here



988 gives more accurate complex conductivity predictions when the inclusion eccentricity  
 989 increases compared to spherical inclusions (Sen *et al.* 1981; Mendelson & Cohen 1982; Sen  
 990 1984).

991 Our model allows determining the effective diameter of the  $k^{\text{th}}$  clay aggregate,  $d_k$  (Eq. 28).

992 The following equation (Mendelson & Cohen 1982) can be solved numerically to determine  
 993 aggregate eccentricity ( $e_c$ ) from the depolarisation factor ( $L$ ) calculation

$$\left| L - \frac{1+e_c^2}{e_c^3} (e_c - \tan^{-1} e_c) \right| = 0, \quad (51)$$

994 and the height of the  $k^{\text{th}}$  aggregate is then given by

$$h_k = \sqrt{\frac{d_k^2}{1+e_c^2}}. \quad (52)$$

995

#### 996 4 CONCLUSIONS

997 We have developed a new mechanistic model to understand and predict laboratory and field  
 998 spectral induced polarisation (SIP) measurements on clay materials including kaolinite, illite  
 999 and montmorillonite minerals from their microstructural and electrochemical properties.  
 1000 Water and surface conductivities, electrical formation factor, cementation exponent, sample  
 1001 porosity, and clay aggregate effective size distribution can be extracted from the comparison  
 1002 of the model to experimental data.

1003 Our model simulates the complex conductivity (for frequencies typically from 1 mHz to tens  
 1004 of kHz) of the different components of the clay material. It considers the polarisation of the  
 1005 Stern layers around clay particles forming aggregates and contributing to surface conductivity  
 1006 as well as montmorillonite interlayer space conduction and polarisation and Maxwell-Wagner

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1007 polarisation. The diffuse layer is assumed to contribute to the water conductivity or to the  
1008 surface conductivity of the particle depending notably if the diffuse layer is thicker or not to  
1009 the clay particle. Our model assumes one main clay mineral contributing to conduction and  
1010 polarisation in the low-frequency range. It also uses parameter values that can be measured in  
1011 the laboratory independently to the SIP measurements like temperature (for temperatures  
1012 between 2 and 87°C where water is liquid), cation exchange capacity (CEC), clay powder  
1013 mass, initial salinity, and sample volume. The parameters to be adjusted are the fraction of the  
1014 counter-charge and the ion effective mobility in the Stern layer, the number of stacked solid  
1015 layers per particle for montmorillonite and the cementation exponent characterizing the shape  
1016 of the aggregates.

1017 The comparison of the model predictions to the experimental data including the optimization  
1018 procedure and the related discussion will be presented in a companion paper. Our model can  
1019 test the validity of some petrophysical models developed at larger scale that are commonly  
1020 used to interpret laboratory and field SIP measurements. In addition, its predictions can be  
1021 checked by purely numerical SIP models developed at the scale of the clay particle and  
1022 constrained by high-resolution characterization measurements.

1023

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1033 No data were used for this theoretical paper.

## 1034 REFERENCES

- 1035 Aizebeokhai, A. P. & Oyeyemi, K. D., 2014. The use of the multiple-gradient array for  
1036 geoelectrical resistivity and induced polarization imaging, *Journal of Applied*  
1037 *Geophysics*, **111**, 364-376, doi:10.1016/j.jappgeo.2014.10.023.
- 1038 Ali, E. S., Askalany, A. A., Harby, K., Diab, M. R., Hussein, B. R. M. & Alsaman, A. S.,  
1039 2021. Experimental adsorption water desalination system utilizing activated clay for  
1040 low grade heat source applications, *Journal of Energy Storage*, **43**, 103219,  
1041 doi:10.1016/j.est.2021.103219.
- 1042 Avena, M. J. & De Pauli, C. P., 1998. Proton adsorption and electrokinetics of an Argentinean  
1043 montmorillonite, *Journal of Colloid and Interface Science*, **202**, 195-204,  
1044 doi:10.1006/jcis.1998.5402.
- 1045 Azua-Bustos, A., Fairén, A. G., Silva, C. G., Carrizo, D., Fernández-Martínez, M. Á., Arenas-  
1046 Fajardo, C., Fernández-Sampedro, M., Gil-Lozano, C., Sánchez-García, L., Ascaso,  
1047 C., Wierzbos, J. & Rampe, E. B., 2020. Inhabited subsurface wet smectites in the  
1048 hyperarid core of the Atacama Desert as an analog for the search for life on Mars, *Sci*  
1049 *Rep*, **10**, doi:10.1038/s41598-020-76302-z.
- 1050 Bandura, A. V. & Lvov, S. N., 2006. The Ionization Constant of Water over Wide Ranges of  
1051 Temperature and Density, *Journal of Physical and Chemical Reference Data*, **35**, 15-  
1052 30, doi:10.1063/1.1928231.
- 1053 Bernard, O., Kunz, W., Turq, P. & Blum, L., 1992. Self-Diffusion in Electrolyte-Solutions  
1054 Using the Mean Spherical Approximation, *Journal of Physical Chemistry*, **96**, 398-  
1055 403, doi:10.1021/J100180a074.
- 1056 Bikerman, J. J., 1940. Electrokinetic equations and surface conductance. A survey of the  
1057 diffuse double layer theory of colloidal solutions *Transactions of the Faraday Society*,  
1058 **35**, 154-160, doi:10.1039/TF9403500154.
- 1059 Binley, A., Hubbard, S. S., Huisman, J. A., Revil, A., Robinson, D. A., Singha, K. & Slater,  
1060 L. D., 2015. The emergence of hydrogeophysics for improved understanding of  
1061 subsurface processes over multiple scales, *Water Resources Research*, **51**, 3837-3866,  
1062 doi: 10.1002/2015WR017016.
- 1063 Binley, A. & Kemna, A., 2005. DC resistivity and induced polarization methods. *in*  
1064 *Hydrogeophysics*, pp. 129-156, ed. Hubbard, Y. R. a. S. S. Springer, New York,
- 1065 Binley, A. & Slater, L., 2020. *Resistivity and Induced Polarization: Theory and Applications*  
1066 *to the Near-Surface Earth*, edn, Vol., Cambridge University Press,  
1067 doi:10.1017/9781108685955.
- 1068 Bø Hunvik, K. W., Loch, P., Wallacher, D., Kirch, A., Cavalcanti, L. P., Rieß, M., Daab, M.,  
1069 Jovsanger, V., Grätz, S., Yokaichiya, F., Knudsen, K. D., Rodrigues Miranda, C.,  
1070 Breu, J. & Fossum, J. O., 2021. CO2 Adsorption Enhanced by Tuning the Layer

- 1071 Charge in a Clay Mineral, *Langmuir*, **37**, 14491-14499,  
 1072 doi:10.1021/acs.langmuir.1c02467.
- 1073 Bourg, I. C., Bourg, A. C. M. & Sposito, G., 2003. Modeling diffusion and adsorption in  
 1074 compacted bentonite: a critical review, *Journal of Contaminant Hydrology*, **61**, 293-  
 1075 302, doi:10.1016/s0169-7722(02)00128-6.
- 1076 Bourg, I. C. & Sposito, G., 2011. Molecular dynamics simulations of the electrical double  
 1077 layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl-CaCl<sub>2</sub>)  
 1078 solutions, *Journal of Colloid and Interface Science*, **360**, 701-715,  
 1079 doi:10.1016/j.jcis.2011.04.063.
- 1080 Bourg, I. C., Sposito, G. & Bourg, A. C. M., 2007. Modeling the acid-base surface chemistry  
 1081 of montmorillonite, *Journal of Colloid and Interface Science*, **312**, 297-310,  
 1082 doi:10.1016/j.jcis.2007.03.062.
- 1083 Brigatti, M., Galán, E. & Theng, B., 2013. 2 Chapter 2 - Structure and Mineralogy of Clay  
 1084 Minerals in *Handbook of Clay Science*, pp. 21-81, ed. Bergaya, F. L., G. Elsevier,  
 1085 Oxford,
- 1086 Bristow, T. F., Rampe, E. B., Achilles, C. N., Blake, D. F., Chipera, S. J., Craig, P., Crisp, J.  
 1087 A., Des Marais, D. J., Downs, R. T., Gellert, R., Grotzinger, J. P., Gupta, S., Hazen, R.  
 1088 M., Horgan, B., Hogancamp, J. V., Mangold, N., Mahaffy, P. R., McAdam, A. C.,  
 1089 Ming, D. W., Morookian, J. M., Morris, R. V., Morrison, S. M., Treiman, A. H.,  
 1090 Vaniman, D. T., Vasavada, A. R. & Yen, A. S., 2018. Clay mineral diversity and  
 1091 abundance in sedimentary rocks of Gale crater, Mars, *Science Advances*, **4**, eaar3330,  
 1092 doi:10.1126/sciadv.aar3330.
- 1093 Bruggeman, D. A. G., 1935. Berechnung verschiedener physikalischer Konstanten von  
 1094 heterogenen Substanzen, *Annalen der Physik*, **416**, 636-664,  
 1095 doi:10.1002/andp.19354160705.
- 1096 Bücker, M., Flores Orozco, A., Undorf, S. & Kemna, A., 2019. On the Role of Stern- and  
 1097 Diffuse-Layer Polarization Mechanisms in Porous Media, *Journal of Geophysical  
 1098 Research: Solid Earth*, **124**, 5656-5677, doi:10.1029/2019jb017679.
- 1099 Busch, A., Bertier, P., Gensterblum, Y., Rother, G., Spiers, C. J., Zhang, M. & Wentinck, H.  
 1100 M., 2016. On sorption and swelling of CO<sub>2</sub> in clays, *Geomechanics and Geophysics  
 1101 for Geo-Energy and Geo-Resources*, **2**, 111-130, doi:10.1007/s40948-016-0024-4.
- 1102 Cadene, A., Rotenberg, B., Durand-Vidal, S., Badot, J. C. & Turq, P., 2006. Dielectric  
 1103 spectroscopy as a probe for dynamic properties of compacted smectites, *Physics and  
 1104 Chemistry of the Earth*, **31**, 505-510, doi:10.1016/j.pce.2006.04.002.
- 1105 Chapman, D. L., 1913. A contribution to the theory of electrocapillarity *Philosophical  
 1106 Magazine Serie 6*, **25**, 475-481, doi: 10.1080/14786440408634187.
- 1107 Charlet, L., Alt-Epping, P., Wersin, P. & Gilbert, B., 2017. Diffusive transport and reaction in  
 1108 clay rocks: A storage (nuclear waste, CO<sub>2</sub>, H<sub>2</sub>), energy (shale gas) and water quality  
 1109 issue, *Advances in Water Resources*, **106**, 39-59,  
 1110 doi:10.1016/j.advwatres.2017.03.019.
- 1111 Chelidze, T. L. & Gueguen, Y., 1999. Electrical spectroscopy of porous rocks: a review - I.  
 1112 Theoretical models, *Geophysical Journal International*, **137**, 1-15,  
 1113 doi:10.1046/j.1365-246x.1999.00799.x.
- 1114 Christidis, G. E., 2010. Industrial Clays, 341-414, doi:10.1180/EMU-notes.9.9.
- 1115 de Lima, O. A. L. & Sharma, M. M., 1992. A generalized Maxwell-Wagner theory for  
 1116 membrane polarization in shaly sands, *Geophysics*, **57**, 431-440,  
 1117 doi:10.1190/1.1443257.
- 1118 Delgado, A. V., Arroyo, F. J., Gonzalez-Caballero, F., Shilov, V. N. & Borkovskaya, Y. B.,  
 1119 1998. The effect of the concentration of dispersed particles on the mechanisms of low-  
 1120 frequency dielectric dispersion (LFDD) in colloidal suspensions, *Colloids and*



