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# 1 Predictive surface complexation model of the calcite-aqueous solution 2 interface: the impact of high concentration and complex composition of brines

3 Jan Vinogradov<sup>a</sup>, Miftah Hidayat<sup>a,b</sup>, Mohammad Sarmadivaleh<sup>b</sup>, Jos Derksen<sup>a</sup>, David Vega-Maza<sup>a,c</sup>,  
4 Stefan Iglauer<sup>d,e</sup>, Damien Jougnot<sup>f</sup>, Mohamed Azaroual<sup>g,h</sup> and Philippe Leroy<sup>h</sup>

5 <sup>a</sup> University of Aberdeen, School of Engineering, Elphinstone Road, AB24 3UE Aberdeen, United Kingdom

6 <sup>b</sup> Curtin University, Discipline of Petroleum Engineering, 26 Dick Perry Avenue, 6151 Kensington, Australia

7 <sup>c</sup> Now at the University of Valladolid, School of Engineering, TermoCal, BioEcoUva, Valladolid, Spain

8 <sup>d</sup> Edith Cowan University, Centre for Sustainable Energy and Resources, 270 Joondalup Drive, 6027  
9 Joondalup, Australia

10 <sup>e</sup> Edith Cowan University, School of Engineering, 270 Joondalup Drive, 6027 Joondalup, Australia

11 <sup>f</sup> Sorbonne Université, CNRS, EPHE, UMR 7619 METIS, F-75005 Paris, France

12 <sup>g</sup> Université d'Orléans, Univ. Orléans, CNRS, BRGM, ISTO, UMR 7327, F-45071, Orléans, France

13 <sup>h</sup> BRGM, French Geological Survey, 45100 Orléans, France

## 14 **Abstract**

15 Electrochemical interactions at calcite-water interface are characterized by the zeta potential and  
16 play an important role in many subsurface applications. In this work we report a new physically  
17 meaningful surface complexation model that is proven to be efficient in predicting calcite-water zeta  
18 potentials for a wide range of experimental conditions.

19 Our model uses a two-stage optimization for matching experimental observations. First, equilibrium  
20 constants are optimized, and the Stern layer capacitance is optimized in the second stage. The  
21 model is applied to a variety of experimental sets that correspond to intact natural limestones  
22 saturated with equilibrated solutions of low-to-high salinity, and crushed Iceland Spar sample  
23 saturated with NaCl at non-equilibrium conditions.

24 The proposed linear correlation of the Stern layer capacitance with the ionic strength is the main  
25 novel contribution to our surface complexation model without which high salinity experiments cannot  
26 be modelled. Our model is fully predictive given accurately known conditions. Therefore, the reported  
27 parameters and modelling protocol are of significant importance for improving our understanding of  
28 the complex calcite-water interfacial interactions. The findings provide a robust tool to predict  
29 electrochemical properties of calcite-water interfaces, which are essential for many subsurface  
30 applications including hydrology, geothermal resources, CO<sub>2</sub> sequestration and hydrocarbon  
31 recovery.

32

33

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40

## 41 1. Introduction

42 Calcite is a very common mineral on the Earth's surface comprising approximately 4% by weight of  
43 Earth's crust. Physico-chemical processes that take place in porous calcite-aqueous solution (water  
44 for simplicity) systems are of great importance for a variety of scientific and technological areas.  
45 Properties of the calcite mineral surface and the interface between calcite and aqueous solution are  
46 important for a broad range of applications including geological storage of nuclear waste and CO<sub>2</sub>  
47 [1], freshwater aquifer management [2,3], hydrocarbon production [4], paper production [5].  
48 However, electrochemical properties of the interfaces between calcite and aqueous solutions  
49 (specifically, electrical surface charge and zeta potential), especially under conditions relevant to  
50 natural subsurface systems (i.e., water chemical composition, temperature, pressure) remain poorly  
51 understood because of their microscopic nature, the high reactivity of the calcite mineral, and the  
52 lack of relevant measurements and models [6].

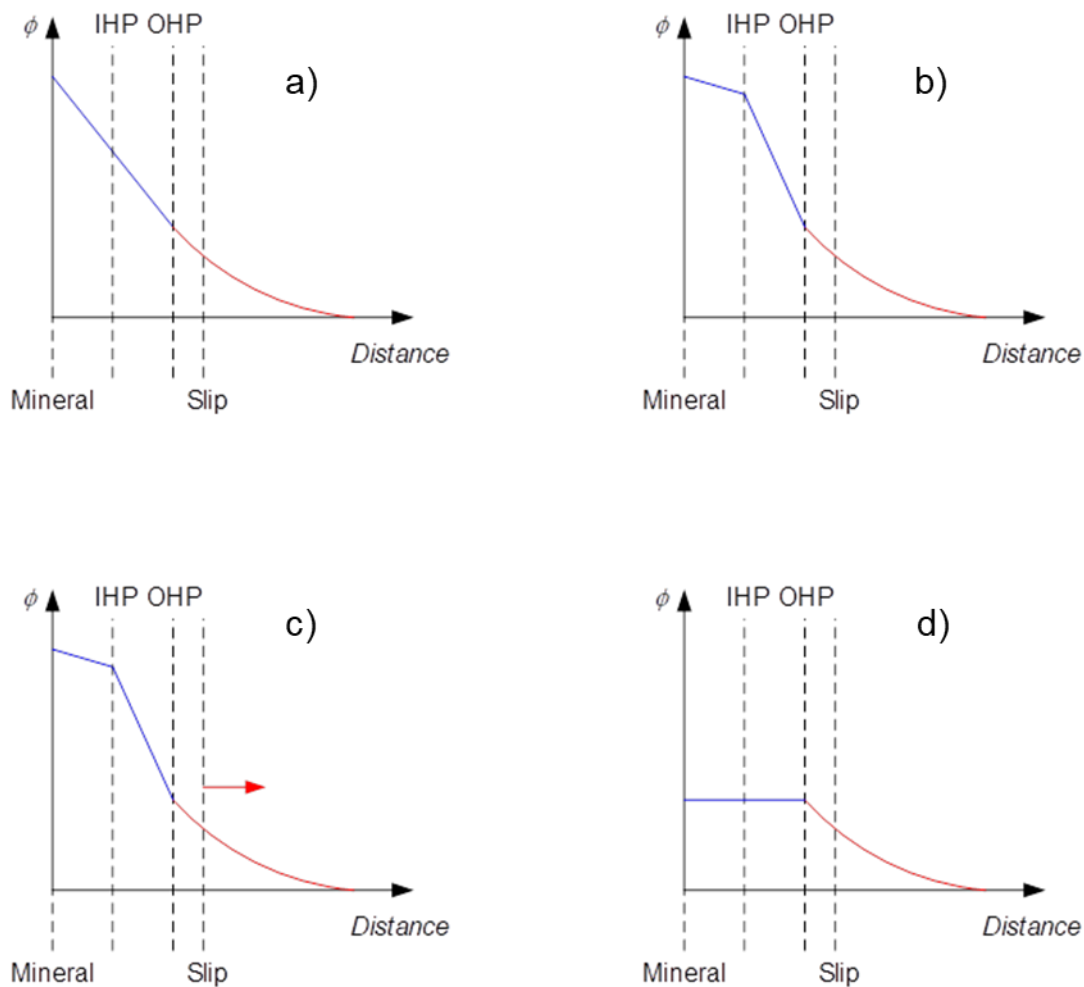
53 The zeta potential is defined as the electrical potential at the shear plane when water flow occurs  
54 parallel to the pore surface [7]. It is most commonly used to estimate the electrochemical properties  
55 of calcite because acid-base potentiometric titration, usually employed to measure the surface  
56 charge of minerals, is extremely difficult to carry out for highly reactive calcite [8]. There are many  
57 studies that have reported measurement of the zeta potential of various calcite-water systems.  
58 However, many reported results are contradictory (see for example Fig. 3 in Jackson et al. [9]). Most  
59 of the experimental studies have reported zeta potential measured with low salinity single-salt  
60 solutions (e.g., [10,11]), and there is inconsistency in the experimental conditions when some  
61 experiments were conducted at equilibrium between the mineral and water while others reported the  
62 zeta potential with non-equilibrium solutions (see for example discussion in Section 3 and 4 Al  
63 Mahrouqi et al. [12]). The experimental studies have also employed a variety of electrokinetic  
64 methods including the electrophoretic mobility (EPM [13]) and streaming potential method (SPM;  
65 [14]). Each of these experimental techniques suffers from several limitations [15]. The EPM applies  
66 an electrical field (of magnitude hundred Volts per meter) that mobilizes charged particles relative to  
67 aqueous solution and measuring the resulting mobility. The EPM is conducted on powdered calcite  
68 samples suspended in aqueous solution thus potentially exposing fresh mineral surfaces. Moreover,  
69 the method is usually limited to solution concentration below 1 M (M = mol/L) [16]. The ratio of the  
70 mineral to the solution is also very low (typically few grams per liter) and not representative of real  
71 rocks. On the other hand, the SPM applies a pressure difference across the sample and measures  
72 a resulting voltage, it can be carried out under equilibrium conditions, on intact rock samples at  
73 salinities up to full saturation (e.g., [17,18]). However, unlike the EPM method, SPM can be time  
74 consuming and very challenging for highly reactive minerals such as calcite in highly saline  
75 conditions thus limiting its ability to cover a wide range of rock-solution permutations (see for  
76 example typical duration of both the equilibration process and individual SPM experiment, as well as  
77 the voltage stability issues at high salinity reported in Alroudhan et al. [19]). Moreover, the zeta  
78 potential values obtained with SPM can be specific to rock type as different carbonate samples may  
79 contain different impurities such as anhydrite and dolomite (e.g., [12]).

80 A model capable of predicting the zeta potential of calcite-water systems at equilibrium as well as  
81 non-equilibrium conditions, low to high salinity, and complex solution composition is crucially  
82 important. Such model will not only be capable of predicting the zeta potential, but also improve our  
83 understanding of the complex electrochemical processes that take place at calcite-water interface.  
84 To date, there have been numerous attempts to develop such model with most of published studies  
85 using the so-called surface complexation modelling (SCM) approach (e.g., [6,10,11]). In this method  
86 the calcite surface is presented as an ensemble of chemically active surface sites that interact with  
87 ions from the adjacent bulk electrolyte. The strength of these interactions is described by the  
88 equilibrium constants (similar to chemical reactions), so that the resulting equilibrium concentration

89 of positive and negative surface complexes establishes the net surface charge and the  
90 corresponding surface potential [20]. Depending on the complexity of the aqueous solution, such  
91 models can be realized analytically (e.g., [21]) or by using numerical methods already available in  
92 software packages such as PHREEQC (e.g., [22]).

93 Studies published to date on SCM have used different approaches to model the zeta potential  
94 (**Figure 1**): Basic Stern Model (BSM, e.g., [10]), Triple Layer Model (TLM, e.g., [23]), Quad-Layer  
95 Model (QLM, e.g. [24]) and Diffuse Layer Model (DLM, e.g. [25]). BSM, TLM and QLM explicitly  
96 describe the Stern layer and a layered arrangement of ionic species adsorbed on the mineral surface  
97 in the diffuse layer. Both the TLM and QLM distinguish between the Inner Helmholtz plane (IHP) and  
98 the Outer Helmholtz plane (OHP), at which adsorption of de-hydrated and hydrated ions,  
99 respectively, takes place [23]. On the other hand, BSM for calcite assumes that adsorption of all ions  
100 in compact layer takes place at the OHP (e.g., [6,10,11]). All three models that explicitly describe the  
101 adsorption layers (i.e., BSM, TLM, QLM) also assume that only protonation/deprotonation of  
102 hydrated calcite lattice ions take place at the mineral surface. In these models, the surface charge  
103 densities are computed at each plane, from which linear, capacitor-like variation of the electric  
104 potential between the planes is obtained. Consequently, TLM and QLM simulate separately  
105 protonation/deprotonation and salt ion adsorption reactions at three different planes (mineral  
106 surface, IHP, OHP), and ascribe two capacitance values to layers confined between the mineral  
107 surface and IHP, and between IHP and OHP. In addition, the QLM considers a stagnant diffuse  
108 layer, implying that the shear plane is located further away from the OHP. This makes these two  
109 models more computationally expensive compared with BSM, which uses only one capacitance and  
110 all adsorption reactions are considered to take place at OHP for calcite.

111 On the other hand, DLM assumes that both the protonation/deprotonation and salt ion adsorption  
112 reactions take place at the mineral surface thus ignoring the complexity of the Stern layer that  
113 comprises the IHP and OHP. Hence, compared to the BSM, TLM, and QLM, the DLM is not sensitive  
114 to the capacitance values and is only sensitive to the location of the so-called shear (or slip) plane  
115 at which ions can be mobilized by the flow and at which the electric potential is defined as the zeta  
116 potential. According to the generally agreed theory of the electrical double layer, concentrations of  
117 counter-ions that populate the region beyond the OHP (in the diffuse layer) obey the Boltzmann  
118 distribution law where they decrease exponentially towards concentrations of ions in electroneutral  
119 bulk electrolyte (outside the diffuse layer). The location of the slip plane is uncertain and is usually  
120 used as a fitting parameter to match the model predictions to experimental data [10]. The assumed  
121 location of the slip plane can also be used in BSM, TLM and QLM as additional fitting parameter, but  
122 in contrast with DLM the modelled zeta potential using these models depends on adjustable  
123 capacitance values and therefore, the location of the slip plane can be kept constant for matching  
124 different experimental datasets. The QLM published by Alizadeh and Wang [24] assumed that the  
125 slip plane was dynamic and moved further away from the mineral surface as the ionic strength of the  
126 bulk electrolyte decreased. Although the dynamic slip plane model successfully reproduced  
127 experimental results, the hypothesis was not clearly justified by the authors or confirmed  
128 experimentally.



