



HAL
open science

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

Jan Vinogradov, Miftah Hidayat, Jos Derksen, David Vega-Maza, Stefan Iglauer, Mohammad Sarmadivaleh, Damien Jougnot, Mohamed Azaroual, Philippe Leroy

► To cite this version:

Jan Vinogradov, Miftah Hidayat, Jos Derksen, David Vega-Maza, Stefan Iglauer, et al.. Predictive surface complexation model of the calcite-aqueous solution interface: The impact of high concentration and complex composition of brines. *Journal of Colloid and Interface Science*, 2022, 609, pp.852 - 867. 10.1016/j.jcis.2021.11.084 . hal-03695223

HAL Id: hal-03695223

<https://hal.sorbonne-universite.fr/hal-03695223v1>

Submitted on 14 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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^a, Miftah Hidayat^{a,b}, Mohammad Sarmadivaleh^b, Jos Derksen^a, David Vega-Maza^{a,c},
4 Stefan Iglauer^{d,e}, Damien Jougnot^f, Mohamed Azaroual^{g,h} and Philippe Leroy^h

5 ^a University of Aberdeen, School of Engineering, Elphinstone Road, AB24 3UE Aberdeen, United Kingdom

6 ^b Curtin University, Discipline of Petroleum Engineering, 26 Dick Perry Avenue, 6151 Kensington, Australia

7 ^c Now at the University of Valladolid, School of Engineering, TermoCal, BioEcoUva, Valladolid, Spain

8 ^d Edith Cowan University, Centre for Sustainable Energy and Resources, 270 Joondalup Drive, 6027
9 Joondalup, Australia

10 ^e Edith Cowan University, School of Engineering, 270 Joondalup Drive, 6027 Joondalup, Australia

11 ^f Sorbonne Université, CNRS, EPHE, UMR 7619 METIS, F-75005 Paris, France

12 ^g Université d'Orléans, Univ. Orléans, CNRS, BRGM, ISTO, UMR 7327, F-45071, Orléans, France

13 ^h 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, CO₂ sequestration and hydrocarbon
31 recovery.

32

33

34 **This work is published in JCIS:**

35 Vinogradov, J., Hidayat, M., Sarmadivaleh, M., Derksen, J., Vega-Maza, D., Iglauer, S., Jougnot, D.,
36 Azaroual, M., Leroy, P. (2022) Predictive surface complexation model of the calcite-aqueous
37 solution interface: the impact of high concentration and complex composition of brines, *Journal of*
38 *Colloids and Interface Sciences*, 609, 852-867. [doi:10.1016/j.jcis.2021.11.084](https://doi.org/10.1016/j.jcis.2021.11.084)

39

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 CO₂
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].