- 1121 *Surfaces a-Physicochemical and Engineering Aspects*, **140**, 139-149,  
1122 doi:10.1016/S0927-7757(97)00272-0.
- 1123 Dufreche, J. F., Marry, V., Bernard, O. & Turq, P., 2001. Models for electrokinetic  
1124 phenomena in montmorillonite, *Colloids and Surfaces a-Physicochemical and*  
1125 *Engineering Aspects*, **195**, 171-180, doi:10.1016/S0927-7757(01)00840-8.
- 1126 El Alam, J., Revil, A. & Dick, P., 2023. Influence of the water content on the complex  
1127 conductivity of bentonite, *Engineering Geology*, **322**,  
1128 doi:10.1016/j.enggeo.2023.107183.
- 1129 Fixman, M., 1980. Charged Macromolecules in External Fields. I. The Sphere, *Journal of*  
1130 *Chemical Physics*, **72**, 5177-5186, doi:10.1063/1.439753.
- 1131 Gehin, A., Greneche, J. M., Tournassat, C., Brendle, J., Rancourt, D. G. & Charlet, L., 2007.  
1132 Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive  
1133 sites on a synthetic clay mineral, *Geochimica Et Cosmochimica Acta*, **71**, 863-876,  
1134 doi:10.1016/j.gca.2006.10.019.
- 1135 Glaser, D. R., Barrowes, B. E., Shubitidze, F. & Slater, L. D., 2023. Laboratory investigation  
1136 of high-frequency electromagnetic induction measurements for macro-scale relaxation  
1137 signatures, *Geophysical Journal International*, **235**, 1274-1291,  
1138 doi:10.1093/gji/ggad298.
- 1139 Gouy, G., 1910. Sur la constitution de la charge électrique à la surface d'un électrolyte,  
1140 *Annales de Physique (Paris) Série 4*, **9**, 457-468, doi:  
1141 10.1051/jphysap:019100090045700.
- 1142 Grahame, D. C., 1947. The Electrical Double Layer and the Theory of Electrocapillarity,  
1143 *Chemical Reviews*, **41**, 441-501, doi:10.1021/cr60130a002.
- 1144 Greathouse, J. A., Cygan, R. T., Fredrich, J. T. & Jerauld, G. R., 2016. Molecular Dynamics  
1145 Simulation of Diffusion and Electrical Conductivity in Montmorillonite Interlayers,  
1146 *The Journal of Physical Chemistry C*, **120**, 1640-1649, doi:10.1021/acs.jpcc.5b10851.
- 1147 Grim, R. E., 1962. *Applied Clay Mineralogy*, edn, Vol., McGraw-Hill, New York,
- 1148 Grosse, C. & Delgado, A. V., 2010. Dielectric dispersion in aqueous colloidal systems,  
1149 *Current Opinion in Colloid & Interface Science*, **15**, 145-159,  
1150 doi:10.1016/j.cocis.2009.11.004.
- 1151 Guggenheim, S. & Martin, R. T., 1995. Definition of Clay and Clay Mineral: Joint Report of  
1152 the AIPEA Nomenclature and CMS Nomenclature Committees, *Clays and Clay*  
1153 *Minerals*, **43**, 255-256, doi:10.1346/ccmn.1995.0430213.
- 1154 Guisseau, D., Mas, P. P., Beaufort, D., Girard, J. P., Inoue, A., Sanjuan, B., Petit, S., Lens, A.  
1155 & Genter, A., 2007. Significance of the depth-related transition montmorillonite-  
1156 beidellite in the Bouillante geothermal field (Guadeloupe, Lesser Antilles), *American*  
1157 *Mineralogist*, **92**, 1800-1813, doi:10.2138/am.2007.2398.
- 1158 Hanai, T., 1968. 5 Electrical properties of emulsions. in *Emulsions Science*, pp. 354-477, ed.  
1159 Sherman, P. Academic Press, New York,
- 1160 Hao, W., Flynn, S. L., Alessi, D. S. & Konhauser, K. O., 2018. Change of the point of zero  
1161 net proton charge (pHPZNPC) of clay minerals with ionic strength, *Chemical*  
1162 *Geology*, **493**, 458-467, doi:10.1016/j.chemgeo.2018.06.023.
- 1163 Hashin, Z. & Shtrikman, S., 1962. A Variational Approach to the Theory of the Effective  
1164 Magnetic Permeability of Multiphase Materials, *Journal of Applied Physics*, **33**, 3125-  
1165 3131, doi:10.1063/1.1728579.
- 1166 Hassan, M. S., Villieras, F., Gaboriaud, F. & Razafitianamaharavo, A., 2006. AFM and low-  
1167 pressure argon adsorption analysis of geometrical properties of phyllosilicates,  
1168 *Journal of Colloid and Interface Science*, **296**, 614-623,  
1169 doi:10.1016/j.jcis.2005.09.028.

- 1170 Hiemstra, T. & Van Riemsdijk, W. H., 2006. On the relationship between charge distribution,  
1171 surface hydration, and the structure of the interface of metal hydroxides, *Journal of*  
1172 *Colloid and Interface Science*, **301**, 1-18, doi:10.1016/j.jcis.2006.05.008.
- 1173 Hiemstra, T. & VanRiemsdijk, W. H., 1996. A surface structural approach to ion adsorption:  
1174 The charge distribution (CD) model, *Journal of Colloid and Interface Science*, **179**,  
1175 488-508, doi:10.1006/jcis.1996.0242.
- 1176 Hunter, R. J., 1981. *Zeta Potential in Colloid Science: Principles and Applications*, edn, Vol.,  
1177 Academic Press, New York, doi: 10.1016/C2013-0-07389-6
- 1178 Ismadji, S., Soetaredjo, F. E. & Ayucitra, A., 2015. *Clay Materials for Environmental*  
1179 *Remediation*, edn, Vol. 25, Springer, Surabaya, doi:10.1007/978-3-319-16712-1.
- 1180 Jougnot, D., Ghorbani, A., Revil, A., Leroy, P. & Cosenza, P., 2010a. Spectral induced  
1181 polarization of partially saturated clay-rocks: a mechanistic approach, *Geophysical*  
1182 *Journal International*, **180**, 210-224, doi:10.1111/j.1365-246X.2009.04426.x.
- 1183 Jougnot, D., Revil, A. & Leroy, P., 2009. Diffusion of ionic tracers in the Callovo-Oxfordian  
1184 clay-rock using the Donnan equilibrium model and the formation factor, *Geochimica*  
1185 *Et Cosmochimica Acta*, **73**, 2712-2726, doi:10.1016/j.gca.2009.01.035.
- 1186 Jougnot, D., Revil, A., Lu, N. & Wayllace, A., 2010b. Transport properties of the Callovo-  
1187 Oxfordian clay rock under partially saturated conditions, *Water Resources Research*,  
1188 **46**, doi:10.1029/2009wr008552.
- 1189 Karaborni, S., Smit, B., Heidug, W., Urai, J. & van Oort, E., 1996. The Swelling of Clays:  
1190 Molecular Simulations of the Hydration of Montmorillonite, *Science*, **271**, 1102-1104,  
1191 doi:10.1126/science.271.5252.1102.
- 1192 Kausar, A., Iqbal, M., Javed, A., Aftab, K., Nazli, Z.-i.-H., Bhatti, H. N. & Nouren, S., 2018.  
1193 Dyes adsorption using clay and modified clay: A review, *Journal of Molecular*  
1194 *Liquids*, **256**, 395-407, doi:10.1016/j.molliq.2018.02.034.
- 1195 Kemna, A., Binley, A., Cassiani, G., Niederleithinger, E., Revil, A., Slater, L., Williams, K.  
1196 H., Orozco, A. F., Haegel, F. H., Hordt, A., Kruschwitz, S., Leroux, V., Titov, K. &  
1197 Zimmermann, E., 2012. An overview of the spectral induced polarization method for  
1198 near-surface applications, *Near Surface Geophysics*, **10**, 453-468, doi: 10.3997/1873-  
1199 0604.2012027.
- 1200 Khaldoun, A., Moller, P., Fall, A., Wegdam, G., De Leeuw, B., Méheust, Y., Otto Fossum, J.  
1201 & Bonn, D., 2009. Quick Clay and Landslides of Clayey Soils, *Physical Review*  
1202 *Letters*, **103**, doi:10.1103/PhysRevLett.103.188301.
- 1203 Khaled, E. M. & Stucki, J. W., 1991. Iron Oxidation State Effects on Cation Fixation in  
1204 Smectites, *Soil Science Society of America Journal*, **55**, 550,  
1205 doi:10.2136/sssaj1991.03615995005500020045x.
- 1206 Leroy, P., Devau, N., Revil, A. & Bizi, M., 2013. Influence of surface conductivity on the  
1207 apparent zeta potential of amorphous silica nanoparticles, *Journal of Colloid and*  
1208 *Interface Science*, **410**, 81-93, doi:10.1016/j.jcis.2013.08.012.
- 1209 Leroy, P., Lassin, A., Azaroual, M. & Andre, L., 2010. Predicting the surface tension of  
1210 aqueous 1:1 electrolyte solutions at high salinity, *Geochimica Et Cosmochimica Acta*,  
1211 **74**, 5427-5442, doi:10.1016/j.gca.2010.06.012.
- 1212 Leroy, P., Li, S., Jougnot, D., Revil, A. & Wu, Y., 2017a. Modeling the evolution of complex  
1213 conductivity during calcite precipitation on glass beads, *Geophysical Journal*  
1214 *International*, **209**, 123-140, doi:10.1093/gji/ggx001.
- 1215 Leroy, P. & Revil, A., 2004. A triple-layer model of the surface electrochemical properties of  
1216 clay minerals, *Journal of Colloid and Interface Science*, **270**, 371-380,  
1217 doi:10.1016/j.jcis.2003.08.007.