129

130 **Figure 1.** Electrical potential distribution at the calcite-water interface: a) – BSM (no distinction between IHP  
 131 and OHP, the slip plane may or may not coincide with OHP); b) – TLM (IHP and OHP are considered separately  
 132 with different surface complexation reactions taking place at each plane, the slip plane coincides with OHP);  
 133 c) – QLM (IHP and OHP are considered separately with different surface complexation reactions taking place  
 134 at each plane, the slip plane does not coincide with OHP and its distance from OHP can be constant or varying  
 135 with salinity); d) – DLM (IHP and OHP are not considered at all as if there is no separation between the mineral  
 136 surface and OHP, the slip plane may or may not coincide with mineral/OHP).

137 However, despite the plethora of published SCM studies, all of the simulated results appear to be  
 138 specific to an experimental dataset. Heberling and co-authors [6,10] used fractional charges of  
 139 individual surface site, the approach that was consistent with that taken by Wolthers et al. [23], who  
 140 used the Charge Distribution MultiSite Ion Complexation or CD-MUSIC modeling approach.  
 141 However, the magnitude of the surface site charges was different. On the other hand, Van Cappellen  
 142 et al. [26] used integer surface site charges in their BSM. Furthermore, Heberling et al. [6,10] used  
 143 equilibrium constants for adsorption reactions at OHP limited by ion-binding ones that corresponded  
 144 to pairing of ions in the bulk electrolyte. In contrast, Pokrovsky and Schott [27] estimated their  
 145 equilibrium constants for adsorption reactions from the correlation between stability of surface sites  
 146 and stability of the same molecules in the solution. As a result, the equilibrium constants used by  
 147 Pokrovsky and Schott [27] in their BSM exceeded by several orders of magnitude those used by  
 148 Heberling et al. [6,10] in their BSM. Considering the equilibrium constants of  
 149 protonation/deprotonation reactions that take place at the mineral surface, a significant variation in  
 150 their values was also evident across different studies. For instance, Heberling et al. [10] used five-  
 151 fold larger equilibrium constant for deprotonation of hydrated Ca site compared with their later study

152 [6]. At the same time, Wolthers et al. [23] used twelve orders of magnitude larger equilibrium constant  
153 for the same reaction compared with Heberling et al. [10].

154 Previously published studies that used either BSM or TLM relied on constant Stern layer  
155 capacitance, but the reported values used in these studies varied between 0.45 F/m<sup>2</sup>, 1.24 F/m<sup>2</sup> [11]  
156 , 17 F/m<sup>2</sup> [27], 52 F/m<sup>2</sup> [28] and 100 F/m<sup>2</sup> [23]. Therefore, the inconsistency in these values suggests  
157 a high degree of freedom and unconstrained variation of simulated zeta potential. Moreover, most  
158 of the published SCM simulated the zeta potential of calcite in contact with low salinity (typically less  
159 than 0.1 M) single salt solutions (e.g., NaCl) therefore ignoring the effect of divalent ions such as  
160 Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> and high ionic strength. Studies that included such reactions reported inconsistent  
161 equilibrium constants, with Heberling et al. [6] predicting adsorption of Ca<sup>2+</sup> on negative surface sites  
162 to be controlled by an equilibrium constant ten orders of magnitude smaller compared with the  
163 equilibrium constant calculated from two consecutive reactions described by Pokrovsky et al. [28]  
164 and Pokrovsky and Schott [29]. All in all, a unique combination of adsorption reactions, their  
165 equilibrium constants, capacitance values and charges of the surface sites used in published studies  
166 appear to be very specific to the modelled experimental datasets, thus limiting the use of each model  
167 for a very narrow range of ionic strength, pH and composition of electrolytes in contact with the  
168 calcite mineral.

169 Therefore, the aim of this study is to develop and validate a new SCM that accurately computes the  
170 zeta potential of any calcite-water system as long as the experimental conditions are reproduced in  
171 the model. The developed model has proven to be accurate in simulating and predicting zeta  
172 potentials at both equilibrium and non-equilibrium conditions, high to low salinity, for any carbonate  
173 rock type as long as the dominating mineral is calcite, and for any solution composition as long as  
174 the dominating salt is NaCl and concentration of SO<sub>4</sub><sup>2-</sup> does not exceed that of Ca<sup>2+</sup> and Mg<sup>2+</sup>.

175

## 176 2. Methodology

177 To develop a robust predictive model requires detailed description of experimental parameters and  
178 conditions. Therefore, we have chosen the data reported by Al Mahrouqi et al. [12] as the most  
179 comprehensive experimental work and will briefly describe the experimental conditions and main  
180 conclusions.

### 181 2.1. Description of the experimental data on zeta potential in intact limestone samples

182 Streaming potential measurements were performed by Al Mahrouqi et al. [12] and Alroudhan et al.  
183 [19] on three different carbonate rock samples: Estailades [12], Ketton [12] and Portland [19]. The  
184 petrophysical and mineralogical properties of the rock samples are shown in **Table 1**.

Property/rock	Ketton	Estailades	Portland
Porosity (%)	23.0 ± 0.5	28.0 ± 0.5	20.0 ± 0.5
Permeability (Darcy)	1.4 ± 0.4	0.13 ± 0.2	0.005 ± 0.001
Formation factor (F)	13.87 ± 0.5	12.92 ± 0.5	22.04 ± 0.5
Composition (%)	97 <sup>a</sup> – calcite	97 <sup>a</sup> (95 <sup>b</sup> ) – calcite	96.6 <sup>a</sup> – calcite
	3 <sup>a</sup> magnesium	3 <sup>a</sup> (4 <sup>b</sup> ) – magnesium	3.4 <sup>a</sup> – quartz
		(1 <sup>b</sup> ) – anhydrite	

185 **Table 1.** Petrophysical and mineralogical properties of three different carbonate rock samples. Ketton and  
186 Estailades were used in the experiments of by Al Mahrouqi et al. [12], Portland was used by Alroudhan et al.  
187 [19].

188 **a** – mineralogy reported by Al Mahrouqi et al. [12] using X-ray diffraction (XRD). Magnesium was reported to  
189 be likely incorporated into the limestone as dolomite.

190 **b** – recent study by Udoh and Vinogradov [30], identified and confirmed that there was 4% dolomite  
191 (CaMg(CO<sub>3</sub>)<sub>2</sub>) and 1% anhydrite (CaSO<sub>4</sub>) in the Estailades sample using XRD.

192

193 The zeta potential measurements were conducted at room temperature (23°C) with NaCl solutions  
194 of varying concentration between 0.05 M (mol/L) and 5.0 M NaCl at equilibrium conditions. Effluent  
195 fluid samples were regularly collected for chemical analyses to determine the concentration of Na<sup>+</sup>,  
196 Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The experimentally confirmed presence of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> was  
197 explained by partial dissolution of rock samples during the equilibration with NaCl solutions and  
198 leaching of these ions.

199 These studies concluded that the zeta potential of carbonate rock samples was controlled by the  
200 concentration of the potential determining ions (PDIs), which were identified to be Ca<sup>2+</sup>, Mg<sup>2+</sup>, and  
201 SO<sub>4</sub><sup>2-</sup>.

### 202 2.2. Calcite surface complexation model development

#### 203 2.2.1. Basic definitions and assumptions

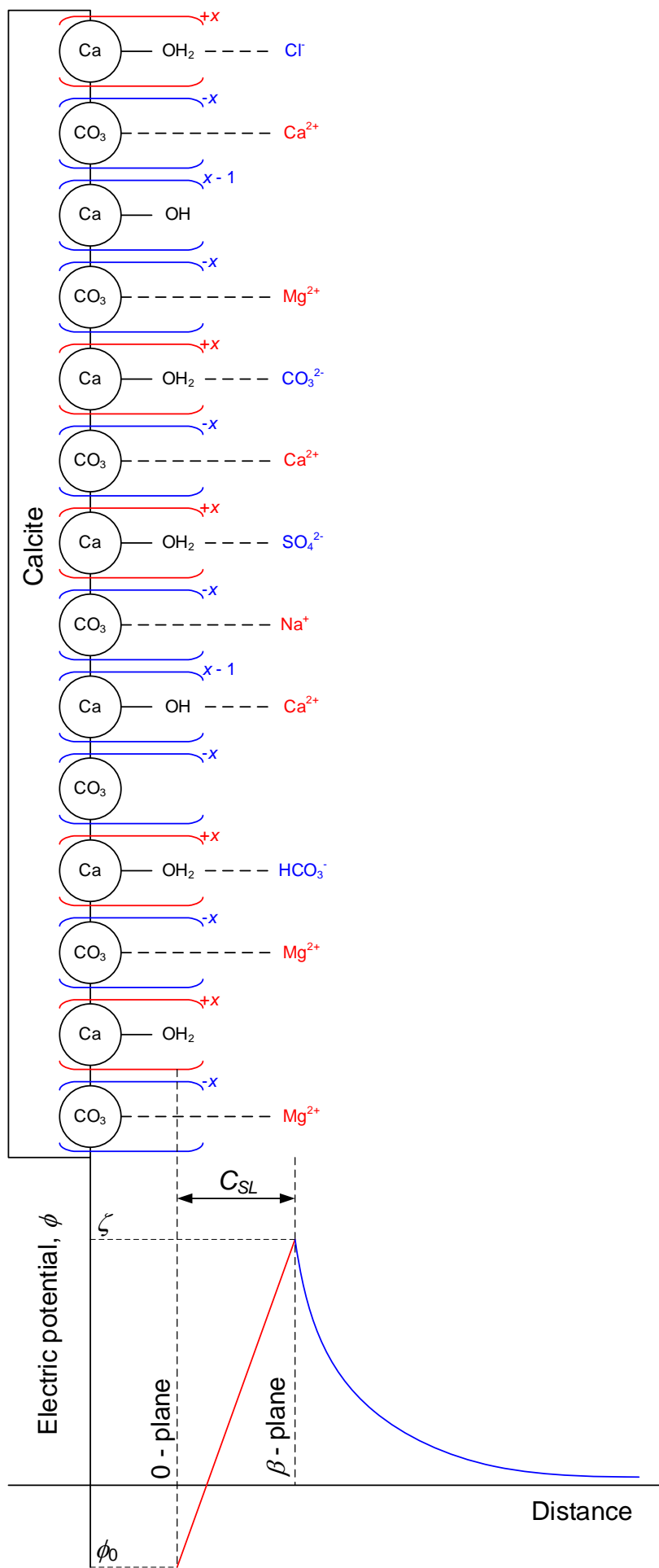
204 A BSM was used in this study to model the zeta potential of pure calcite in contact with aqueous  
205 solutions. The modelling approach was consistent with the most comprehensive and empirically  
206 justified model developed by Heberling et al. [6,10]. Since the content of calcite in all three tested  
207 carbonate rock samples (Estailades, Ketton, Portland) was found to be greater than 95%, it was  
208 assumed that calcite was the most dominant mineral in the samples so that only calcite surface sites  
209 were considered in the model.

210 The measured zeta potential with all tested carbonate rocks reflected presence of minerals other  
211 than calcite (e.g., dolomite and anhydrite), which led to a non-zero concentration of  $Mg^{2+}$  and  $SO_4^{2-}$   
212 found in the bulk solution as a result of mineral dissolution during the equilibration process.  
213 Therefore, we artificially added the equilibrium concentration of  $Mg^{2+}$  and  $SO_4^{2-}$  measured in the  
214 experiment to our geochemical model of pure calcite. The amount of  $Ca^{2+}$  leached into NaCl  
215 solutions during the equilibration was either added artificially to the model and equilibration was  
216 switched off, or it was not added to the initial solution while the equilibration was activated (see  
217 Section 2.3 for details).

218 Consistent with Heberling et al. [6,10], calcite (1 0 4) face was assumed to dominate the interface  
219 due to its high abundance and the total surface site density of calcium and carbonate surface sites  
220 on the calcite (1 0 4) face was set to 4.95 sites per  $nm^2$  for each type of site. However, unlike  
221 Heberling et al. [6], this study assumed that the zeta potential could be calculated by considering the  
222 shear plane coinciding with the OHP (see **Figure 2**), i.e.,  $\phi_\beta = \phi_d = \zeta$  – the assumption that was  
223 also used by Li et al. [11] (no stagnant diffuse layer). Li et al. [11] considered that the assumption of  
224 the presence of a stagnant diffuse layer in Heberling et al. [10] was due to the nature of electrokinetic  
225 measurements that were not corrected for surface conductivity effects thus reducing the  
226 experimental zeta potentials and then necessitating smaller modelled zeta potentials to be further  
227 away from the mineral surface, to match the data.