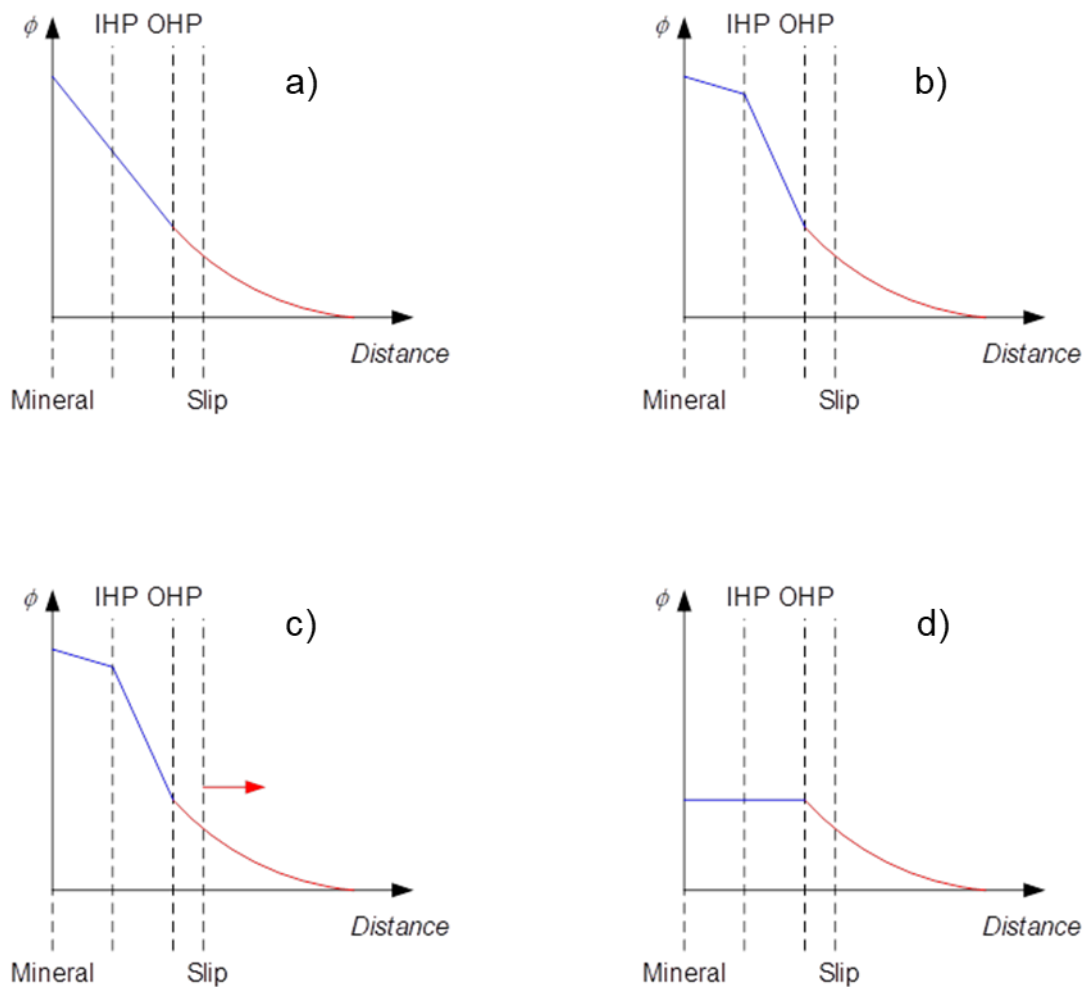
53 The zeta potential is defined as the electrical potential at the shear plane when water flow occurs
54 parallel to the pore surface [7]. It is most commonly used to estimate the electrochemical properties
55 of calcite because acid-base potentiometric titration, usually employed to measure the surface
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/m², 1.24 F/m² [11]
156 , 17 F/m² [27], 52 F/m² [28] and 100 F/m² [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 Mg²⁺ and SO₄²⁻ and high ionic strength. Studies that included such reactions reported inconsistent
161 equilibrium constants, with Heberling et al. [6] predicting adsorption of Ca²⁺ 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 SO₄²⁻ does not exceed that of Ca²⁺ and Mg²⁺.

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 ^a – calcite	97 ^a (95 ^b) – calcite	96.6 ^a – calcite
	3 ^a magnesium	3 ^a (4 ^b) – magnesium	3.4 ^a – quartz
		(1 ^b) – 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(CO₃)₂) and 1% anhydrite (CaSO₄) 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⁺,
196 Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻. The experimentally confirmed presence of Ca²⁺, Mg²⁺, and SO₄²⁻ 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 Ca²⁺, Mg²⁺, and
201 SO₄²⁻.