- 1218 Leroy, P. & Revil, A., 2009. A mechanistic model for the spectral induced polarization of  
1219 clay materials, *Journal of Geophysical Research-Solid Earth*, **114**, 1-21,  
1220 doi:10.1029/2008jb006114.
- 1221 Leroy, P., Revil, A., Altmann, S. & Tournassat, C., 2007. Modeling the composition of the  
1222 pore water in a clay-rock geological formation (Callovo-Oxfordian, France),  
1223 *Geochimica Et Cosmochimica Acta*, **71**, 1087-1097, doi:10.1016/j.gca.2006.11.009.
- 1224 Leroy, P., Revil, A., Kemna, A., Cosenza, P. & Ghorbani, A., 2008. Complex conductivity of  
1225 water-saturated packs of glass beads, *Journal of Colloid and Interface Science*, **321**,  
1226 103-117, doi:10.1016/j.jcis.2007.12.031.
- 1227 Leroy, P., Tournassat, C., Bernard, O., Devau, N. & Azaroual, M., 2015. The electrophoretic  
1228 mobility of montmorillonite. Zeta potential and surface conductivity effects, *Journal*  
1229 *of Colloid and Interface Science*, **451**, 21-39, doi:10.1016/j.jcis.2015.03.047.
- 1230 Leroy, P., Tournassat, C. & Bizi, M., 2011. Influence of surface conductivity on the apparent  
1231 zeta potential of TiO<sub>2</sub> nanoparticles, *Journal of Colloid and Interface Science*, **356**,  
1232 442-453, doi:10.1016/j.jcis.2011.01.016.
- 1233 Leroy, P., Weigand, M., Mériguet, G., Zimmermann, E., Tournassat, C., Fagerlund, F.,  
1234 Kemna, A. & Huisman, J. A., 2017b. Spectral induced polarization of Na-  
1235 montmorillonite dispersions, *Journal of Colloid and Interface Science*, **505**, 1093-  
1236 1110, doi:10.1016/j.jcis.2017.06.071.
- 1237 Lesmes, D. P. & Morgan, F. D., 2001. Dielectric spectroscopy of sedimentary rocks, *Journal*  
1238 *of Geophysical Research-Solid Earth*, **106**, 13329-13346, doi:10.1029/2000jb900402.
- 1239 Li, S., Leroy, P., Heberling, F., Devau, N., Jougnot, D. & Chiaberge, C., 2016. Influence of  
1240 surface conductivity on the apparent zeta potential of calcite, *Journal of Colloid and*  
1241 *Interface Science*, **468**, 262-275, doi:10.1016/j.jcis.2016.01.075.
- 1242 Li, Z., Dong, M., Li, S. & Huang, S., 2006. CO<sub>2</sub> sequestration in depleted oil and gas  
1243 reservoirs—caprock characterization and storage capacity, *Energy Conversion and*  
1244 *Management*, **47**, 1372-1382, doi:10.1016/j.enconman.2005.08.023.
- 1245 Lide, D. R., 1990. *CRC Handbook of Chemistry and Physics* edn, Vol., CRC Press, Boca  
1246 Raton,
- 1247 Liu, J., Wang, S., Javadpour, F., Feng, Q. & Cha, L., 2022. Hydrogen Diffusion in Clay Slit:  
1248 Implications for the Geological Storage, *Energy & Fuels*, **36**, 7651-7660,  
1249 doi:10.1021/acs.energyfuels.2c01189.
- 1250 Lyklema, J., Dukhin, S. S. & Shilov, V. N., 1983. The relaxation of the double-layer around  
1251 colloidal particles and the low-frequency dielectric-dispersion. Part I. Theoretical  
1252 Considerations, *Journal of Electroanalytical Chemistry*, **143**, 1-21,  
1253 doi:10.1016/S0022-0728(83)80251-4.
- 1254 Lyklema, J. & Minor, M., 1998. On surface conduction and its role in electrokinetics,  
1255 *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, **140**, 33-41,  
1256 doi:10.1016/S0927-7757(97)00266-5.
- 1257 Madden, T. R., 1976. Random Networks and Mixing Laws, *Geophysics*, **41**, 1104-1125,  
1258 doi:10.1190/1.2035907.
- 1259 Mainault, A., Leroy, P., Mendieta, A. & Jougnot, D., 2024. A mechanistic model for the  
1260 complex conductivity of clay materials. II. Comparison to experimental data,  
1261 *submitted to Geophysical Journal International*.
- 1262 Malusis, M. A., Shackelford, C. D. & Olsen, H. W., 2003. Flow and transport through clay  
1263 membrane barriers, *Engineering Geology*, **70**, 235-248, doi:10.1016/s0013-  
1264 7952(03)00092-9.
- 1265 Marshall, D. J. & Madden, T. R., 1959. Induced Polarization, a Study of Its Causes,  
1266 *Geophysics*, **24**, 790-816, doi:10.1190/1.1438659.

- 1267 Martin, T., Günther, T., Orozco, A. F. & Dahlin, T., 2020. Evaluation of spectral induced  
 1268 polarization field measurements in time and frequency domain, *Journal of Applied*  
 1269 *Geophysics*, **180**, doi:10.1016/j.jappgeo.2020.104141.
- 1270 Massat, L., Cuisinier, O., Bihannic, I., Claret, F., Pelletier, M., Masrouri, F. & Gaboreau, S.,  
 1271 2016. Swelling pressure development and inter-aggregate porosity evolution upon  
 1272 hydration of a compacted swelling clay, *Applied Clay Science*, **124-125**, 197-210,  
 1273 doi:10.1016/j.clay.2016.01.002.
- 1274 Maxwell, J. C., 1892. *A Treatise on Electricity and Magnetism*, third edition edn, Vol.,  
 1275 Oxford University Press, London,
- 1276 Mc Bride, E. F., 2012. Petrology of the Eureka Quartzite (Middle and Late Ordovician), Utah  
 1277 and Nevada, U.S.A, *Rocky Mountain Geology*, **47**, 81-111,  
 1278 doi:10.2113/gsrocky.47.2.81.
- 1279 Mc Bride, M. B. & Baveye, P., 2002. Diffuse double-layer models, long-range forces, and  
 1280 ordering in clay colloids, *Soil Science Society of America Journal*, **66**, 1207-1217,  
 1281 doi:10.2136/sssaj2002.1207.
- 1282 Melkior, T., Gaucher, E. C., Brouard, C., Yahiaoui, S., Thoby, D., Clinard, C., Ferrage, E.,  
 1283 Guyonnet, D., Tournassat, C. & Coelho, D., 2009. Na<sup>+</sup> and HTO diffusion in  
 1284 compacted bentonite: Effect of surface chemistry and related texture, *Journal of*  
 1285 *Hydrology*, **370**, 9-20, doi:10.1016/j.jhydrol.2009.02.035.
- 1286 Mendelson, K. S. & Cohen, M. H., 1982. The effect of grain anisotropy on the electrical-  
 1287 properties of sedimentary-rocks, *Geophysics*, **47**, 257-263, doi:10.1190/1.1441332.
- 1288 Mendieta, A., Jougnot, D., Leroy, P. & Mainault, A., 2021. Spectral Induced Polarization  
 1289 Characterization of Non-Consolidated Clays for Varying Salinities—An Experimental  
 1290 Study, *Journal of Geophysical Research: Solid Earth*, **126**,  
 1291 doi:10.1029/2020jb021125.
- 1292 Mouzon, J., Bhuiyan, I. U. & Hedlund, J., 2016. The structure of montmorillonite gels  
 1293 revealed by sequential cryo-XHR-SEM imaging, *Journal of Colloid and Interface*  
 1294 *Science*, **465**, 58-66, doi:10.1016/j.jcis.2015.11.031.
- 1295 Nagendrappa, G., 2011. Organic synthesis using clay and clay-supported catalysts, *Applied*  
 1296 *Clay Science*, **53**, 106-138, doi:10.1016/j.clay.2010.09.016.
- 1297 Neuzil, C. E., 1994. How permeable are clays and shales?, *Water Resources Research*, **30**,  
 1298 145-150, doi:10.1029/93wr02930.
- 1299 O'Konski, C. T., 1960. Electric properties of macromolecules. V. Theory of ionic polarization  
 1300 in polyelectrolytes, *The Journal of Physical Chemistry*, **64**, 605-619,  
 1301 doi:10.1021/j100834a023.
- 1302 Okay, G., Leroy, P., Ghorbani, A., Cosenza, P., Camerlynck, C., Cabrera, J., Florsch, N. &  
 1303 Revil, A., 2014. Spectral induced polarization of clay-sand mixtures: Experiments and  
 1304 modeling, *Geophysics*, **79**, E353-E375, doi:10.1190/Geo2013-0347.1.
- 1305 Olhoeft, G. R., 1981. Electrical properties of rocks. in *Physical properties of rocks and*  
 1306 *minerals*, pp. 257–339, ed. Y. S. Touloukian, W. R. J., and R. F. Roy. McGraw-Hill,  
 1307 New York,
- 1308 Parkhurst, D. L. & Appelo, C. A. J., 2013. 43 Description of Input and Examples for  
 1309 PHREEQC Version 3--a Computer Program for Speciation, Batch-reaction, One-  
 1310 dimensional Transport, and Inverse Geochemical Calculations. in *U.S. Geological*  
 1311 *Survey Techniques and Methods, Book 6, Modeling Techniques*, pp. 497, ed. Reston,  
 1312 U. S. G. S., Denver,
- 1313 Pelton, W. H., Ward, S. H., Hallof, P. G., Sill, W. R. & Nelson, P. H., 1978. Mineral  
 1314 Discrimination and Removal of Inductive Coupling with Multifrequency-Ip,  
 1315 *Geophysics*, **43**, 588-609, doi:10.1190/1.1440839.