228 The 0-plane was defined as the hydrolysis layer located 2.3 Å from the calcite surface defined by  
229 the surface of calcium ions, at which only protonation/deprotonation of surface sites took place [6].  
230 The surface charge at 0-plane was found to be negative regardless of the concentration and  
231 composition of the adjacent solution and pH range of 5-11 tested in our study, similar to the results  
232 reported by Heberling et al. [6]. On the other hand, the  $\beta$ -plane was set at a distance of 4.6 Å from  
233 the surface [6], and we assumed that all the specific adsorption reactions between the surface sites  
234 and salt ions from the bulk electrolyte only occurred at the OHP where ions are adsorbed as outer-  
235 sphere complexes.





237 **Figure 2.** Illustration of the Basic Stern Model used in this study. The 0-plane corresponds to the mineral  
238 surface where only protonation/deprotonation reactions take place. We used fractional surface charge  $x = 0.5$   
239 for all surface sites. The Stern Layer is confined between the 0-plane and  $\beta$ -plane, with the latter corresponding  
240 to the OHP where all adsorption reactions take place and where the zeta potential ( $\zeta$ ) is defined.  $C_{SL}$  is the  
241 Stern layer capacitance.

242

### 243 2.2.2. Adsorption reactions and equilibrium constants

244 All modelled adsorption reactions between calcite surface sites and ions are listed in **Table 2**. The  
245 original set of adsorption reactions proposed by Heberling et al. [6,10] and Li et al. [11] was extended  
246 to include the reactions between the surface sites and  $Mg^{2+}$  and  $SO_4^{2-}$  (R9 – R11 in **Table 2**). The  
247 equilibrium constant of R1 that corresponds to deprotonation of hydrated calcium surface sites was  
248 fixed to the value of  $\text{Log}K_1 = -0.5$  to yield the relative abundance of positive and negative surface  
249 complexes at 0-plane according to Heberling et al. [6].

250 Among published studies on SCM of calcite, there is no consensus on whether protonation of  
251  $>CO_3^{-0.5}$  surface sites on 0-plane should be considered. Some of these studies included the reaction  
252  $>CO_3^{-0.5} + H^+ \rightleftharpoons >CO_3H^{+0.5}$  (e.g., [10,23,27]), while other studies (e.g., [6,11]) disregarded it. We  
253 could not find any published justification for inclusion of  $>CO_3^{-0.5}$  protonation based on the  
254 experimental data or theoretical analysis. However, there have been several publications in support  
255 of excluding the protonation of the  $>CO_3^{-0.5}$  surface sites. One theoretical study on hydration of (1 0  
256 4) calcite surface [31] demonstrated that neutral  $H_2O$  molecules preferentially ‘chemisorbed’ into  $>$   
257  $Ca^{+0.5}$  to form  $>CaOH_2^{+0.5}$  site, and existence of  $>CO_3H^{+0.5}$  surface sites was attributed to hydration  
258 of carbonate surface groups ( $>CO_3OH_2^{-0.5}$ ) but not direct protonation of the  $>CO_3^{-0.5}$  sites.  
259 Therefore, in the absence of  $>CO_3OH_2^{-0.5}$  there could be no  $>CO_3H^{+0.5}$  sites resulting from  
260 subsequent dissociation of water molecules  $>CO_3OH_2^{-0.5} \rightleftharpoons >CO_3H^{+0.5} + OH^-$ . These conclusions  
261 were supported by a variety of experimental measurements reported in the paper. Another numerical  
262 study [32] also predicted low fraction of protonated  $>CO_3H^{+0.5}$  sites (<20%) on a variety of calcite  
263 mineral geometries for pH between 5 and 11, which is consistent with pH values tested with our  
264 model. For pH greater than 7, the fraction of protonated carbonate sites decreased to below 5%  
265 according to this study. Moreover, inclusion of the  $>CO_3^{-0.5}$  surface site protonation would result in  
266 increased pH under simulated equilibrium conditions, thus mismatching the experimentally  
267 measured values. Effect of  $>CO_3^{-0.5}$  protonation on equilibrium pH will be discussed in more detail  
268 in Section 3. For these reasons and following Heberling et al., [6] we did not consider hydration of  
269 carbonate surface sites in our model.

270

No	Reactions	LogK <sup>min</sup>	LogK <sup>max</sup>	LogK <sup>opt</sup>
0-plane reactions				
R1	$> \text{CaOH}_2^{+0.5} \Leftrightarrow \text{CaOH}^{-0.5} + \text{H}^+$	-0.5	-0.5	-0.5
$\beta$ -plane reactions				
R2	$> \text{CaOH}^{-0.5} + \text{Na}^+ \Leftrightarrow \text{CaOH}^{-0.5} - \text{Na}^+$	0.09 <sup>a</sup>	0.56 <sup>b</sup>	0.56
R3	$> \text{CaOH}_2^{+0.5} + \text{Cl}^- \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{Cl}^-$	-2.10 <sup>c</sup>	0.45 <sup>d</sup>	-0.64
R4	$> \text{CaOH}^{-0.5} + \text{Ca}^{2+} \Leftrightarrow \text{CaOH}^{-0.5} - \text{Ca}^{2+}$	1.68 <sup>b</sup>	3.40 <sup>e</sup>	3.40
R5	$> \text{CaOH}_2^{+0.5} + \text{HCO}_3^- \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{HCO}_3^-$	0.04 <sup>b</sup>	12.50 <sup>f</sup>	10.65
R6	$> \text{CaOH}_2^{+0.5} + \text{CO}_3^{2-} \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{CO}_3^{2-}$	-7.07 <sup>b</sup>	6.00 <sup>g</sup>	-4.59
R7	$> \text{CO}_3^{-0.5} + \text{Ca}^{2+} \Leftrightarrow \text{CO}_3^{-0.5} - \text{Ca}^{2+}$	1.68 <sup>b</sup>	3.40 <sup>h</sup>	3.40
R8	$> \text{CO}_3^{-0.5} + \text{Na}^+ \Leftrightarrow \text{CO}_3^{-0.5} - \text{Na}^+$	0.56 <sup>b</sup>	3.40 <sup>i</sup>	0.56
R9	$> \text{CaOH}^{-0.5} + \text{Mg}^{2+} \Leftrightarrow \text{CaOH}^{-0.5} - \text{Mg}^{2+}$	1.66 <sup>a</sup>	3.40 <sup>j</sup>	2.81
R10	$> \text{CaOH}_2^{+0.5} + \text{SO}_4^{2-} \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{SO}_4^{2-}$	-2.10 <sup>g</sup>	3.30 <sup>k</sup>	3.30 $\rightarrow$ 11.9
R11	$> \text{CO}_3^{-0.5} + \text{Mg}^{2+} \Leftrightarrow \text{CO}_3^{-0.5} - \text{Mg}^{2+}$	1.68 <sup>l</sup>	3.40 <sup>l</sup>	2.81

272 **Table 2.** Adsorption reactions and their equilibrium constants. Equilibrium constant for R1 was not optimised.

273 **a** – Song et al. [33].

274 **b** – Heberling et al. [6].

275 **c** – only one value for the equilibrium constant for R3 was found in the literature (0.45), hence we considered

276 LogK<sup>min</sup> to be equal to that of R10 due to similarity.

277 **d** – Li et al. [11].

278 **e** – only one value for the equilibrium constant for R8 was found in the literature (1.68), hence we considered

279 LogK<sup>max</sup> to be equal to that of R7 due to similarity.

280 **f** – combined from two reactions reported in Pokrovsky and Schott [29].

281 **g** – Qiao et al. [34].

282 **h** – combined from two reactions reported in Pokrovsky et al. [28].

283 **i** – only one value for the equilibrium constant for R8 was found in the literature (0.56), hence we considered

284 LogK<sup>max</sup> to be equal to that of R7 due to similarity.

285 **j** – only one value for the equilibrium constant for R9 was found in the literature (1.66), hence we considered

286 LogK<sup>max</sup> to be equal to that of R4 due to similarity.

287 **k** – Qiao et al. [35].

288 **l** – this is a new additional reaction introduced in our model with no values for the equilibrium constant found

289 in the literature, hence we assumed both LogK<sup>min</sup> and LogK<sup>max</sup> to be equal to those of R7 due to similarity.

290

291 For reactions R2 – R11 we identified ranges of possible variation of equilibrium constants. The

292 ranges were based on previously published values thus defining the minimum and maximum

293 possible equilibrium constant for each reaction, LogK<sup>min</sup> and LogK<sup>max</sup>, respectively. Note, that due to

294 lack of published information on some equilibrium constants, their maximum and minimum values

295 were assumed to be similar to those of other adsorption reactions or calculated from published  
296 values of consecutive reactions (see caption of **Table 2** for details).

297 We used the Pitzer theory (pitzer.dat database of PREEQC [36,37]) to calculate the ion activity  
298 coefficients for all complexation reactions that take place in the bulk solution at high ionic strength  
299 systems ( $> 0.5$  M). For ionic strengths below 0.5 M it was found that there was no noticeable  
300 difference in the modelled results obtained using either the Debye-Huckel (phreeqc.dat database of  
301 PHREEQC) or Pitzer theory to calculate the ion activity coefficients. Therefore, the Pitzer theory was  
302 used throughout the entire range of tested ionic strengths.

### 303 **2.2.3. BSM – capacitance of the Stern layer and electric potential distribution within EDL**

304 The electric potential distribution within the Stern layer, between 0-plane and  $\beta$ -plane, is described  
305 by a linear variation, similar to the concept of two parallel plates capacitor which it can be expressed  
306 as follows:

$$\sigma_0 = C_{SL} (\phi_0 - \phi_\beta), \quad (1)$$

307 where  $\sigma_0$  is the surface charge density at 0-plane ( $C \cdot m^{-2}$ ),  $C_{SL}$  is the specific Stern layer capacitance  
308 (or Stern layer capacitance for simplicity) between 0-plane and  $\beta$ -plane ( $F \cdot m^{-2}$ ),  $\phi_0$  is the electric  
309 potential at 0-plane (V) and  $\phi_\beta$  is the electric potential at  $\beta$ -plane (V). The Stern layer capacitance  
310 can also be expressed as:

$$C_{SL} = \frac{\epsilon_0 \epsilon_r}{x}, \quad (2)$$

311 where  $\epsilon_0$  is vacuum permittivity ( $F \cdot m^{-1}$ ),  $\epsilon_r$  is relative permittivity of the Stern layer and  $x$  is the  
312 distance between 0-plane and  $\beta$ -plane or the thickness of the Stern layer (m). Beyond the  $\beta$ -plane,  
313 in the diffuse layer, the electrical potential distribution is described using the Gouy-Chapman theory  
314 based on the Poisson-Boltzmann equation. The electrical potential magnitude decreases  
315 exponentially with the distance from the mineral surface and ion concentrations follow a Boltzmann  
316 distribution.

### 317 **2.2.4. Two-step optimization**

318 Our model was developed through a two-step optimization process applied to experimental zeta  
319 potential results obtained with Estailades and Ketton rock samples saturated with equilibrated NaCl  
320 solutions of ionic strengths between 0.05 M and 5 M.

321 The first-step optimization aimed at determining the equilibrium constants of R2-R11, while the  
322  $\log K_{R1}$  and the Stern layer capacitance ( $C_{SL}$ ) were kept constant and equal to -0.5 and 1.24  $F/m^2$ ,  
323 respectively, in accordance with the study of Li et al. [11]. The optimization of equilibrium constants  
324 of the surface complexation reactions and Stern layer capacitance was a necessary step, as  
325 previous studies considered either low salinity (e.g., [11]) or moderate salinity solutions (e.g.,  
326 seawater model by Song et al. [33]) using different sets of the parameters for each ionic strength,  
327 thus making their models suitable to very specific experimental conditions. To the best of our  
328 knowledge there has been no study that tried SCM for a range of salinities, and especially for ionic  
329 strengths above 0.5 M which are typical for many subsurface settings. The first-step optimization  
330 was conducted in the following manner:

- 331 • Concentration of all ions ( $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$ ) and pH reported by Al Mahrouqi et al.  
332 [12] were used as input parameters. The concentration of carbon related ions ( $HCO_3^-$ ,  $CO_3^{2-}$ ),  
333 termed C(4) ions in PHREEQC, was not reported in the corresponding paper, therefore it was  
334 calculated from the charge balance equation. It was also assumed that the calculated C(4)

335 concentration could exceed that of Ca<sup>2+</sup> and C(4) ions that originate from the dissolved  
 336 atmospheric CO<sub>2</sub> in aqueous solution at equilibrium with air. This assumption is consistent with  
 337 the experimentally confirmed dissolution of CaCO<sub>3</sub> during the equilibration process that  
 338 resulted in 10<sup>-3</sup> M of dissolved Ca<sup>2+</sup>, and hence the same concentration of C(4) [12,19], which  
 339 is higher than the equilibrium concentration of 1.5×10<sup>-5</sup>M of C(4) in solution at equilibrium with  
 340 air [11].

- 341 • The dissolution and precipitation of calcite was switched off at this optimization step by  
 342 implementing PREEQC code 'Calcite 0 0' in 'equilibrium\_phases' section [6,22].
- 343 • The R2 – R11 equilibrium constants were optimized by minimizing the objective function,  $f$ ,  
 344 that defines the normalized difference between the observed and the simulated zeta potential  
 345 and pH:

$$f = \sum \left( \frac{\zeta_{obs} - \zeta_{sim}}{\delta_{\zeta}} \right)^2 + \sum \left( \frac{pH_{obs} - pH_{sim}}{\delta_{pH}} \right)^2, \quad (3)$$

346 where  $\zeta_{obs}$  is the observed zeta potential (mV),  $\zeta_{sim}$  is the simulated zeta potential (mV),  $\delta_{\zeta}$  is  
 347 the experimental uncertainty of the zeta potential (mV),  $pH_{obs}$  is the observed pH,  $pH_{sim}$  is the  
 348 simulated pH and  $\delta_{pH}$  is the experimental uncertainty of pH. Note that pH was included in the  
 349 objective function since the computed value for a given set of equilibrium constants could be  
 350 different from the input (experimental) value. Therefore, both directly measured properties  
 351 (zeta potential and pH) were included in **Eq. 3**. The optimization was conducted by combining  
 352 the PHREEQC geochemical code with an optimization software, PEST, in which the Gauss  
 353 Marquardt Levenberg method was implemented.

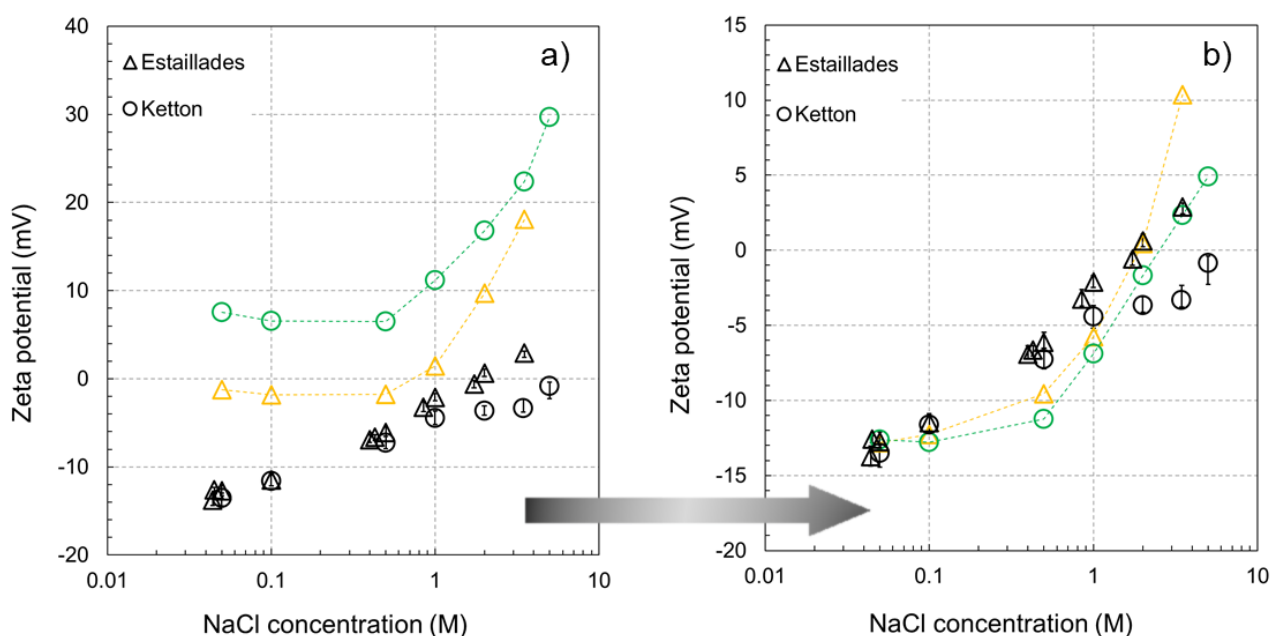
- 354 • The optimization was repeated three times, with the initial values of all equilibrium constants  
 355 being either i) the minimum found in literature ( $\text{Log}K^{\text{min}}$ ), ii) the maximum reported in the  
 356 literature ( $\text{Log}K^{\text{max}}$ ), or iii) the median within the tested range (see more details in **Table 2**  
 357 caption). This repetitive optimization procedure was required to find the global minimum of  $f$ ,  
 358 which corresponded to the best match between the experimentally measured and computed  
 359 zeta potential and pH, so that the equilibrium constants that corresponded to the smallest  $f$   
 360 were taken forward.

- 361 • The results of the first step optimization procedure are shown in **Table 2** ( $\text{Log}K^{\text{opt}}$  column).

362 It was found that the calculated zeta potentials of Estailades and Ketton were positive except for  
 363 Estailades at ionic strength below 1 M. In contrast, the experimental results showed that the zeta  
 364 potential of both rock samples remained negative at low ionic strength to become less  
 365 negative/positive at high ionic strength (**Figure 3a**). Moreover, the calculated Ketton zeta potential  
 366 was more positive compared with that of Estailades, while the experimental data showed an  
 367 opposite trend. The more positive zeta potential measured in Estailades sample could not be  
 368 explained by different rates of calcite dissolution as the equilibrium Ca<sup>2+</sup> concentration was found to  
 369 be higher in Ketton sample (Figure 9a in Al Mahrouqi et al. [12]), which would imply a more positive  
 370 zeta potential, consistent with our model.

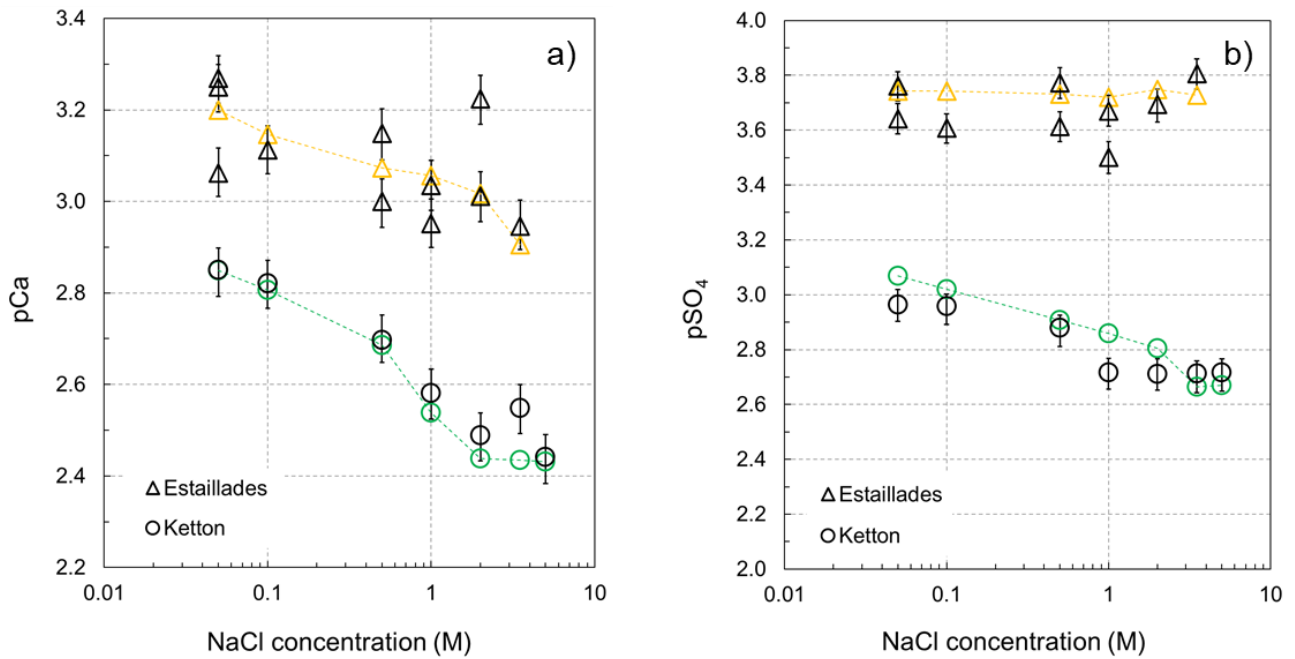
371 However, a considerably higher concentration of SO<sub>4</sub><sup>2-</sup> was also reported in experiments with Ketton  
 372 (Figure 9b in Al Mahrouqi et al. [12]), and more negative zeta potential compared with that of  
 373 Estailades sample was attributed to it. The authors demonstrated that the zeta potential was not  
 374 very sensitive to SO<sub>4</sub><sup>2-</sup> concentration (Figure 8b in Al-Mahrouqi et al. [12]), as long as concentration  
 375 of all other ions remained unchanged thus implying that high sensitivity to SO<sub>4</sub><sup>2-</sup> only took place when  
 376 sulfate content was less or equal to that of the divalent cations. However, the paper did not consider

377 a possibility of  $\text{Ca}^{2+}$  ions acting as bridges to  $\text{SO}_4^{2-}$  ions [38–40] thus enhancing sulfate adsorption  
 378 when elevated concentration of  $\text{Ca}^{2+}$  is found in bulk solution. Such bridging ability of  $\text{Ca}^{2+}$  implies  
 379 that higher concentration of  $\text{Ca}^{2+}$  (and/or  $\text{Mg}^{2+}$ ) combined with higher concentration of  $\text{SO}_4^{2-}$  (as was  
 380 observed by Al Mahrouqi et al. [12]) should result in overall higher adsorption of sulfate and more  
 381 negative zeta potential. Keeping in mind that dissolved  $\text{SO}_4^{2-}$  could only originate from undetected  
 382 minerals such as anhydrite ( $\text{CaSO}_4$ ) or epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), a higher concentration of sulfate  
 383 ions would always be accompanied by a higher equilibrium concentration of  $\text{Ca}^{2+}$  and/or  $\text{Mg}^{2+}$  as it  
 384 was indeed reported by Al-Mahrouqi et al. [12]. Therefore, we assumed that the reactivity of calcite  
 385 to  $\text{SO}_4^{2-}$  was considerably higher for rock samples that leached more sulfate and the constraint on  
 386  $\text{Log}K^{\text{max}}$  for R10 was removed, which resulted in a substantially better match to the experimental  
 387 data (**Figure 3b**) and the corresponding value of the optimized equilibrium constant,  $\text{Log}K^{\text{opt}}$ , of 11.9  
 388 (Table 2). We expect that including  $\text{Ca}^{2+}$ – $\text{SO}_4^{2-}$  ion bridging in the surface complexation reactions  
 389 would lower  $\text{Log}K^{\text{opt}}$ . Such inclusion implemented in SCM, would require currently unavailable  
 390 experimental data to validate the model and therefore, data acquisition and the corresponding SCM  
 391 adjustments will be conducted in a follow-up study.



392  
 393 **Figure 3.** Calculated zeta potential after the first step optimization a) with the constraint  $-2.10 \leq \log K_{\text{R10}} \leq$   
 394  $3.30$ , b) without the constraint  $-2.10 \leq \log K_{\text{R10}}$ . Black symbols denote the experimental results from  
 395 AlMahrouqi et al. [12].

396 The calculated concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (note, that input pH and concentration of  $\text{Mg}^{2+}$  were  
 397 constant at 8.3 and  $\text{pMg} = 4.19$ , respectively, as reported by Al-Mahrouqi et al. [12],  $\text{pMg} = -\log C_{\text{Mg}}$   
 398 with  $C$  denoting the ion concentration in M) for both rock samples is shown in **Figure 4**. The  
 399 computed solution pH and concentration of all other ions (those that are not shown in **Figure 4**)  
 400 remained unchanged and equal to the input values regardless of  $\text{Log}K^{\text{opt}}$  for R10, hence the  
 401 corresponding plots for these ions are not included in the figure.



402

403 **Figure 4.** Computed pCa (a) and pSO<sub>4</sub> (b) from the first optimization step. Black symbols represent the  
 404 experimental data [12]. The results in color correspond to the modelled zeta potential that appears in **Figure**  
 405 **3b**.

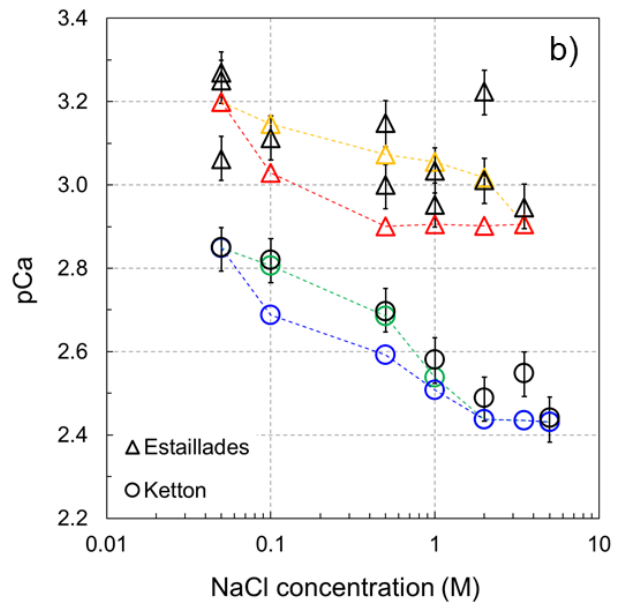
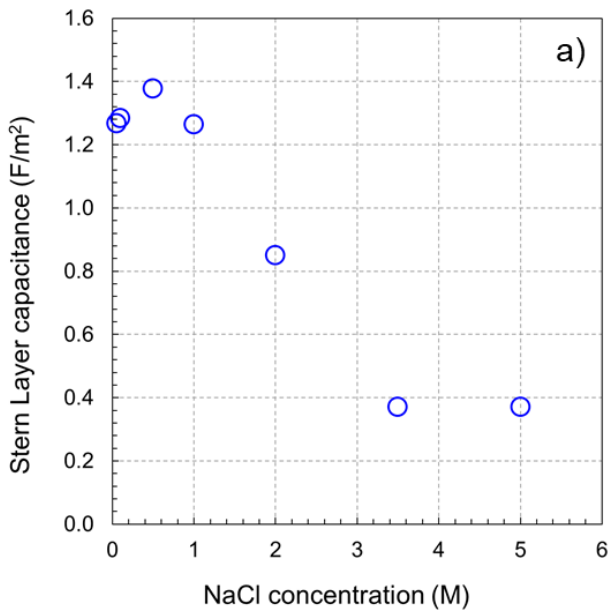
406

407 After increasing the LogK<sup>opt</sup> for R10 to the value of 11.9, the match to the experimental results  
 408 significantly improved as shown in **Figure 3b** for ionic strength ≤ 2 M. However, the simulated zeta  
 409 potential at ionic strength greater than 2 M remained significantly more positive compared with the  
 410 observed values, and for the Ketton sample it became positive as opposed to the negative zeta  
 411 potential obtained from the experiments. Therefore, additional modification to the model was made.