- 1316 Petraglia, M. D., Ashton, N., Lewis, S. G., De Groote, I., Duffy, S. M., Bates, M., Bates, R.,  
1317 Hoare, P., Lewis, M., Parfitt, S. A., Peglar, S., Williams, C. & Stringer, C., 2014.  
1318 Hominin Footprints from Early Pleistocene Deposits at Happisburgh, UK, *Plos One*,  
1319 **9**, e88329, doi:10.1371/journal.pone.0088329.
- 1320 Porté, J., Bretaudeau, F. & Girard, J. F., 2023. 3-D complex resistivity imaging using  
1321 controlled source electromagnetic data: a multistage procedure using a second order  
1322 polynomial parametrization, *Geophysical Journal International*, **233**, 839-860,  
1323 doi:10.1093/gji/ggac486.
- 1324 Pride, S., 1994. Governing Equations for the Coupled Electromagnetics and Acoustics of  
1325 Porous-Media, *Physical Review B*, **50**, 15678-15696,  
1326 doi:10.1103/PhysRevB.50.15678.
- 1327 Qi, Y. & Wu, Y., 2022. Electrical Conductivity of Clayey Rocks and Soils: A Non-Linear  
1328 Model, *Geophysical Research Letters*, **49**, doi:10.1029/2021gl097408.
- 1329 Qi, Y. & Wu, Y., 2024. Induced Polarization of Clayey Rocks and Soils: Non-Linear  
1330 Complex Conductivity Models, *Journal of Geophysical Research: Solid Earth*, **129**,  
1331 doi:10.1029/2023jb028405.
- 1332 Rasmusson, M., Rowlands, W., O'Brien, R. W. & Hunter, R. J., 1997. The dynamic mobility  
1333 and dielectric response of sodium bentonite, *Journal of Colloid and Interface Science*,  
1334 **189**, 92-100, doi:10.1006/jcis.1997.4793.
- 1335 Revil, A., 2012. Spectral induced polarization of shaly sands: Influence of the electrical  
1336 double layer, *Water Resources Research*, **48**, 1-23, doi:10.1029/2011WR011260.
- 1337 Revil, A., Cathles, L. M., Losh, S. & Nunn, J. A., 1998. Electrical conductivity in shaly sands  
1338 with geophysical applications, *Journal of Geophysical Research-Solid Earth*, **103**,  
1339 23925-23936, doi:10.1029/98JB02125.
- 1340 Revil, A. & Florsch, N., 2010. Determination of permeability from spectral induced  
1341 polarization in granular media, *Geophysical Journal International*, **181**, 1480-1498,  
1342 doi:10.1111/j.1365-246X.2010.04573.x.
- 1343 Revil, A., Ghorbani, A., Jougnot, D. & Yven, B., 2023. Induced polarization of clay-rich  
1344 materials — Part 1: The effect of desiccation, *Geophysics*, **88**, MR195-MR210,  
1345 doi:10.1190/geo2022-0510.1.
- 1346 Revil, A. & Glover, P. W. J., 1997. Theory of ionic-surface electrical conduction in porous  
1347 media, *Physical Review B*, **55**, 1757-1773, doi:10.1103/PhysRevB.55.1757.
- 1348 Revil, A. & Leroy, P., 2001. Hydroelectric coupling in a Clayey Material, *Geophysical  
1349 Research Letters*, **28**, 1643-1646, doi:10.1029/2000GL012268.
- 1350 Revil, A. & Leroy, P., 2004. Constitutive equations for ionic transport in porous shales,  
1351 *Journal of Geophysical Research-Solid Earth*, **109**, 1-19, doi:10.1029/2003jb002755.
- 1352 Revil, A., Leroy, P. & Titov, K., 2005. Characterization of transport properties of argillaceous  
1353 sediments: Application to the Callovo-Oxfordian argillite, *Journal of Geophysical  
1354 Research-Solid Earth*, **110**, B06202, doi:10.1029/2004jb003442.
- 1355 Revil, A. & Linde, N., 2006. Chemico-electromechanical coupling in microporous media, *J  
1356 Colloid Interface Sci*, **302**, 682-694, doi:10.1016/j.jcis.2006.06.051.
- 1357 Revil, A. & Skold, M., 2011. Salinity dependence of spectral induced polarization in sands  
1358 and sandstones, *Geophysical Journal International*, **187**, 813-824, doi:10.1111/j.1365-  
1359 246X.2011.05181.x.
- 1360 Richter, S. M. & Sevic-Muraca, E. M., 2000. Characterization of concentrated colloidal  
1361 suspensions using time-dependent photon migration measurements, *Colloids and  
1362 Surfaces A: Physicochemical and Engineering Aspects*, **172**, 163-173,  
1363 doi:10.1016/s0927-7757(00)00581-1.

- 1364 Robinson, D. A., 2004. Measurement of the solid dielectric permittivity of clay minerals and  
1365 granular samples using a time domain reflectometry immersion method, *Vadose Zone*  
1366 *Journal*, **3**, 705-713, doi:10.2136/vzj2004.0705.
- 1367 Rotenberg, B., Cadéne, A., Dufrière, J. F., Durand-Vidal, S., Badot, J. C. & Turq, P., 2005.  
1368 An Analytical Model for Probing Ion Dynamics in Clays with Broadband Dielectric  
1369 Spectroscopy, *The Journal of Physical Chemistry B*, **109**, 15548-15557,  
1370 doi:10.1021/jp051586k.
- 1371 Ruiz Pestana, L., Kolluri, K., Head-Gordon, T. & Lammers, L. N., 2016. Direct Exchange  
1372 Mechanism for Interlayer Ions in Non-Swelling Clays, *Environmental Science &*  
1373 *Technology*, **51**, 393-400, doi:10.1021/acs.est.6b04747.
- 1374 Sahai, N. & Sverjensky, D. A., 1997. Evaluation of internally consistent parameters for the  
1375 triple-layer model by the systematic analysis of oxide surface titration data,  
1376 *Geochimica Et Cosmochimica Acta*, **61**, 2801-2826, doi:10.1016/S0016-  
1377 7037(97)00128-2.
- 1378 Schlumberger, C., 1920. *Study of underground electrical prospecting*, edn, Vol., Paris,
- 1379 Schramm, L. L. & Kwak, J. C. T., 1982. Influence of Exchangeable Cation Composition on  
1380 the Size and Shape of Montmorillonite Particles in Dilute Suspension, *Clays and Clay*  
1381 *Minerals*, **30**, 40-48, doi:10.1346/Ccmn.1982.0300105.
- 1382 Schroeder, P. A., 2018. *Clays in the Critical Zone*, edn, Vol., Cambridge University Press,  
1383 Cambridge, UK, doi:10.1017/9781316480083.
- 1384 Schurr, J. M., 1964. On the Theory of the Dielectric Dispersion of Spherical Colloidal  
1385 Particles in Electrolyte Solution, *The Journal of Physical Chemistry*, **68**, 2407-2413,  
1386 doi:10.1021/j100791a004.
- 1387 Schwarz, G., 1962. A theory of the low-frequency dielectric dispersion of colloidal particles  
1388 in electrolyte solution *The Journal of Physical Chemistry*, **66**, 2636-2642,  
1389 doi:10.1021/j100818a067.
- 1390 Secor, R. B. & Radke, C. J., 1985. Spillover of the diffuse double layer on montmorillonite  
1391 particles, *Journal of Colloid and Interface Science*, **103**, 237-244, doi:10.1016/0021-  
1392 9797(85)90096-7.
- 1393 Sellin, P. & Leupin, O. X., 2013. The Use of Clay as an Engineered Barrier in Radioactive-  
1394 Waste Management – A Review, *Clays and Clay Minerals*, **61**, 477-498,  
1395 doi:10.1346/ccmn.2013.0610601.
- 1396 Sen, P. N., 1984. Grain Shape Effects on Dielectric and Electrical-Properties of Rocks,  
1397 *Geophysics*, **49**, 586-587, doi:10.1190/1.1441695.
- 1398 Sen, P. N., Scala, C. & Cohen, M. H., 1981. A self-similar model for sedimentary rocks with  
1399 application to the dielectric constant of fused glass beads, *Geophysics*, **46**, 781-795,  
1400 doi:10.1190/1.1441215.
- 1401 Sondi, I., Biscan, J. & Pravidic, V., 1996. Electrokinetics of pure clay minerals revisited,  
1402 *Journal of Colloid and Interface Science*, **178**, 514-522, doi:10.1006/jcis.1996.0146.
- 1403 Sposito, G., 1989. *The Chemistry of Soils* edn, Vol., Oxford University Press, New York,
- 1404 Sposito, G., Skipper, N. T., Sutton, R., Park, S. h., Soper, A. K. & Greathouse, J. A., 1999.  
1405 Surface geochemistry of the clay minerals, *Proceedings of the National Academy of*  
1406 *Sciences*, **96**, 3358-3364, doi:10.1073/pnas.96.7.3358.
- 1407 Tombacz, E. & Szekeres, M., 2004. Colloidal behavior of aqueous montmorillonite  
1408 suspensions: the specific role of pH in the presence of indifferent electrolytes, *Applied*  
1409 *Clay Science*, **27**, 75-94, doi:10.1016/j.clay.2004.01.001.
- 1410 Tombacz, E. & Szekeres, M., 2006. Surface charge heterogeneity of kaolinite in aqueous  
1411 suspension in comparison with montmorillonite, *Applied Clay Science*, **34**, 105-124,  
1412 doi:10.1016/j.clay.2006.05.009.