412 The second step optimization was initiated by fixing the optimal values of all equilibrium constants  
 413 obtained from the first step optimization. Then, using the same objective function as in the 1<sup>st</sup>  
 414 optimization step (**Eq. 3**), the 2<sup>nd</sup> step optimization was implemented for each rock sample and each  
 415 concentration of NaCl solution using the following variables:

- 416 • The concentration of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> was allowed to vary within the reported experimental  
 417 uncertainty.
- 418 • A variable capacitance of the Stern layer was assumed and allowed to vary between 0.2 F·m<sup>-2</sup>  
 419 and 1.4 F·m<sup>-2</sup> (see more detailed discussion in section 2.2.5).

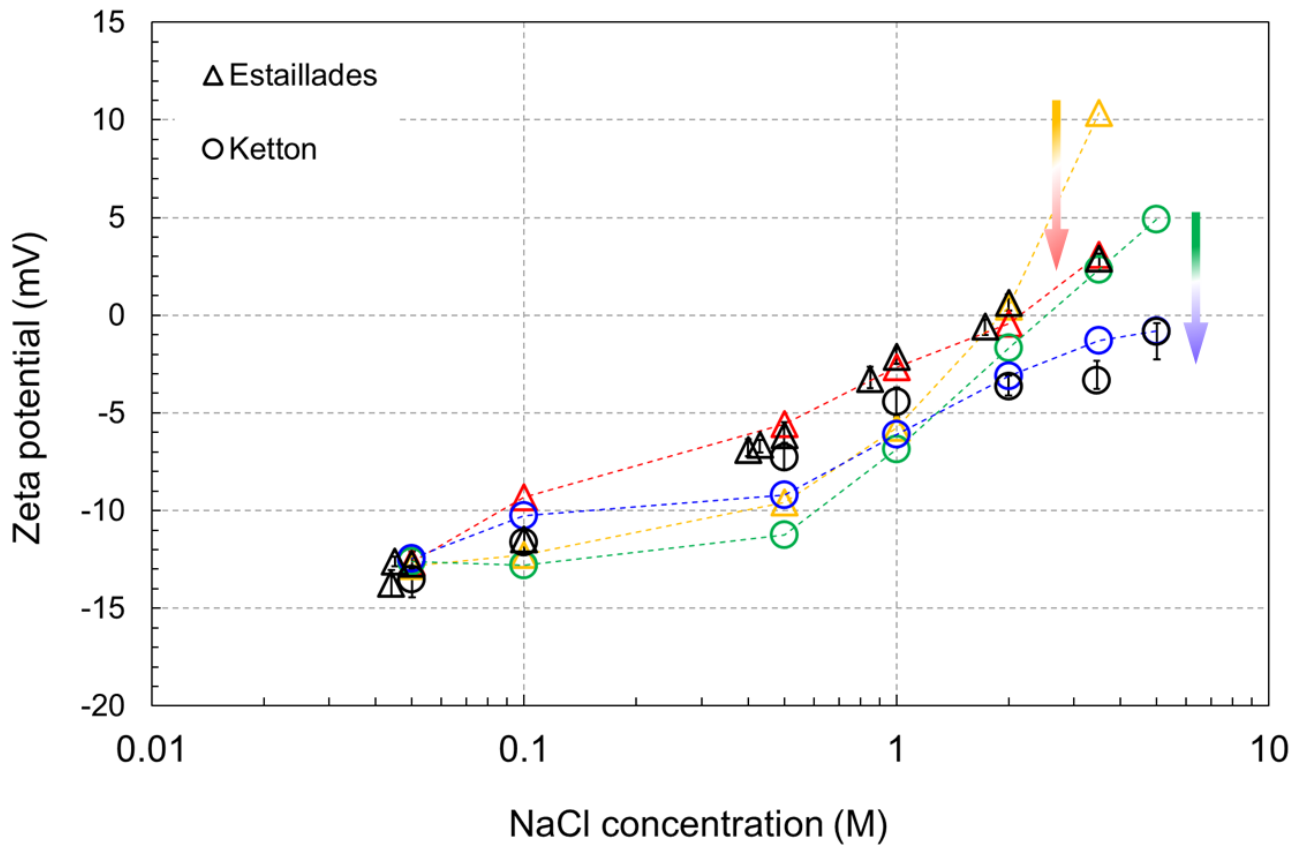
420 The resulting from the 2<sup>nd</sup> optimization step pH and concentration of SO<sub>4</sub><sup>2-</sup> and Mg<sup>2+</sup> remained the  
 421 same compared with the results of the 1<sup>st</sup> optimization step. However, to obtain a better match to the  
 422 experimentally measured zeta potential required a non-monotonic change of the optimized Stern  
 423 layer capacitance (**Figure 5a**) and increased concentration of Ca<sup>2+</sup> (see the yellow→red shift for  
 424 Estailades and green→blue shift for Ketton in **Figure 5b**). The computed zeta potential was found  
 425 to be in a good agreement with the experimental data after the variable capacitance was  
 426 implemented (see the yellow→red shift for Estailades and green→blue shift for Ketton in **Figure 6**).



427

428 **Figure 5.** Optimized Stern layer capacitance (a) and pCa as a function of NaCl concentration. Black symbols  
 429 in b) correspond to the experiments of Al Mahrouqi et al., [12]. The yellow→red and green→blue shift represent  
 430 manual adjustment of pCa to obtain a better match to the computed zeta potential in **Fig. 6**.

431



432

433 **Figure 6.** Calculated zeta potential after the first and the second step optimization. Black symbols correspond  
 434 to the experimental data of Al Mahrouqi et al. [12]. The yellow→red (Estailades) and green→blue (Ketton)  
 435 shifts demonstrate a significant improvement of the match after applying variable Stern layer capacitance.

436

437 **2.2.5. Variable Stern layer capacitance**



438 As mentioned in the previous section, in order to obtain a good match with the experimentally  
 439 measured zeta potential it was required to allow the Stern layer capacitance ( $C_{SL}$ ) to vary and to  
 440 decrease globally. Following the definition of  $C_{SL}$  (**Eq. 2**), its optimized concentration dependence  
 441 (**Figure 5a**) can be explained by either: i) constant distance between the 0-plane and  $\beta$ -plane,  $x$ , and  
 442 decreasing relative permittivity of the Stern layer,  $\varepsilon_r$ , with increasing NaCl concentration; ii) constant  
 443 relative permittivity and increasing with salinity  $x$ ; iii) increasing with salinity  $x$  and decreasing  $\varepsilon_r$ ; or  
 444 iv) decreasing  $x$  and  $\varepsilon_r$  with increasing salinity so that the rate of decrease of  $\varepsilon_r$  exceeds that of  $x$ .  
 445 Previously published studies have suggested that hydration diameter of cations decreases  
 446 considerably with increasing salinity, hence  $x$  might become smaller as smaller in diameter ions may  
 447 have a closer distance of approach to the mineral surface (see for example, results obtained from  
 448 an analytical model for  $Mg^{2+}$  in Afanas'ev and Ustinov [41] and for  $Na^+$  in Afanasiev et al. [42] using  
 449 the same approach, both verified by various experimental data) thus restricting the possible  
 450 explanation for the decreasing  $C_{SL}$  to option iv). This assumption is also supported by Brown et al.  
 451 [43] who suggested a substantial compression of the Stern layer with increasing electrolyte salinity,  
 452 which was interpreted from experimental observations including EPM. In contrast, some molecular  
 453 dynamics studies (e.g., [44]) suggest that there is no change in  $x$  with increasing salt concentration  
 454 due to the presence of the hydrolysis layer. At the same time, an electric field within the Stern layer  
 455 that is exerted on polar water molecules results in its polarization and may lead to a substantial  
 456 decrease in  $\varepsilon_r$  with increasing salinity (e.g., [45]), consistent with options i), iii) and iv). In the light of  
 457 the above arguments, we assumed option i) in our model, implying constant  $x$  and decreasing with  
 458 salinity  $\varepsilon_r$ . Note, that we tested hypothesis iv) and found that  $C_{SL}$  is significantly less sensitive to the  
 459 variation of  $x$  (even assuming the maximum possible range between fully hydrated  $Na^+$  radius of 4.5  
 460 Å and crystallographic  $Na^+$  radius of 0.5 Å at 5 M [46]) compared with allowed variation of  $\varepsilon_r$  (between  
 461 the value that corresponds to diluted electrolyte, ~80 at a temperature of 20°C and that of structured  
 462 water in the Stern layer, ~6 [10]), but this sensitivity analysis is not presented here.

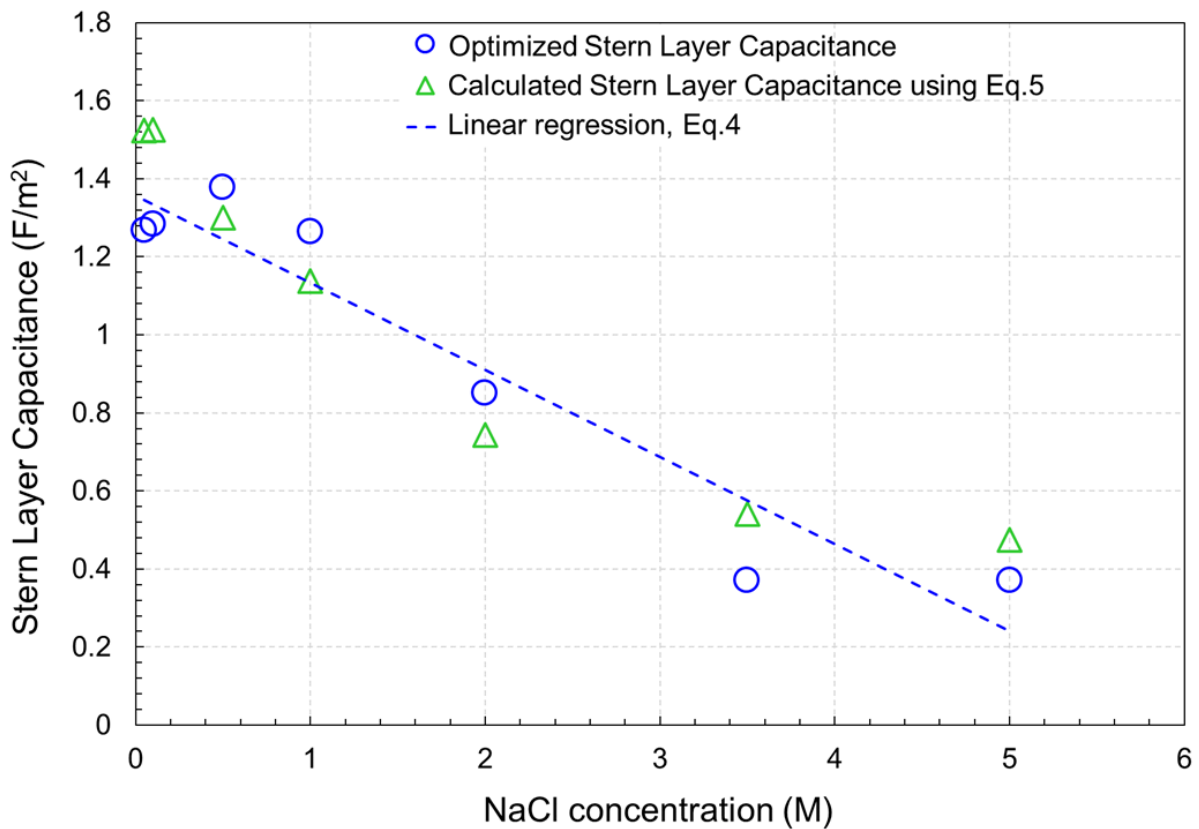
463 For simplicity we used a linear regression through optimized values of  $C_{SL}$  as shown in **Figure 7**:

$$C_{SL} = -0.2232 \times IS + 1.357 [F \cdot m^{-2}] \quad (4)$$

464 Where  $IS$  is the ionic strength of the solution of interest (M). To verify the regression is physically  
 465 meaningful we assumed a constant distance between 0-plane and  $\beta$ -plane of  $x = 2.3$  Å [6] and used  
 466 a published equation for the Stern layer relative permittivity [47,48]:

$$\varepsilon_r = \frac{\varepsilon_z - \varepsilon_s}{1 + b \left( -\frac{d\phi}{x} \right)^2} + \varepsilon_s \quad (5)$$

467 where  $\varepsilon_z$  is the relative permittivity of the bulk electrolyte (at a given ionic strength and temperature),  
 468  $\varepsilon_s$  is the relative permittivity near the mineral surface (~6 [48]),  $d\phi$  is the electrical potential difference  
 469 (V) between 0-plane with  $\beta$ -plane calculated by our model, and  $b = 1.2 \times 10^{-17} m \cdot V^{-1}$  is a constant  
 470 [48]. The values of  $C_{SL}$  calculated using  $\varepsilon_r$  computed from Eq. 5, and  $x = 2.3$  Å are plotted in **Figure**  
 471 **7** and are in good agreement with the optimized values thus confirming the validity of our approach.  
 472 Note, that  $d\phi$  for Eq.5 were computed by PHREEQC using the linear regression of  $C_{SL}$  (blue line in  
 473 **Figure 7**) and provided an excellent match to the zeta potentials, so that non-linear regressions for  
 474  $C_{SL}$  were not tried as this was not the focus of this study.