- 1413 Tournassat, C. & Appelo, C. A. J., 2011. Modelling approaches for anion-exclusion in  
1414 compacted Na-bentonite, *Geochimica Et Cosmochimica Acta*, **75**, 3698-3710,  
1415 doi:10.1016/j.gca.2011.04.001.
- 1416 Tournassat, C., Bizi, M., Braibant, G. & Crouzet, C., 2011. Influence of montmorillonite  
1417 tactoid size on Na-Ca cation exchange reactions, *Journal of Colloid and Interface*  
1418 *Science*, **364**, 443-454, doi:10.1016/j.jcis.2011.07.039.
- 1419 Tournassat, C., Bourg, I. C., Steefel, C. I. & Bergaya, F., 2015. Surface Properties of Clay  
1420 Minerals, pp. 5-31, doi:10.1016/b978-0-08-100027-4.00001-2.
- 1421 Tournassat, C., Chapron, Y., Leroy, P., Bizi, M. & Boulahya, F., 2009. Comparison of  
1422 molecular dynamics simulations with triple layer and modified Gouy-Chapman  
1423 models in a 0.1 M NaCl-montmorillonite system, *Journal of Colloid and Interface*  
1424 *Science*, **339**, 533-541, doi:10.1016/j.jcis.2009.06.051.
- 1425 Tournassat, C., Davis, J. A., Chiaberge, C., Grangeon, S. & Bourg, I. C., 2016a. Modeling the  
1426 Acid-Base Properties of Montmorillonite Edge Surfaces, *Environmental Science &*  
1427 *Technology*, **50**, 13436-13445, doi:10.1021/acs.est.6b04677.
- 1428 Tournassat, C., Gaboreau, S., Robinet, J. C., Bourg, I. & Steefel, C. I., 2016b. Impact of  
1429 microstructure on anion exclusion in compacted clay media, **22**, 137-149,  
1430 doi:10.1346/cms-wls-21.11.
- 1431 Tournassat, C., Grangeon, S., Leroy, P. & Giffaut, E., 2013. Modeling specific pH dependent  
1432 sorption of divalent metals on montmorillonite surfaces. A review of pitfalls, recent  
1433 achievements and current challenges, *American Journal of Science*, **313**, 395-451,  
1434 doi:10.2475/05.2013.01.
- 1435 Tournassat, C. & Steefel, C. I., 2019. Reactive Transport Modeling of Coupled Processes in  
1436 Nanoporous Media, *Reviews in Mineralogy and Geochemistry*, **85**, 75-109,  
1437 doi:10.2138/rmg.2019.85.4.
- 1438 Triantafylis, J. & Lesch, S. M., 2005. Mapping clay content variation using electromagnetic  
1439 induction techniques, *Computers and Electronics in Agriculture*, **46**, 203-237,  
1440 doi:10.1016/j.compag.2004.11.006.
- 1441 Udonne, J. D., 2011. A comparative study of recycling of used lubrication oils using  
1442 distillation, acid and activated charcoal with clay methods, *Journal of Petroleum and*  
1443 *Gas Engineering*, **2**, 12-19, doi:10.5897/JPGE.9000001.
- 1444 Vandiver, P. B., Soffer, O., Klima, B. & Svoboda, J., 1989. The Origins of Ceramic  
1445 Technology at Dolni Věstonice, Czechoslovakia, *Science*, **246**, 1002-1008,  
1446 doi:10.1126/science.246.4933.1002.
- 1447 Vinegar, H. J. & Waxman, M. H., 1984. Induced Polarization of Shaly Sands, *Geophysics*, **49**,  
1448 1267-1287, doi:10.1190/1.1441755.
- 1449 Viseras, C., Carazo, E., Borrego-Sánchez, A., García-Villén, F., Sánchez-Espejo, R., Cerezo,  
1450 P. & Aguzzi, C., 2019. Clay Minerals in Skin Drug Delivery, *Clays and Clay*  
1451 *Minerals*, **67**, 59-71, doi:10.1007/s42860-018-0003-7.
- 1452 Viseras, C., Cerezo, P., Sanchez, R., Salcedo, I. & Aguzzi, C., 2010. Current challenges in  
1453 clay minerals for drug delivery, *Applied Clay Science*, **48**, 291-295,  
1454 doi:10.1016/j.clay.2010.01.007.
- 1455 Von Smoluchowski, M., 1905. Zur theorie der elektrischen kataphorese und der  
1456 oberflächenleitung, *Physikalische Zeitschrift* **6**, 529-531.
- 1457 Von Smoluchowski, M., 1921. edn, Vol. II, pp. 366-428, L. Graetz, Leipzig,
- 1458 Wander, M. C. F. & Clark, A. E., 2008. Structural and Dielectric Properties of Quartz-Water  
1459 Interfaces, *Journal of Physical Chemistry C*, **112**, 19986-19994,  
1460 doi:10.1021/Jp803642c.
- 1461 Waxman, M. H. & Smits, L. J. M., 1968. Electrical conductivities in oil bearing shaly sands,  
1462 *Society of Petroleum Engineers Journal*, **8**, 107-122, doi:10.2118/1863-A.

- 1463 Weller, A., Slater, L., Huisman, J. A., Esser, O. & Haegel, F. H., 2015. On the specific  
1464 polarizability of sands and sand-clay mixtures, *Geophysics*, **80**, A57-A61,  
1465 doi:10.1190/Geo2014-0509.1.
- 1466 Weller, A., Slater, L. & Nordsiek, S., 2013. On the relationship between induced polarization  
1467 and surface conductivity: Implications for petrophysical interpretation of electrical  
1468 measurements, *Geophysics*, **78**, D315-D325, doi:10.1190/Geo2013-0076.1.
- 1469 Xu, T., Sonnenthal, E., Spycher, N. & Pruess, K., 2006. TOUGHREACT—A simulation  
1470 program for non-isothermal multiphase reactive geochemical transport in variably  
1471 saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological  
1472 sequestration, *Computers & Geosciences*, **32**, 145-165,  
1473 doi:10.1016/j.cageo.2005.06.014.
- 1474 Yang, D., Peng, S., Hartman, M. R., Gup-ton-Campolongo, T., Rice, E. J., Chang, A. K., Gu,  
1475 Z., Lu, G. Q. & Luo, D., 2013. Enhanced transcription and translation in clay hydrogel  
1476 and implications for early life evolution, *Sci Rep*, **3**, doi:10.1038/srep03165.
- 1477 Yates, D. E., Levine, S. & Healy, T. W., 1974. Site-binding Model of the Electrical Double  
1478 Layer at the Oxide/Water interface, *Journal of the Chemical Society, Faraday  
1479 Transactions*, **70**, 1807-1818, doi:10.1039/F19747001807.
- 1480 Yven, B., Sammartino, S., Geraud, Y., Homand, F. & Villieras, F., 2007. Mineralogy, texture  
1481 and porosity of Callovo-Oxfordian argillites of the Meuse/Haute-Marne region  
1482 (eastern Paris Basin), *Mémoires de la Société géologique de France*, **178**, 73-90.
- 1483 Zhang, L., Lu, X., Liu, X., Zhou, J. & Zhou, H., 2014. Hydration and Mobility of Interlayer  
1484 Ions of (Nax, Cay)-Montmorillonite: A Molecular Dynamics Study, *The Journal of  
1485 Physical Chemistry C*, **118**, 29811-29821, doi:10.1021/jp508427c.
- 1486 Zimmermann, E., Kemna, A., Berwix, J., Glaas, W., Munch, H. M. & Huisman, J. A., 2008.  
1487 A high-accuracy impedance spectrometer for measuring sediments with low  
1488 polarizability, *Measurement Science & Technology*, **19**, 105603, doi:10.1088/0957-  
1489 0233/19/10/105603.
- 1490
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1492 **APPENDIX A. COMPUTED VOLUMES OF THE COMPONENTS OF THE CLAY**  
 1493 **MATERIAL**

1494 The volume of the solid part of the clay sample (not considering the interlayer space) (in m<sup>3</sup>)  
 1495 is given by

$$V_s = \frac{10^{-3} \delta_s}{\rho_s}. \quad (\text{A1})$$

1496 The volumes of the solid part of the main clay mineral and of the remaining minerals in the  
 1497 sample are determined, respectively, from

$$V_{sc} = V_s \xi_c, \quad (\text{A2})$$

$$V_{so} = V_s (1 - \xi_c), \quad (\text{A3})$$

1498 assuming that the minerals have roughly the same volumetric mass density.

1499 The volume of the diffuse layer water is calculated using

$$V_w^d = S_o \chi_d, \quad (\text{A4})$$

1500 where  $S_o$  is the outer surface area of the main clay mineral in the mud (in m<sup>2</sup>) and  $\chi_d = 2\chi_D$ .

1501 The Debye length is calculated as a function of the bulk water chemical composition using

$$\chi_D = \sqrt{\frac{\epsilon_w k_B T}{e^2 10^3 N_A \sum_{i=1}^N z_i^2 C_i^b}}; \quad (\text{A5})$$

1502 The quantity  $S_o$  in Eq. A4 is given by

$$S_o = \delta_{sc} S S_o, \quad (\text{A6})$$

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1503 where  $\delta_{sc} = \delta_s \xi_c$  is the solid mass of the main clay mineral in the mud (in g) and  $SS_o$  is the  
 1504 outer specific surface area of the main clay mineral in the mud (in  $\text{m}^2 \text{g}^{-1}$ ), which is computed  
 1505 using

$$SS_o = SS_e + \frac{SS_b}{n_c}, \quad (\text{A7})$$

1506 where  $n_c$  is the number of solid layers per clay particle (Tournassat *et al.* 2011). In Eq. A7,  
 1507 the  $SS_e$  quantity can be neglected for Mt and illite (see Section 2.1.).

1508 The volume of the Stern layers is calculated using

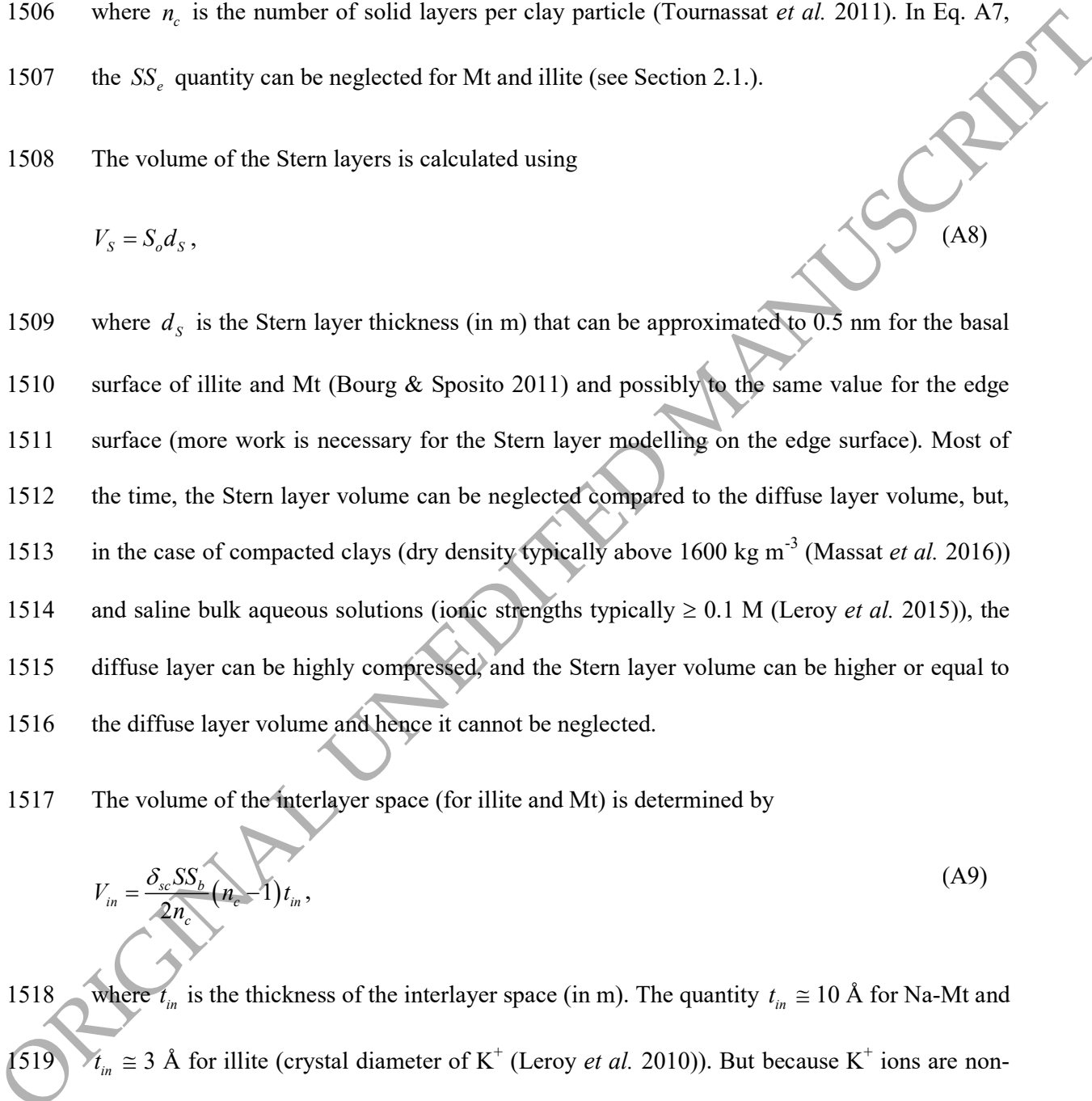
$$V_s = S_o d_s, \quad (\text{A8})$$

1509 where  $d_s$  is the Stern layer thickness (in m) that can be approximated to 0.5 nm for the basal  
 1510 surface of illite and Mt (Bourg & Sposito 2011) and possibly to the same value for the edge  
 1511 surface (more work is necessary for the Stern layer modelling on the edge surface). Most of  
 1512 the time, the Stern layer volume can be neglected compared to the diffuse layer volume, but,  
 1513 in the case of compacted clays (dry density typically above  $1600 \text{ kg m}^{-3}$  (Massat *et al.* 2016))  
 1514 and saline bulk aqueous solutions (ionic strengths typically  $\geq 0.1 \text{ M}$  (Leroy *et al.* 2015)), the  
 1515 diffuse layer can be highly compressed, and the Stern layer volume can be higher or equal to  
 1516 the diffuse layer volume and hence it cannot be neglected.

1517 The volume of the interlayer space (for illite and Mt) is determined by

$$V_{in} = \frac{\delta_{sc} SS_b}{2n_c} (n_c - 1) t_{in}, \quad (\text{A9})$$

1518 where  $t_{in}$  is the thickness of the interlayer space (in m). The quantity  $t_{in} \cong 10 \text{ \AA}$  for Na-Mt and  
 1519  $t_{in} \cong 3 \text{ \AA}$  for illite (crystal diameter of  $\text{K}^+$  (Leroy *et al.* 2010)). But because  $\text{K}^+$  ions are non-



1520 solvated and for the mud we can take the mass of the clay powder containing already  $K^+$  ions  
 1521 for  $V_s$ , we can assume  $t_{in} \cong 0 \text{ \AA}$  for illite (Tournassat *et al.* 2015) ( $t_{in} \cong 0 \text{ \AA}$  also for  
 1522 kaolinite).

1523 Finally, the volume of bulk water is calculated according to the volume of the sample minus  
 1524 the estimated volumes of the other components of the mud:

$$V_w^b = V_t - V_s - V_w^d - V_s - V_{in}. \quad (\text{A10})$$

1525

## 1526 APPENDIX B. COMPUTATION OF MODEL PARAMETER VALUES FROM 1527 TEMPERATURE AND SALINITY

1528 In the model, the liquid water permittivity, for temperatures ranging from  $2^\circ\text{C}$  to  $87^\circ\text{C}$  (Lide  
 1529 1990) and minus the decimal logarithm of the dissociation constant of water molecules (  
 1530  $pK_w = -\log K_w$ ), for temperatures ranging from  $0^\circ\text{C}$  to  $100^\circ\text{C}$  (Bandura & Lvov 2006), are  
 1531 computed as a function of the temperature in degree Celsius using

$$\varepsilon_w = \varepsilon_0 (a_0 + a_1 T_C + a_2 T_C^2 + a_3 T_C^3), \quad (\text{B1})$$

$$pK_w = b_0 + b_1 T_C + b_2 T_C^2 + b_3 T_C^3, \quad (\text{B2})$$

1532 where  $a_0 = 87.895$ ,  $a_1 = -4.0029 \times 10^{-1}$ ,  $a_2 = 8.6132 \times 10^{-4}$ ,  $a_3 = -9.565 \times 10^{-7}$ ,  $b_0 = 14.95$ ,  
 1533  $b_1 = -4.38 \times 10^{-2}$ ,  $b_2 = 2.32 \times 10^{-4}$ , and  $b_3 = -6.4 \times 10^{-7}$  in order to reproduce the related  
 1534 measurements.

1535 The ion  $i$  mobility in bulk water at a temperature  $T$  (in K) is calculated from

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$$T = T_c + 273.15, \quad (\text{B3})$$

$$\beta_i^b(T) = \beta_i^b(298) \frac{T}{298} \frac{\eta_w(298)}{\eta_w}, \quad (\text{B4})$$

1536 where  $\beta_i^b(298)$  is the ion  $i$  mobility in bulk water at a temperature of 298.15 K,  $\eta_w(298)$  is  
 1537 the liquid water dynamic viscosity at a temperature of 298.15 K ( $\sim 0.8905 \times 10^{-3}$  Pa s), and  $\eta_w$   
 1538 is the liquid water dynamic viscosity at a temperature  $T$ .

1539 Ions of opposite charge decrease ion mobility in bulk water because of their mutual  
 1540 interaction (e.g., Bernard *et al.* 1992).  $\text{Na}^+$  and  $\text{Cl}^-$  ion mobilities in bulk water at a  
 1541 temperature of 298.15 K are determined as a function of NaCl concentration in bulk water  
 1542 using

$$\beta_{\text{Na}^+}^b(298) = (a_0 + a_1 C_{\text{NaCl}}^b + a_2 C_{\text{NaCl}}^{b2}) 10^{-8}, \quad (\text{B5})$$

1543 for  $C_{\text{NaCl}}^b \leq 0.1\text{M}$ ,

$$\beta_{\text{Na}^+}^b(298) = (a_0' + a_1' C_{\text{NaCl}}^b) 10^{-8}, \quad (\text{B6})$$

1544 for  $C_{\text{NaCl}}^b > 0.1\text{M}$ ,

$$\beta_{\text{Cl}^-}^b(298) = (b_0 + b_1 C_{\text{NaCl}}^b + b_2 C_{\text{NaCl}}^{b2}) 10^{-8}, \quad (\text{B7})$$

1545 for  $C_{\text{NaCl}}^b \leq 0.1\text{M}$ , and

$$\beta_{\text{Cl}^-}^b(298) = (b_0' + b_1' C_{\text{NaCl}}^b) 10^{-8}, \quad (\text{B8})$$

1546 for  $C_{\text{NaCl}}^b > 0.1\text{M}$ ,

1547 where  $a_0 = 5.07490$ ,  $a_1 = -9.55617$ ,  $a_2 = 7.73145$ ,  $a_0' = 4.32333$ ,  $a_1' = -1.07333$ ,  
 1548  $b_0 = 7.77572$ ,  $b_1 = 10.77742$ ,  $b_0' = 6.92256$ , and  $b_1' = 1.14556$  in order to reproduce the  
 1549 corresponding values simulated by the mean spherical approximation (MSA) method  
 1550 (Bernard *et al.* 1992; Leroy *et al.* 2015). For other types of ions (here  $H^+$ ,  $OH^-$ , and  $Ca^{2+}$  and  
 1551  $SO_4^{2-}$  ions from the interlayer space and dissolved clay minerals, according to Leroy *et al.*  
 1552 2017b), we use for ion  $i$  mobility in bulk water

$$\beta_i^b(298) = \frac{\overline{D}_i^b(298)|q_i|}{k_B 298}, \quad (B9)$$

1553 where  $\overline{D}_i^b(298)$  is the measured ion  $i$  self-diffusion coefficient in distilled (bulk) water at a  
 1554 temperature of 298.15 K (in  $m^2 s^{-1}$ ) (Table B1 (Parkhurst & Appelo 2013)) (Eq. B9 is the  
 1555 Nernst-Einstein equation).