475

476 **Figure 7.** Optimized Stern layer capacitance compared with values obtained using **Eq. 5** and approximated  
 477 by the linear regression fitted to the optimized values in blue (**Eq. 4**; quality of match to the optimized values  
 478 of capacitance in blue is  $R^2 = 0.91$ ) as a function of ionic strength.

479

### 480 2.3. Calcite surface complexation model implementation

481 To use our model for predicting the zeta potential of calcite in contact with aqueous solutions requires  
 482 identification of input parameters and model options that accurately replicated the reported  
 483 experimental conditions. Therefore, the following steps should be taken to obtain an accurate  
 484 prediction of the zeta potential:

- 485 • Define the *saturation index* and the *amount* (typically, 10 mol to 20 mol to allow sufficient  
 486 amount of calcite to equilibrate with the solution of interest) in 'EQUILIBRIUM\_PHASES'  
 487 section (see **Appendix A**). A non-zero *amount* should be chosen to replicate chemical  
 488 equilibration between calcite and water of the experiment of interest, while the *saturation index*  
 489 should be adjusted so that the computed  $\text{Ca}^{2+}$  concentration matches the experimental value.
- 490 • Define input concentrations of all ions in the modelled solution consistent with the reported  
 491 values. Note, that the input concentration of  $\text{Ca}^{2+}$  should be kept at zero and  
 492 dissolution/precipitation of calcite switched on, when simulating the zeta potential experiments  
 493 under equilibrium conditions, in which case content of  $\text{Ca}^{2+}$  in the solution is computed by  
 494 PHREEQC and cross-compared with the experimental data. Otherwise, the measured  
 495 concentration of  $\text{Ca}^{2+}$  should be used while switching off the calcite dissolution option (see  
 496 examples in the **Appendix A**).
- 497 • Use the optimized equilibrium constants for R1-R11 (**Table 2**).

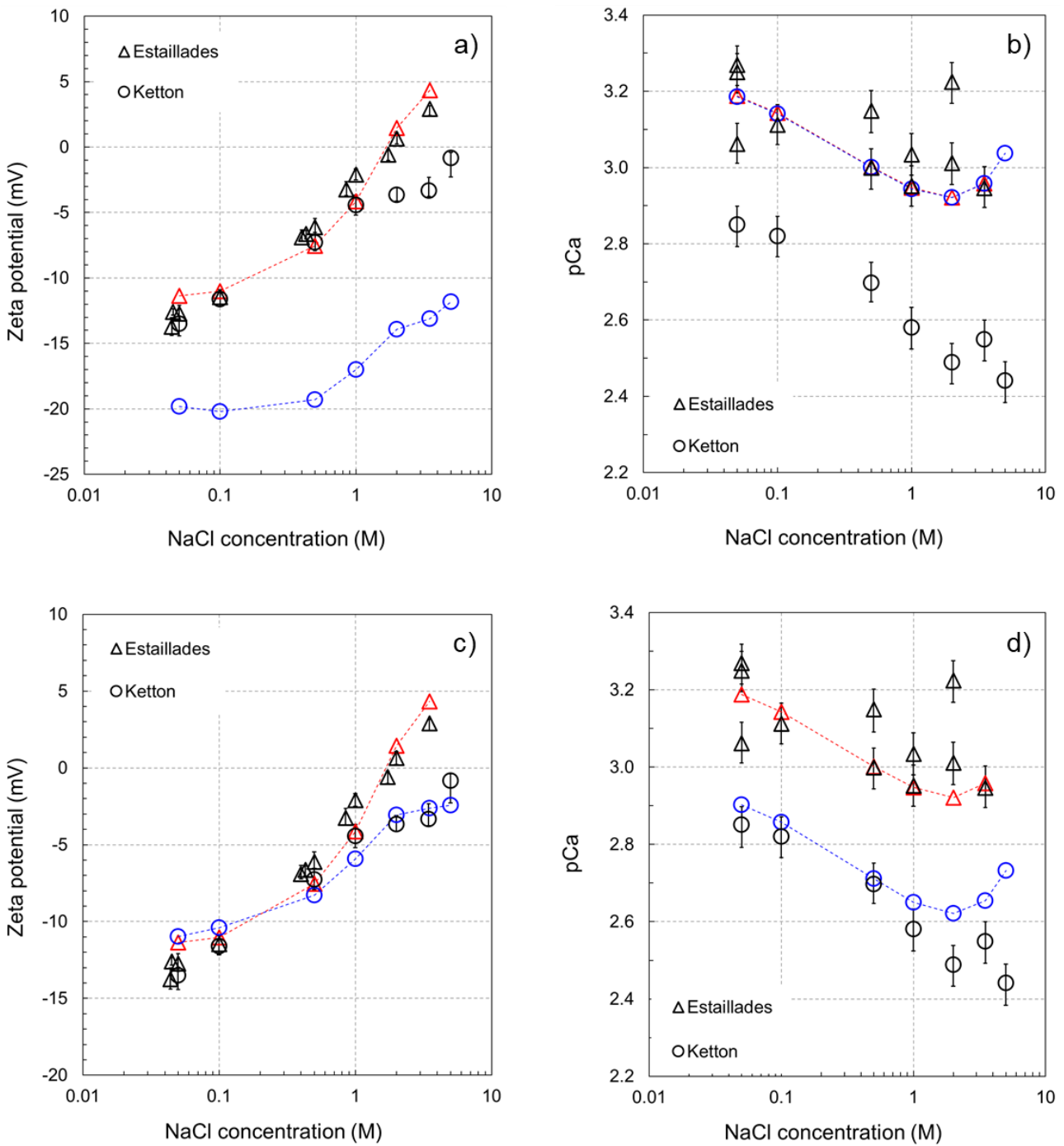
- 498 • For a given ionic strength, calculate the Stern layer capacitance using the linear regression  
499 equation (**Eq. 4**) and allow PHREEQC to compute the zeta potential. To validate the result  
500 cross-compare the simulated pH and concentrations of all ions against the measured values.  
501

### 502 3. Model validation, results and discussion

503 Our model described in previous sections was tested against the experimentally measured zeta  
504 potential in intact carbonate core samples saturated with aqueous solutions reported by Al Mahrouqi  
505 et al. [12], Jackson et al. [49] and Li et al. [11]. The developed model simulated the zeta potential  
506 from SPM conducted on three different intact carbonate samples saturated with equilibrated NaCl  
507 solutions [12], one intact carbonate sample saturated with equilibrated artificial solutions [49], and  
508 crushed Iceland spar sample saturated with unequilibrated NaCl solutions [11].

#### 509 3.1. Estailades and Ketton samples saturated with equilibrated NaCl solution [12]

510 We began modelling the zeta potential with defining the input equilibrium concentration of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  
511  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  as reported in the paper. The initial input concentration of  $\text{Ca}^{2+}$  was set to zero M, partial  
512  $\text{CO}_2$  pressure is set to  $10^{-3.44}$  atm (consistent with atmospheric  $\text{CO}_2$ ), and dissolution of calcite is  
513 switched on (zero default value of the *saturation index* and 20 mol *amount*) to replicate the  
514 equilibrium experimental conditions. Applying the specific capacitance values calculated using **Eq.**  
515 **4** for each value of tested ionic strength our model computed the zeta potential and the resulting  
516 equilibrium concentration of  $\text{Ca}^{2+}$ , and the results are shown in **Figures 8a** and **8b** (note, that  
517 simulated pH and concentration of all ions except  $\text{Ca}^{2+}$  were found to be identical to the experimental  
518 values used as input parameters). It can be seen from **Figures 8a** and **8b** that simulated results for  
519 the Ketton sample underestimate the concentration of  $\text{Ca}^{2+}$  and consequently overestimate the  
520 negative zeta potential. To be consistent with the experimental data, the calcite dissolution rate for  
521 Ketton was enhanced by setting the *saturation index* to 0.8, so that the modelled equilibrium  
522 concentration of  $\text{Ca}^{2+}$  became comparable with the measured one, which resulted in an excellent  
523 correlation between the modelled and measured zeta potential (**Figures 8c** and **8d**).



524

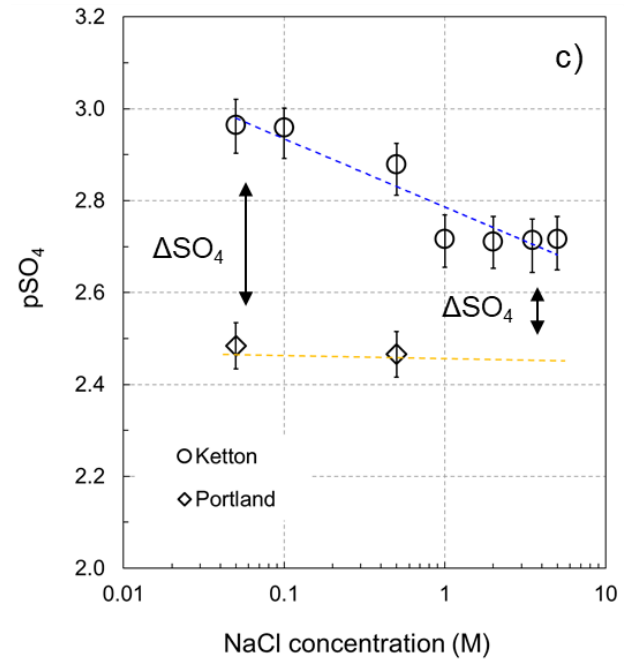
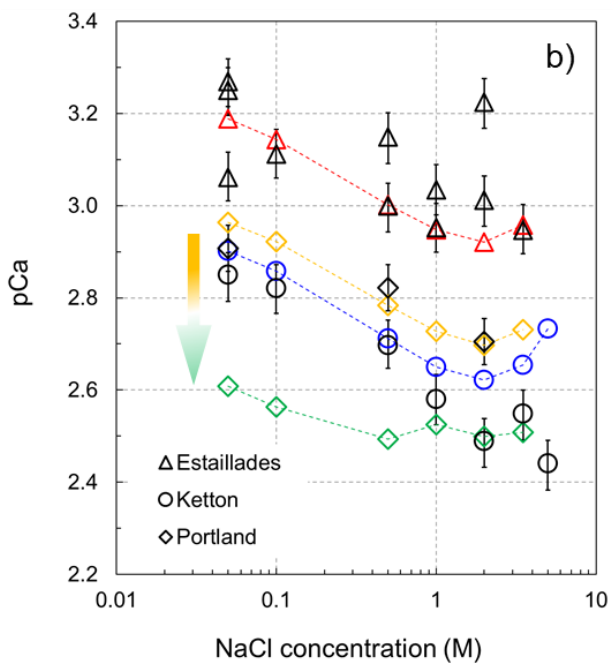
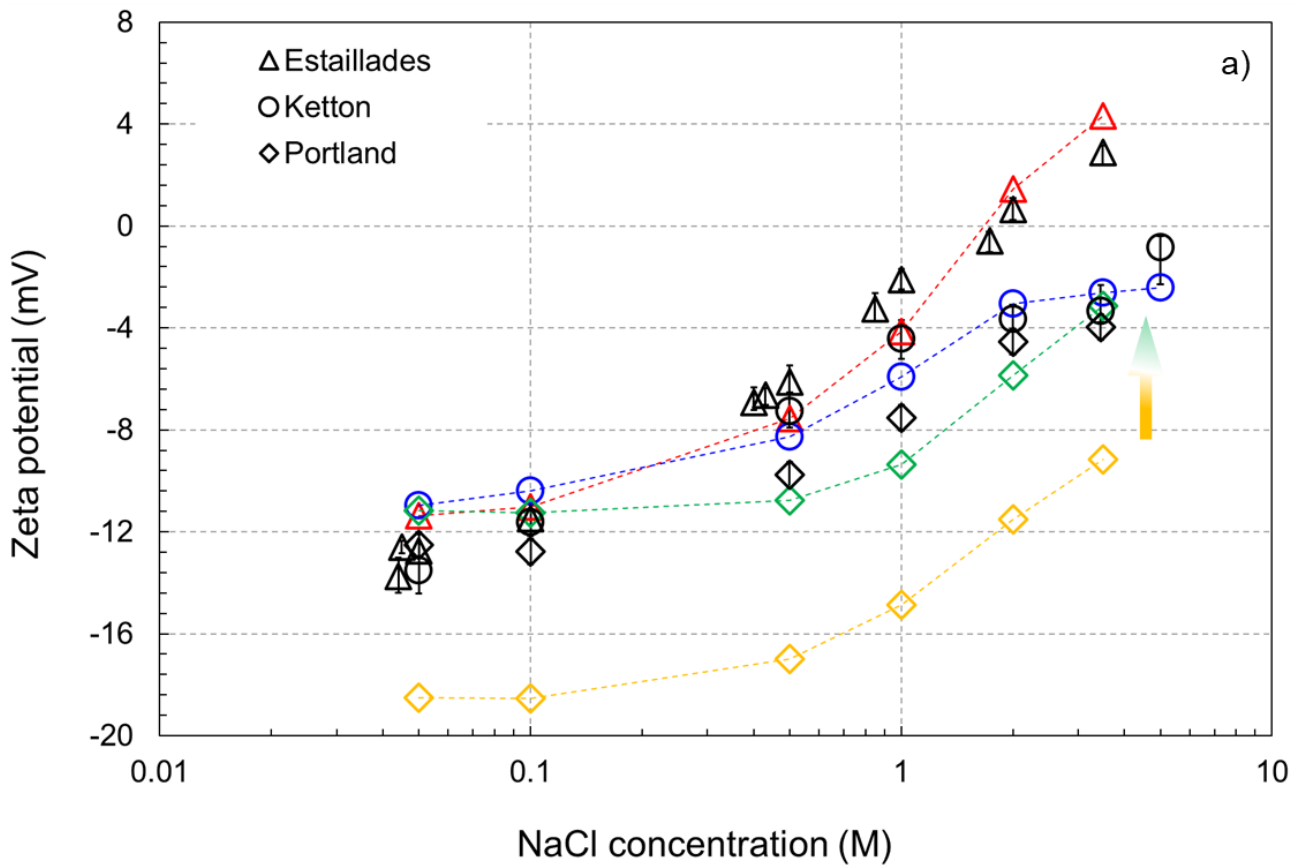
525 **Figure 8.** Experimentally measured (black symbols) and simulated zeta potential (a, c) and pCa (b, d) at  
 526 equilibrium conditions for Estailades and Ketton samples saturated with NaCl solutions. The modelled results  
 527 were obtained assuming identical *saturation index* for both rock samples toward NaCl solutions (a, b), and  
 528 higher *saturation index* for Ketton (0.80) sample relative to the default value (0) of Estailades (c, d).

529

### 530 3.2. Portland sample saturated with equilibrated NaCl solution [12]

531 Our model was then applied to simulate the zeta potential obtained from Portland limestone. To  
 532 evaluate the equilibrium concentration of  $\text{Ca}^{2+}$  dissolved from the Portland sample we implemented  
 533 a similar procedure by comparing the computed and measured equilibrium concentration of  $\text{Ca}^{2+}$ ,  
 534 which was reported to be slightly lower than that for the Ketton sample (compare diamonds and  
 535 squares in Figure 10a of Al Mahrouqi et al. [12]). A good agreement between the computed and  
 536 measured  $\text{Ca}^{2+}$  concentration corresponded to the *saturation index* of 0.6. However, a significantly

537 higher, compared with either Estailades or Ketton, concentration of  $\text{SO}_4^{2-}$  was reported for  
538 equilibrated solutions in contact with Portland (compare diamonds with squares in Figure 10b of Al  
539 Mahrouqi et al. [12]), while the reported concentration of  $\text{Mg}^{2+}$  in all rock samples was the same (pMg  
540 = 4.19). Since  $\text{SO}_4^{2-}$  in the equilibrated solution could only originate from dissolution of sulfate  
541 containing minerals (anhydrite or epsomite), the equilibrium concentration of  $\text{SO}_4^{2-}$  would not be  
542 expected to exceed that of the total concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which was not the case reported  
543 for Portland sample. We could not explain this discrepancy, and thus assumed that the reported  
544 concentration of  $\text{Ca}^{2+}$  was inaccurate and contained an experimental uncertainty, which resulted in  
545 underestimated concentration of the cation. Therefore, we artificially added  $\text{Ca}^{2+}$  to our simulated  
546 aqueous solution, so that the concentration of the added cation was equal to the difference in sulfate  
547 concentration across the salinity range:  $\Delta[\text{SO}_4^{2-}] = [\text{SO}_4^{2-}]_{\text{Portland}} - [\text{SO}_4^{2-}]_{\text{Ketton}}$ . Note that the  
548 difference in sulfate concentration depends on the salinity as shown in **Figure 9c**, so that a single  
549 value of the *saturation index* could not be used thus justifying our approach of adding  $\text{Ca}^{2+}$  to the  
550 solution artificially. Keeping the *saturation index* equal to 0.6, the total computed concentration of  
551  $\text{Ca}^{2+}$  increased by the amount equal to  $\Delta[\text{SO}_4^{2-}]$  (as denoted by the yellow→green shift in **Figure**  
552 **9b**), and we successfully modelled the zeta potential as presented in Figure 9a (the yellow→green  
553 shift in **Figure 9a** shows the effect on the computed zeta potential made by adding  $\text{Ca}^{2+}$  to the  
554 solution).



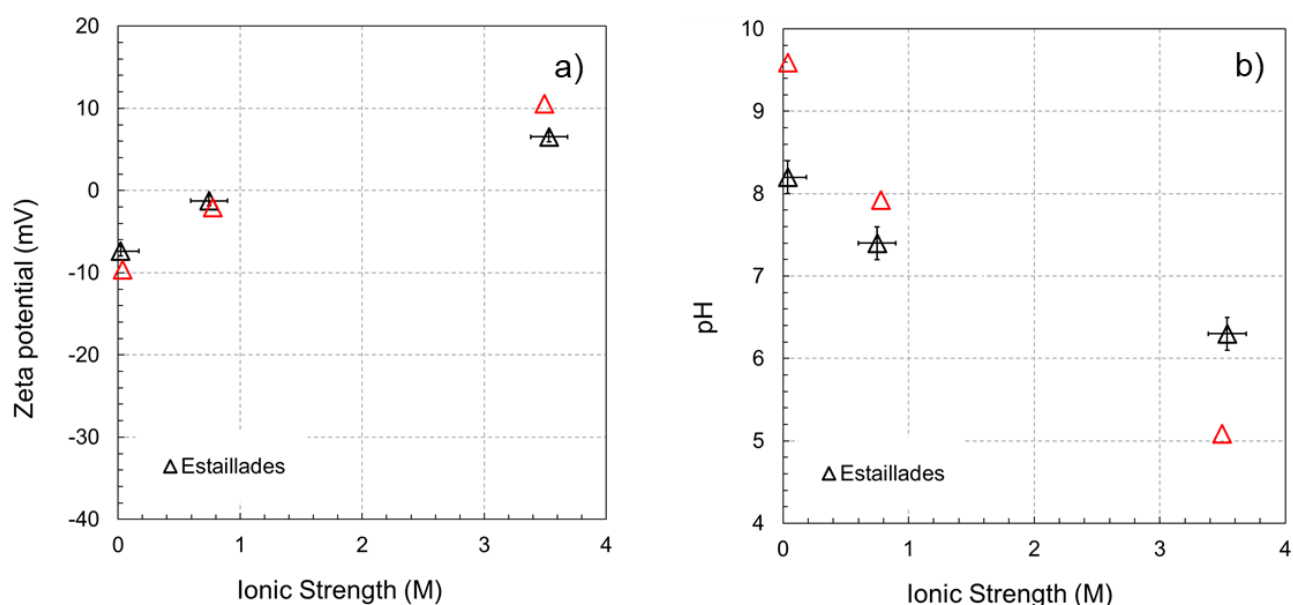
555

556 **Figure 9.** Measured and modelled zeta potential (a), pCa (b) and  $\text{SO}_4^{2-}$  (c) of three natural rock samples. The  
 557 amount of artificially added  $\text{Ca}^{2+}$  to the model of Portland equals the reported difference in concentration of  
 558  $\text{SO}_4^{2-}$  as shown in (c) and explained in Section 3.2. Yellow diamonds represent the modelled zeta potential (a)  
 559 and pCa (b) assuming *saturation index* of 0.6 and zero artificially added  $\text{Ca}^{2+}$ . The results of the model with  
 560 artificially added  $\text{Ca}^{2+}$  are denoted by green diamonds.

561

562 **3.3. Estailades sample saturated with artificial natural solutions [49]**

563 Jackson et al. [49] measured zeta potential on Estailades rock sample saturated with three different  
 564 equilibrated solutions: low salinity 20dSW (20 times diluted seawater), SW (seawater) representing  
 565 moderate ionic strength of 0.749 M, and 3.537 M high salinity FMB (formation brine), with detailed  
 566 composition provided in Table 1 in Jackson et al. [49]. The purpose of these experiments was to  
 567 simulate the conventional and/or inverted low salinity waterflooding used to maximize oil recovery.  
 568 To simulate the results, we modelled equilibrium conditions between calcite and the aqueous  
 569 solutions by using zero initial concentration of  $\text{Ca}^{2+}$  and the same calcite dissolution rate as in Section  
 570 3.1. for Estailades (default zero value of *saturation index*). The results of modelled zeta potential for  
 571 all three solutions are presented in **Figure 10**. Our model could successfully reproduce the measured  
 572 zeta potential (**Figure 10a**). However, the modelled equilibrium pH was significantly higher with  
 573 20dSW and significantly lower with FMB experimental data (**Figure 10b**) despite the fact that  
 574 modelled concentrations of all ionic species were found to be identical to the measured ones. We  
 575 hypothesize that such discrepancy could result from the experimental protocol reported by Jackson  
 576 et al. [49] who reported the initial (at time of preparation) pH and ionic concentration of solutions but  
 577 not the final values established after equilibration with the rock sample.



578  
 579 **Figure 10.** Simulated zeta potential (a) and pH (b) of three different brine compositions for Estailades rock  
 580 sample plotted as a function of ionic strength. The experimental data denoted by black symbols are extracted  
 581 from Jackson et al. [49].

582  
 583 It is worth mentioning, that equilibrium pH computed by our model in all tested aqueous solutions  
 584 and rock samples matched the experimentally measured values apart from the results presented in  
 585 **Figure 10**, where the simulated equilibrium pH was higher than experimental for 20dSW and SW and  
 586 lower than experimental for FMB. Inclusion of protonation of  $> \text{CO}_3^{-0.5}$  surface sites without changing  
 587 the optimized equilibrium constants resulted in increased simulated equilibrium pH compared with  
 588 the experimental values. Thus, the assumed exclusion of protonation of the  $> \text{CO}_3^{-0.5}$  surface sites  
 589 was confirmed for all tested parameters except for FMB, for which such reaction might need to be  
 590 included, and this will be tested in a follow-up study.

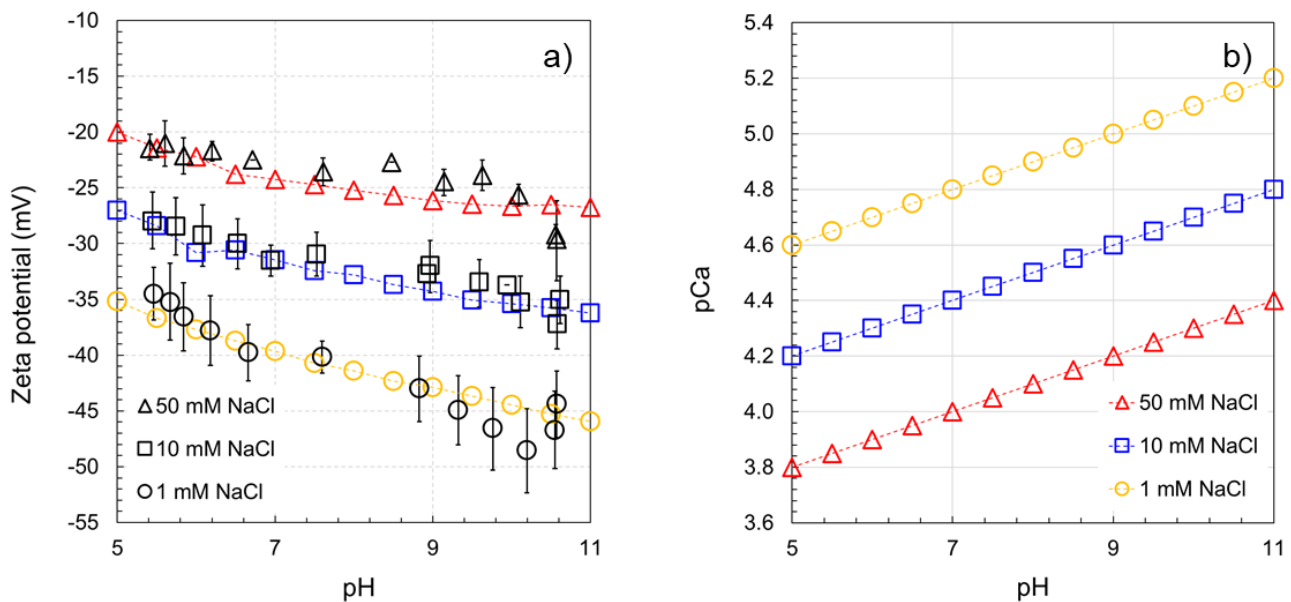
591  
 592 **3.4. Iceland spar saturated with NaCl at non-equilibrium conditions [11]**

593 Finally, our model was tested against the data reported by Li et al. [11] on crushed Iceland spar  
 594 saturated with  $10^{-3}$  M,  $10^{-2}$  M, and  $5 \times 10^{-2}$  M NaCl not equilibrated with the mineral. Description of the



595 experimental procedure reported by Li et al. [11] did not provide detailed information on the duration  
596 of the streaming potential measurements. However, considering the expected high permeability of  
597 the crushed samples (comparable to permeability of sandpacks reported by Vinogradov et al. [50])  
598 and low salinity solutions used by Li et al. [11], it was assumed that the reported streaming potential  
599 measurements on crushed Iceland spar did not last hundreds of hours required for complete  
600 equilibration between the mineral and the tested solutions. Therefore, we assumed that only partial  
601 equilibration was reached during the experiments and for that reason we modelled the data reported  
602 by Li et al. [11] as obtained at non-equilibrium conditions so that any equilibration of calcite was  
603 disabled in the model (zero *amount* was set, Section 2.3 and **Appendix A**). However, due to partial  
604 equilibration expected in the experiments, we artificially added some non-zero initial concentration  
605 of  $\text{Ca}^{2+}$  to the modelled solution. The concentration of dissolved  $\text{Ca}^{2+}$  in 0.05 M NaCl was adjusted  
606 to  $10^{-4.2}$  M (expressed as  $\text{pCa} = 4.2$  in **Figure 11b**) at pH 9, consistent with observations reported by  
607 Alroudhan et al. [19]. Firstly, we assumed that the amount of dissolved (and therefore artificially  
608 added to the model)  $\text{Ca}^{2+}$  should depend on pH (lower pH would lead to higher concentration of  
609 dissolved  $\text{Ca}^{2+}$ , consistent with higher dissolution rate reported by Anabaraonye et al. [51]).  
610 Furthermore, the pH dependence of  $\text{pCa}$  in 0.05 M NaCl experiments was extended throughout the  
611 entire range of pH (5-11) using a linear slope of  $\Delta \text{pCa} / \Delta \text{pH} = 0.1$ , consistent with calcite dissolution  
612 rate reported by Chou et al. [52].