1556 **Table B1**

1557 Ion self-diffusion coefficient values in distilled water from the phreeqc.dat database

	Na <sup>+</sup>	Cl <sup>-</sup>	H <sup>+</sup>	OH <sup>-</sup>	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
$\overline{D}_i^b(298)$ ( $10^{-9} m s^{-1}$ )	1.33	2.03	9.31	5.27	0.793	1.07

1558

1559 In Eq. B3, the liquid water dynamic viscosity at a temperature  $T$  (in K) is computed from

$$\eta_w = \frac{\eta_w(293)}{10^{A/B}}, \quad (B10)$$

$$A = 1.37023(T - 293.15) + 8.36 \times 10^{-4}(T - 293.15)^2, \quad (B11)$$

$$B = T - 164.15, \quad (B12)$$

1560

1560 where  $\eta_w(293)$  is the liquid water dynamic viscosity at a temperature of 293 K ( $\sim 1.002 \times 10^{-3}$   
 1561 Pa s).

1562 The ion mobility of the counter-ions in the Stern layer at a temperature  $T$  (K) is calculated  
 1563 from

$$\beta_s = \beta_s(298) [1 + v_s (T - 298.15)], \quad (\text{B13})$$

$$\beta_s = \bar{\beta}_i^b(298) m r_s [1 + v_s (T - 298.15)], \quad (\text{B14})$$

1564 where  $v_s = 0.037 \text{ K}^{-1}$  for sodium ion (Revil *et al.* 1998) (there are other  $v_s$  values for  
 1565 monovalent and divalent cations reported in Revil *et al.* 1998) and  $m r_s$  is the mobility ratio  
 1566 between a ion in the Stern layer and the same ion in bulk and distilled water at a temperature  
 1567 of 298.15 K ( $I$  is the ionic strength in M),

$$m r_s = \frac{\beta_s(298)}{\bar{\beta}_i^b(298)}, \quad (\text{B15})$$

$$\bar{\beta}_i^b(298) = \lim_{I \rightarrow 0} \beta_i^b(298), \quad (\text{B16})$$

$$I = 0.5 \sum_{i=1}^N z_i^2 C_i^b. \quad (\text{B17})$$

1568 The Stern layer of clays is mostly occupied by ions with the same sign of the charge. This is  
 1569 the reason why we use in Eqs B14 and B15  $\bar{\beta}_i^b(298)$  instead of  $\beta_i^b(298)$ . Indeed, because of  
 1570 the mutual interaction of anions and cations in bulk water,  $\beta_i^b(298)$  decreases when salt  
 1571 concentration increases, which is not expected in the Stern layer of clays containing usually

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1572 mostly cations counter-ions. In our model,  $\overline{\beta}_i^b$  (298) is a constant that is not decreasing with  
 1573 salinity on the contrary to  $\beta_i^b$  (298).

1574

## 1575 APPENDIX C. COMPUTED BULK WATER CHEMICAL COMPOSITION

1576 In our model, NaCl concentration in bulk water after evaporation,  $C_{\text{NaCl}}^b$ , is determined by:

$$C_{\text{NaCl}}^b = C_{\text{NaCl}}^0 \frac{\delta_t^0}{\delta_i^1}. \quad (\text{C1})$$

1577 HCl and NaOH electrolytes can also be added to NaCl electrolyte to change the pH. Hence,  
 1578 their concentrations after evaporation become

$$C_{\text{HCl}}^b = C_{\text{HCl}}^0 \frac{\delta_t^0}{\delta_i^1}, \quad (\text{C2})$$

$$C_{\text{NaOH}}^b = C_{\text{NaOH}}^0 \frac{\delta_t^0}{\delta_i^1}. \quad (\text{C3})$$

1579 Ion concentrations in bulk water,  $C_i^b$ , are calculated according to:

$$a_{\text{H}^+}^b = 10^{-\text{pH}}, \quad (\text{C4})$$

$$a_{\text{OH}^-}^b = K_w / a_{\text{H}^+}^b, \quad (\text{C5})$$

$$C_{\text{H}^+}^b \cong a_{\text{H}^+}^b, \quad (\text{C6})$$

$$C_{\text{OH}^-}^b \cong a_{\text{OH}^-}^b, \quad (\text{C7})$$

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$$C_{\text{Cl}^-}^b = C_{\text{NaCl}}^b + C_{\text{HCl}}^b + \overline{C_{\text{Cl}^-}^b}, \quad (\text{C8})$$

$$C_{\text{Na}^+}^b = C_{\text{NaCl}}^b + C_{\text{NaOH}}^b + \sum_i -z_i \overline{C_{i^{z_i^+}}^b} + \sum_{i \neq j} z_j \overline{C_{j^{z_j^-}}^b} - C_{\text{H}^+}^b + C_{\text{OH}^-}^b + C_{\text{Cl}^-}^b, \quad (\text{C9})$$

1580 where  $\overline{C_{i^{z_i^+}}^b}$  and  $\overline{C_{j^{z_j^-}}^b}$  are ion (cation and anion) concentrations from dissolved minerals and  
 1581 Mt interlayer space. It should be noted that more complex electrolytes can be considered in  
 1582 our model, but here we focus on an electrolyte containing mostly  $\text{Na}^+$ ,  $\text{Cl}^-$  and leached ions  
 1583 because we will show in Mainault *et al.* (2024) the comparison of our SIP model predictions to  
 1584 the corresponding measurements reported by Mendieta *et al.* (2021).

1585

#### 1586 APPENDIX D. COMPUTED ELECTRICAL POTENTIAL AT THE D-PLANE AND 1587 SURFACE CONDUCTIVITY OF THE DIFFUSE LAYER.

1588 The  $\varphi_d$  potential is calculated by minimizing the following function:

$$|Q_{d1} - Q_{d2}| = 0, \quad (\text{D1})$$

$$Q_{d1} = \sqrt{2\varepsilon_w k_B T 10^3 N_A \sum_{i=1}^N C_i^b \left[ \exp\left(-\frac{q_i \varphi_d}{k_B T}\right) - 1 \right]}, \quad (\text{D2})$$

$$Q_{d2} = -Q_0 (1 - f_Q), \quad (\text{D3})$$

1589 where  $Q_{d1}$  is the surface charge density of the diffuse layer calculated from the Gouy-  
 1590 Chapman theory (Hunter 1981) based on the assumption that the electrical potential in the  
 1591 diffuse layer does not change with the distance from the mineral surface at the end of the



1592 diffuse layer, i.e.  $(d\phi/dx)_{x=\chi_d} = 0 \text{ V m}^{-1}$ . The expression of the surface charge density of the  
 1593 diffuse layer  $Q_{d2}$  (Eq. D3) was determined from

$$f_Q = \frac{Q_\beta}{Q_\beta + Q_{d2}}, \text{ and} \quad (\text{D4})$$

$$Q_{d2} = -(Q_0 + Q_\beta), \quad (\text{D5})$$

1594 which make

$$f_Q = -\frac{Q_\beta}{Q_0}, \quad (\text{D6})$$

1595 and finally

$$Q_{d2} = -Q_0(1 - f_Q). \quad (\text{D7})$$

1596 Eq. D5 is the electroneutrality condition.

1597 According to Schurr 1964, the low-frequency conductivity of a spherical particle of diameter  
 1598  $d$  due to EDL polarisation and conduction is given by

$$\sigma_s = \frac{4}{d} \left( \Sigma_s \frac{i\omega\tau}{1+i\omega\tau} + \Sigma_s^d \right), \quad (\text{D8})$$

1599 where the first term in brackets represents conductivity from the polarisation of the bounded  
 1600 ion layer with surface conductivity  $\Sigma_s$  (in S) (Schwarz 1962) and the second term in brackets  
 1601 represents conductivity from ion electro-migration in the diffuse layer with surface  
 1602 conductivity  $\Sigma_s^d$  (Leroy *et al.* 2008).