613 Secondly, we assumed that dissolved  $\text{Ca}^{2+}$  concentration should also depend on NaCl concentration  
614 (higher NaCl concentration would lead to higher concentration of dissolved  $\text{Ca}^{2+}$  as reported in Al  
615 Mahrouqi et al. [12]). Therefore, for NaCl solutions of  $10^{-2}$  M and  $10^{-3}$  M the end-points of  $\text{pCa}$  were  
616 moved up the vertical scale by 0.4 units relative to one another to reflect on the salinity dependence  
617 of calcite dissolution. The value of 0.4 was approximated from the reported calcite dissolution rate  
618 as a function of NaCl concentration [53] and assuming duration of the steaming potential  
619 measurement experiments conducted by Li et al. [11] to be approximately 10 hours. Ultimately,  
620 ascribing the end-point values for  $\text{Ca}^{2+}$  concentration for each tested NaCl solution on the pH scale  
621 (**Figure 11b**) and applying linear variation of  $\text{pCa}$  between these end-points, our model successfully  
622 predicted the measured zeta potential (**Figure 11a**). Moreover, our model predicts that  $\text{Ca}^{2+}$  must  
623 be added to the modelled solution in order to replicate the experimentally measured zeta potential.  
624 Note, that  $\text{C}(4)$  of the amount equal to the added  $\text{Ca}^{2+}$  must also be added to the solution in addition  
625 to the initial concentration of  $\text{C}(4)$  that reflects the equilibrium content of dissolved  $\text{CO}_2$ . Despite the  
626 fact that the computed from calcite dissolution or artificially added  $\text{Ca}^{2+}$  and  $\text{C}(4)$  to the bulk  
627 electrolyte was not reported by Li et al. [11], the adsorption reactions for these ions were included in  
628 their SCM. Therefore, we are confident that our approach is consistent with Li et al. [11]. Our results  
629 also explain how the experimental data from Li et al. [11] was successfully matched by means of  
630 non-zero concentration of  $\text{Ca}^{2+}$  and  $\text{C}(4)$  in the solution, both of which should increase with  
631 decreasing pH. If such pH dependence of  $\text{Ca}^{2+}$  and  $\text{C}(4)$  concentration was not applied to the model  
632 of Li et al. [11], the simulated zeta potential would become more positive with increasing pH, which  
633 is an inverted trend relative to that reported in the paper.



634

635 **Figure 11.** Modelled zeta potential (a) and pCa (b) of crashed Iceland spar samples saturated with three  
 636 different NaCl solutions under non-equilibrium conditions. The modelled zeta potential is plotted in comparison  
 637 with the experimental data [11] denoted by black symbols. The slopes and intercepts of the pCa as a function  
 638 of pH are discussed and defined in Section 3.4.

639

### 640 3.5. Model capabilities, limitations and implication to carbonate-water subsurface settings

641 The developed robust SCM uses a set of justified and well-defined calcite surface sites and surface  
 642 reactions' equilibrium constants combined with physically meaningful salinity dependence of the  
 643 Stern layer capacitance. The model is capable to accurately predict zeta potential of a variety of  
 644 carbonate-aqueous solution systems as long as calcite is the dominating mineral comprising natural  
 645 rocks and the aqueous solution is dominated by NaCl. Moreover, an additional requirement for  
 646 predictive capability of our model relates to the naturally occurring concentration of  $\text{SO}_4^{2-}$  in the  
 647 solution, which has to reflect dissolution of sulfate containing minerals such as anhydrite or epsomite  
 648 over geological deposition timescale. This requirement implies that the equilibrium concentration of  
 649  $\text{SO}_4^{2-}$  should not exceed the combined concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

650 The set of equilibrium constants proposed in this paper for ambient conditions (25°C and 1 atm) has  
 651 not been tested to model experimental results obtained with aqueous solutions with artificially added  
 652  $\text{SO}_4^{2-}$  beyond natural occurrence, so that some amendments could be required to model such  
 653 experiments. Moreover, we have not considered elevated temperature experimental conditions,  
 654 which would require additional adjustments to the model: i) the equilibrium constants should be  
 655 adjusted for elevated temperature by using for example the Van't Hoff equation; ii) the relative  
 656 permittivity of the Stern layer should be recalculated; iii) the distance between the 0-plane and the  
 657  $\beta$ -plane should be reduced to account for reduced hydrated diameter of cations at elevated  
 658 temperature (consistent with [50,54]); iv) the salinity dependence of the Stern layer capacitance  
 659 should be amended taking into account ii) and iii) so that a new temperature specific regression is  
 660 used.

661 Capabilities of our model have a broad range of applications since the approach reported here has  
 662 demonstrated to provide an accurate prediction of the zeta potential of natural carbonate rock in  
 663 contact with aqueous solutions, subject to the above conditions. Our model works best for equilibrium  
 664 experimental conditions as long as concentration of all major ionic species is known. In this sense,  
 665 our model can significantly improve our understanding of streaming potential measurements and

666 associated flows in shallow aquifers where temperature and pressure are low and therefore,  
667 laboratory measurements of pH and concentration of all ions of the solution at aquifer conditions are  
668 straight forward. Laboratory experiments should, in this case, assure establishment of full equilibrium  
669 between rock and the solution of interest and fluid samples should be analyzed for molar  
670 concentration of all ions to be used as input parameters of the model. The modelled zeta potential  
671 can then be used to predict flow patterns in critical zones (e.g., [55]), permeability heterogeneities  
672 (e.g., [56]) or even serve as an early warning of saline intrusion (e.g., [2,3]).

673 Our model is useful in situations where the exact concentration of all ions is unknown. For example,  
674 the model can accurately assess the initial estimate of CO<sub>2</sub> geological storage efficiency. The model  
675 would require input from the experimental data, given that laboratory experiments are conducted to  
676 establish full chemical equilibrium between carbonate rock and a CO<sub>2</sub>-saturated aqueous solution at  
677 the target formation conditions of temperature and pressure. Such experiment should report at least  
678 one measured concentration (of constituent ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> or protons, pH) to validate  
679 the simulated by our model concentrations (similar to the experiments reported by Li et al. [57]). The  
680 modelled zeta potential then can be used to interpret the wetting state using Derjaguin-Landau-  
681 Verwey- Overbeek (DLVO) theory (e.g.,[58]) and the resulting residual trapping of the gas.

682

#### 683 4. Conclusions

684 We report a robust surface complexation model of calcite-water interfaces. The model was  
685 developed adopting a two-step optimization, in which the equilibrium constants of surface reactions  
686 were initially optimized to match two experimental datasets, while the ionic strength dependence of  
687 the Stern layer capacitance was obtained in the second optimization step. The model was applied  
688 to successfully predict multiple experimental datasets with an excellent quality of match, and the  
689 modelling results demonstrate that:

- 690 • The unique set of the optimized equilibrium constants can be used universally to simulate the  
691 calcite-water zeta potentials obtained from the streaming potential measurements for all tested  
692 systems and conditions.
- 693 • The Stern layer capacitance should decrease with increasing salinity to replicate high salinity zeta  
694 potentials; the range of varying capacitances was found to be consistent with analytically  
695 predicted values [48] and with values used in previously published numerical studies [45].
- 696 • Using experimental composition of investigated solutions as the only input, our model accurately  
697 predicts zeta potentials of all tested systems and conditions including natural limestones  
698 equilibrated with simple salt and complex solutions of ionic strengths between 0.05 M and 5 M,  
699 and crushed calcite not equilibrated with NaCl solutions of ionic strength between 0.001 M and  
700 0.01 M.
- 701 • To simulate zeta potentials of natural carbonate-water systems at equilibrium conditions, the  
702 developed model requires knowledge of concentration of  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$  that leach from dolomite  
703 and anhydrite inclusions, while the equilibrium concentration of  $\text{Ca}^{2+}$  is produced by the model.
- 704 • To simulate zeta potentials of calcite in contact with water under non-equilibrium conditions  
705 requires knowledge of either measured in *real-time*  $\text{Ca}^{2+}$  concentration or duration of the  
706 simulated experiment.
- 707 • Our model is fully predictive given the required input parameters (e.g., ion concentration) are  
708 provided. However, additional surface reactions and/or model adjustments might be required to  
709 simulate the zeta potentials for carbonate rock in contact with aqueous solutions in which  $\text{SO}_4^{2-}$   
710 concentration exceeds that of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  combined, this will be investigated in a follow-up  
711 study.

712 Future work will also aim at acquiring additional experimental data obtained with varying  
713 concentration of  $\text{C}(4)$  and  $\text{SO}_4^{2-}$  ions under equilibrium conditions to inform the surface complexation  
714 model, which will be updated and/or modified to include the hypothesis of ion bridging outside OHP.

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- 897



898 **Appendix A – PHREEQC code examples**

899 In examples below, text that follows the # symbol is not part of the code, but comments aimed at  
900 clarifying the meaning of program keywords and values

901

902 **EQUILIBRIUM\_PHASES** #basic description

903 **Calcite 0 20**

904 # 0 is the default *saturation index*; 20 is the available *amount* of calcite in mol. The *saturation index*  
905 can be either negative or positive to hinder or enhance calcite dissolution, respectively. To prevent  
906 any dissolution or precipitation of calcite during the equilibration, the *amount* should be set to zero.

907

908 **CO2(g) -3.44**# defines partial CO<sub>2</sub> pressure at equilibrium with atmospheric air equal to 10<sup>-3.44</sup> atm

909 -----

910

911 **EQUILIBRIUM\_PHASES** #example 1 – simulation of established equilibrium between calcite and  
912 water, *default* saturation index (Estailades). The computed equilibrium concentration of Ca<sup>2+</sup>  
913 dissolved in 0.05 M NaCl is pCa=3.18

914 **Calcite 0 20**

915 **CO2(g) -3.44**

916

917 **SOLUTION 1**

918 **temp 25**

919 **units mol/L**

920 **Na 0.05**

921 **Cl 0.05 charge** #the **charge** keyword forces charge balance of the solution by adjusting  
922 concentration of Cl

923 **Mg 0.0000645** #experimental

924 **S(6) 1.800E-4** #experimental

925 **SAVE SOLUTION 1**

926 -----

927

928 **EQUILIBRIUM\_PHASES** #example 2 – simulation of established equilibrium between calcite and  
929 water, *adjusted* saturation index (Ketton). The computed equilibrium concentration of Ca<sup>2+</sup> dissolved  
930 in 0.05 M NaCl is pCa=2.90

931 **Calcite 0.80 20**

932 **CO2(g) -3.44**

933

934 **SOLUTION 2**

935 **temp 25**

936 **units mol/L**

937 **Na 0.05**

938 **Cl 0.05 charge**

939 **Mg 0.0000645** #experimental

940 **S(6) 0.011** #experimental

941 **SAVE SOLUTION 2**

942 -----

943  
944 **EQUILIBRIUM\_PHASES** #example 3 – simulation of no established equilibrium between calcite and  
945 water (Iceland Spar), default saturation index non-zero input concentration of Ca<sup>2+</sup>.  
946 **Calcite 0 0**  
947 **CO2(g) -3.44**  
948  
949 **SOLUTION 3**  
950       **temp 25**  
951       **units mol/L**  
952       **Na 0.05**  
953       **Cl 0.05 charge**  
954       **Ca 0.0000631** #equivalent to pCa=4.2 interpreted from Figure 2a (Alroudhan, et al., 2016)  
955 assuming 10 hours of partial equilibration during the experiment, which results in pH=9.  
956 **SAVE SOLUTION 3**  
957 -----