1603 Leroy *et al.* 2017b) showed that the first term in brackets of Eq. D8 significantly  
 1604 underestimates the complex conductivity magnitude of clay aggregates because it does not

1605 consider the surface area of the clay particles inside the aggregate. To reproduce the measured  
 1606 Na-Mt complex conductivity magnitude, they therefore proposed to multiply this term by the  
 1607 ratio of the surface area of the clay particles inside the aggregate ( $S_o$ ) to the surface area of  
 1608 the non-porous spherical particle with the same effective diameter  $d_k$  ( $S_k$ ). We used the same  
 1609 method than Leroy *et al.* 2017b) to calculate aggregate conductivity considering EDL  
 1610 polarisation and conduction in the case here of a thin diffuse layer. After some algebraic  
 1611 developments, we obtained the following equation for aggregate conductivity

$$\sigma_s = \frac{2}{3} \phi_a \beta_s f_Q Q_V \frac{i\omega\tau}{1+i\omega\tau} - \frac{2}{3\theta} \phi_a \frac{\Sigma_s^d}{Q_0} Q_V. \quad (\text{D9})$$

1612 In Eq. D9, the surface conductivity of the diffuse layer can be calculated from

$$\Sigma_s^d = 10^3 N_A \int_0^{\lambda_d} \left\{ \sum_{i=1}^N |q_i| [\beta_i^d C_i^d(x) - \beta_i^b C_i^b] + q_i C_i^d(x) \beta_{eo}^d(x) \right\} dx, \quad (\text{D10})$$

1613 where the first term of Eq. D10 represents diffuse layer surface conductivity due to ion  
 1614 electro-migration and the second term of Eq. D10 is diffuse layer surface conductivity due to  
 1615 electro-osmosis (Leroy *et al.* 2011). By assuming that ion concentration in the diffuse layer  
 1616 follows a Boltzmann's distribution, i.e.  $C_i^d(x) = C_i^b \exp[-q_i \varphi(x) / k_B T]$  and that ion mobility  
 1617 in the diffuse layer is equal to ion mobility in bulk water, i.e.  $\beta_i^d = \beta_i^b$ , and using Eq. 29, Eq.  
 1618 D10 reduces to

$$\Sigma_s^d = 10^3 N_A \int_0^{\lambda_d} \left\{ \sum_{i=1}^N |q_i| \beta_i^b C_i^b \left\{ \exp\left[-\frac{q_i \varphi(x)}{k_B T}\right] - 1 \right\} + \right. \\ \left. q_i C_i^b \exp\left[-\frac{q_i \varphi(x)}{k_B T}\right] \frac{\bar{\epsilon}_w}{\eta_w} [\varphi(x) - \varphi_d] \right\} dx, \quad (\text{D11})$$

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1619 where the electrical potential distribution in the diffuse layer  $\varphi(x)$  is given by Eq. 37 or Eq.  
1620 38.

1621 According to Revil & Glover 1997), Eq. D11 can be simplified to

$$\Sigma_s^d = \chi_d 10^3 N_A \sum_{i=1}^N |q_i| B_i^d C_i^b \left[ \exp\left(-\frac{q_i \varphi_d}{2k_B T}\right) - 1 \right], \quad (\text{D12})$$

$$B_i^d = \beta_i^b + m_i^d, \quad (\text{D13})$$

1622 where  $m_i^d$  (in  $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$ ) in Eq. D13 is related to the increase of electrical conductivity of the  
1623 diffuse layer due to electro-osmosis (Bikerman 1940; Revil & Glover 1997; Leroy *et al.*  
1624 2011). The term  $m_i^d$  is written as

$$m_i^d = \frac{2\bar{\varepsilon}_w k_B T}{\eta_w |q_i|}. \quad (\text{D14})$$

1625 Eqs D12-D14 have been developed considering a symmetric electrolyte where cation valence  
1626  $z_+$  is equal to anion valence  $z_-$  (Pride 1994; Lyklema & Minor 1998). In the case of an  
1627 asymmetric electrolyte, Eqs D12-D14 can be used to compute the diffuse layer surface  
1628 conductivity despite being more approximate than in the case of a symmetric electrolyte  
1629 (Revil & Glover 1997). Eqs D12-D14 are strictly valid for  $|\varphi_d| < k_B T / (ze)$  where  $z$  is the  
1630 valence of the symmetric electrolyte ( $k_B T / e \cong 25.7 \text{ mV}$  at a temperature of 298.15 K).  
1631 Indeed, they are based on the Debye-Hückel (D-H) approximation, i.e.  $|\varphi| \ll k_B T / (ze)$ , to  
1632 compute the electrical potential distribution in the diffuse layer from the  $\varphi_d$  potential and the  
1633 Poisson-Boltzmann (P-B) equation, i.e.  $\varphi(x) = \varphi_d \exp(-x / \chi_d)$  (Hunter 1981; Pride 1994). In  
1634 our model, we consider that the diffuse layer can contribute to the surface conductivity of the  
1635 aggregate when the diffuse layer is thinner than the particle. For illite and Mt, this occurs

1636 typically when the diffuse layer is highly compressed (see end of section 3.3) at high ionic  
 1637 strengths typically  $\geq 0.1$  M where the  $\phi_d$  potential magnitude should be low satisfying  
 1638  $|\phi_d| < k_B T / (ze)$  (Sondi *et al.* 1996; Leroy *et al.* 2015). Therefore, in this condition, Eqs D12-  
 1639 D14 are valid for our calculation of the surface conductivity of the diffuse layer within the  
 1640 aggregate. It should be noted that Eq. D11 with Eq. 37 or 38 or Eqs D12-D14 can be used to  
 1641 compute the diffuse layer surface conductivity of kaolinite and illite particles at typically  
 1642 lower ionic strengths than Mt particles because kaolinite and in a lesser extent illite particles  
 1643 are thicker than Na-Mt particles and they do not have interlayer space containing hydrated  
 1644 and mobile cations.

1645 If the ion mobilities are similar in the diffuse layer, Eq. D12 can be reduced to

$$\Sigma_s^d = B_d Q_d, \quad (\text{D15})$$

1646 and Eq. D9 finally becomes

$$\sigma_s = \frac{2}{3} \phi_a \left[ \beta_s f_Q \frac{i\omega\tau}{1+i\omega\tau} + \frac{B_d}{g} (1-f_Q) \right] Q_v, \quad (\text{D16})$$

$$\sigma_s = \frac{2}{3} \phi_a \left[ \beta_s f_Q \frac{i\omega\tau}{1+i\omega\tau} + \widetilde{B}_d (1-f_Q) \right] Q_v. \quad (\text{D17})$$

1647 The  $g$  ratio can be computed using Eq. A6

$$g = \frac{S_o}{S_k} = \frac{\delta_{sc} S S_o}{\pi d_k^2}. \quad (\text{D18})$$

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1651 **APPENDIX E. COMPUTED AVERAGE ELECTRICAL POTENTIAL IN THE**  
 1652 **DIFFUSE LAYER AND INTERLAYER SPACE OF NA-MT**

1653 We use the volume averaging method to compute  $\varphi_m$  as a function of CEC and bulk water  
 1654 chemical composition (Revil & Leroy 2004; Leroy *et al.* 2007; Leroy *et al.* 2017b). We  
 1655 assume that the (usually negative) surface charge of the clay mineral is compensated by the  
 1656 excess of counter-charge per unit pore volume in the Stern and diffuse layers and interlayer  
 1657 space of Na-Mt, i.e.

$$\frac{1}{V_t} \left( \int_0^{S_{in}} Q_0 dS + \int_0^{V_{in}} Q_V^{in} dV + \int_0^{S_o} Q_0 dS + \int_0^{V_S+V_w^d} Q_V^o dV \right) = 0, \quad (E1)$$

1658 where  $S_{in}$  is the surface area of the interlayer space (in  $m^2$ ),  $Q_V^{in}$  is the excess of charge per  
 1659 unit interlayer space volume (in  $C m^{-3}$ ) and  $Q_V^o$  is the excess of charge per unit Stern and  
 1660 diffuse layer volumes. In the case of kaolinite and illite, the first two terms in Eq. E1 can be  
 1661 assumed to be zero (no interlayer space and interlayer space containing non-solvated  $K^+$  ions,  
 1662 respectively). In the case of Na-Mt, we assume that  $Q_V^{in} = Q_V^o$ . Eq. E1 then becomes

$$\frac{1}{V_t} \left( \int_0^{S_{in}+S_o} Q_0 dS + \int_0^{V_{in}+V_S+V_w^d} Q_V^o dV \right) = 0. \quad (E2)$$

1663 If  $Q_0$  and  $Q_V^o$  are assumed constant throughout the pore surface and volume, respectively,  
 1664 and, according to Eq. A6, Eq. E2 simplifies to:

$$Q_V^o = - \frac{\delta_{sc} SS}{V_{in} + V_S + V_w^d} Q_0, \quad (E3)$$

1665 for Na-Mt, and

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$$Q_V^o = -\frac{\delta_{sc}SS}{V_S + V_w^d} Q_0, \quad (E4)$$

1666 for kaolinite and illite. The excess of charge per unit pore volume in the diffuse layer and  
 1667 interlayer space of Na-Mt (contributing solely to conduction due to ion electro-migration) is  
 1668 written as:

$$Q_V^d = 10^3 N_A \sum_{i=1}^N q_i \overline{C_i^d}, \quad (E5)$$

$$Q_V^d = (1 - f_Q) Q_V^o, \quad (E6)$$

1669 and, finally, using Eqs E3, E5, and E6 for Na-Mt and Eqs E4, E5, and E6 for kaolinite and  
 1670 illite, the  $\varphi_m$  potential was computed from

$$10^3 N_A \sum_{i=1}^N q_i C_i^b \exp\left(-\frac{q_i \varphi_m}{k_B T}\right) + (1 - f_Q) \frac{\delta_{sc}SS}{V_{in} + V_S + V_w^d} Q_0 = 0, \quad (E7)$$

1671 for Na-Mt, and

$$10^3 N_A \sum_{i=1}^N q_i C_i^b \exp\left(-\frac{q_i \varphi_m}{k_B T}\right) + (1 - f_Q) \frac{\delta_{sc}SS}{V_S + V_w^d} Q_0 = 0, \quad (E8)$$

1672 for kaolinite and illite, where  $\overline{C_i^d} = C_i^b \exp(-q_i \varphi_m / k_B T)$  is the average ion concentration in  
 1673 the diffuse layer and interlayer space of Na-Mt or in the diffuse layer of kaolinite and illite,  
 1674 which follows a Boltzmann's distribution. The  $Q_0$  quantity is expressed as a function of CEC  
 1675 using Eq. 14. We assume in Eq. E7 that the interlayer space of Na-Mt behaves like the EDL  
 1676 on the clay external surface. This assumption could be considered rather crude but we do not  
 1677 want to complicate more our model and hence add additional parameter values to be fitted in  
 1678 our model.