202 2.2. Calcite surface complexation model development

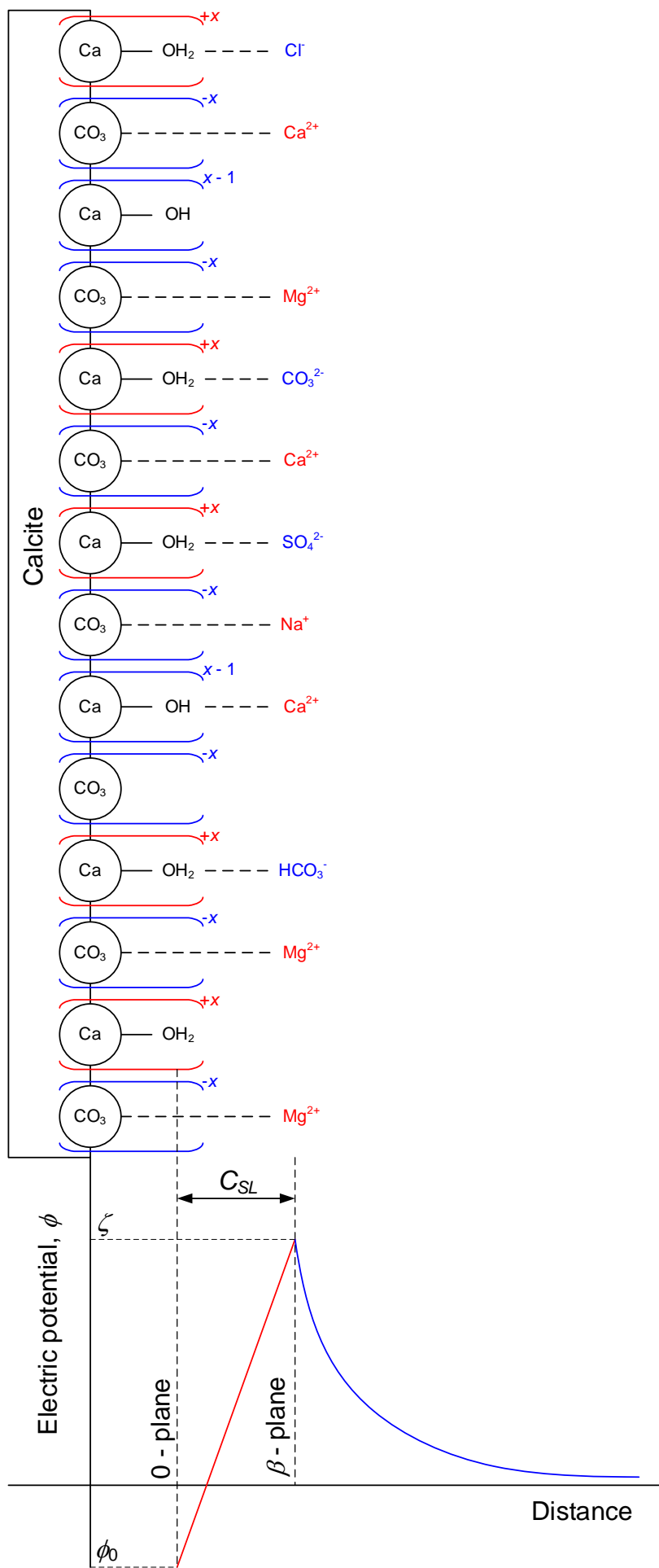
203 2.2.1. Basic definitions and assumptions

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 β -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 β -plane, with the latter corresponding
240 to the OHP where all adsorption reactions take place and where the zeta potential (ζ) 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 ^{min}	LogK ^{max}	LogK ^{opt}
0-plane reactions				
R1	$> \text{CaOH}_2^{+0.5} \Leftrightarrow \text{CaOH}^{-0.5} + \text{H}^+$	-0.5	-0.5	-0.5
β -plane reactions				
R2	$> \text{CaOH}^{-0.5} + \text{Na}^+ \Leftrightarrow \text{CaOH}^{-0.5} - \text{Na}^+$	0.09 ^a	0.56 ^b	0.56
R3	$> \text{CaOH}_2^{+0.5} + \text{Cl}^- \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{Cl}^-$	-2.10 ^c	0.45 ^d	-0.64
R4	$> \text{CaOH}^{-0.5} + \text{Ca}^{2+} \Leftrightarrow \text{CaOH}^{-0.5} - \text{Ca}^{2+}$	1.68 ^b	3.40 ^e	3.40
R5	$> \text{CaOH}_2^{+0.5} + \text{HCO}_3^- \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{HCO}_3^-$	0.04 ^b	12.50 ^f	10.65
R6	$> \text{CaOH}_2^{+0.5} + \text{CO}_3^{2-} \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{CO}_3^{2-}$	-7.07 ^b	6.00 ^g	-4.59
R7	$> \text{CO}_3^{-0.5} + \text{Ca}^{2+} \Leftrightarrow \text{CO}_3^{-0.5} - \text{Ca}^{2+}$	1.68 ^b	3.40 ^h	3.40
R8	$> \text{CO}_3^{-0.5} + \text{Na}^+ \Leftrightarrow \text{CO}_3^{-0.5} - \text{Na}^+$	0.56 ^b	3.40 ⁱ	0.56
R9	$> \text{CaOH}^{-0.5} + \text{Mg}^{2+} \Leftrightarrow \text{CaOH}^{-0.5} - \text{Mg}^{2+}$	1.66 ^a	3.40 ^j	2.81
R10	$> \text{CaOH}_2^{+0.5} + \text{SO}_4^{2-} \Leftrightarrow \text{CaOH}_2^{+0.5} - \text{SO}_4^{2-}$	-2.10 ^g	3.30 ^k	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 ^l	3.40 ^l	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^{min} 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^{max} 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^{max} 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^{max} 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^{min} and LogK^{max} 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^{min} and LogK^{max}, 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 β -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 σ_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 β -plane ($F \cdot m^{-2}$), ϕ_0 is the electric
309 potential at 0-plane (V) and ϕ_β is the electric potential at β -plane (V). The Stern layer capacitance
310 can also be expressed as:

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

311 where ϵ_0 is vacuum permittivity ($F \cdot m^{-1}$), ϵ_r is relative permittivity of the Stern layer and x is the
312 distance between 0-plane and β -plane or the thickness of the Stern layer (m). Beyond the β -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 Ca²⁺ and C(4) ions that originate from the dissolved
 336 atmospheric CO₂ in aqueous solution at equilibrium with air. This assumption is consistent with
 337 the experimentally confirmed dissolution of CaCO₃ during the equilibration process that
 338 resulted in 10⁻³ M of dissolved Ca²⁺, and hence the same concentration of C(4) [12,19], which
 339 is higher than the equilibrium concentration of 1.5×10⁻⁵M 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 ζ_{obs} is the observed zeta potential (mV), ζ_{sim} is the simulated zeta potential (mV), δ_{ζ} is
 347 the experimental uncertainty of the zeta potential (mV), pH_{obs} is the observed pH, pH_{sim} is the
 348 simulated pH and δ_{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.

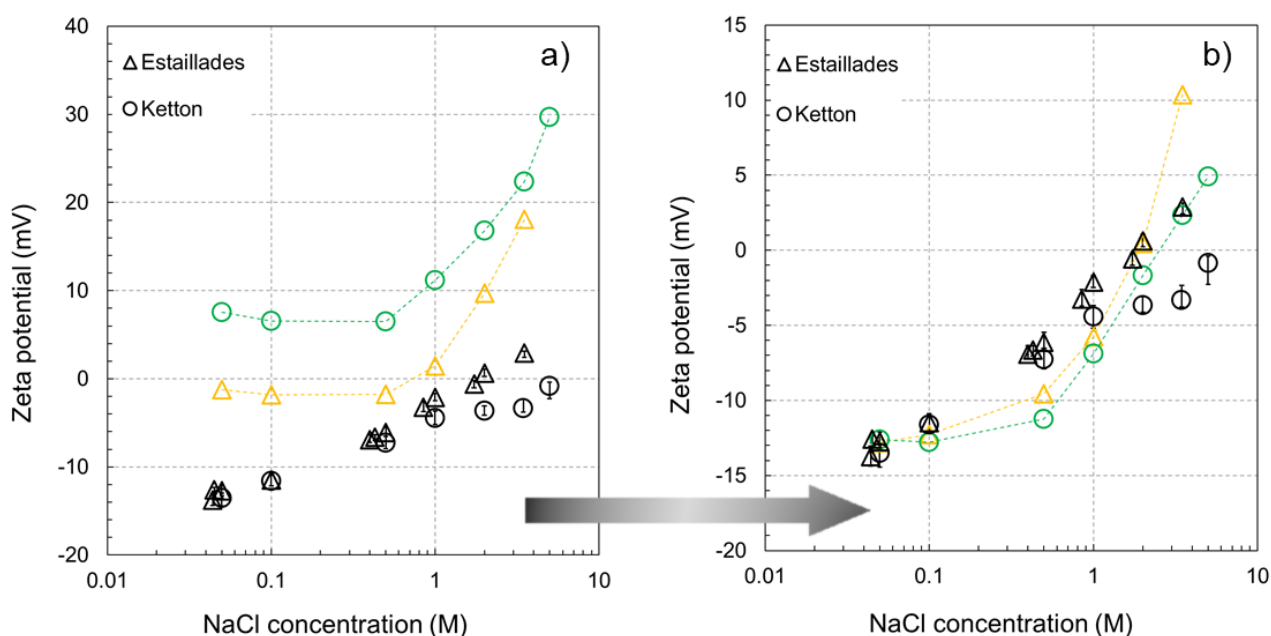
- 354 • The optimization was repeated three times, with the initial values of all equilibrium constants
 355 being either i) the minimum found in literature ($\text{Log}K^{\text{min}}$), ii) the maximum reported in the
 356 literature ($\text{Log}K^{\text{max}}$), or iii) the median within the tested 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 Ca²⁺ 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.

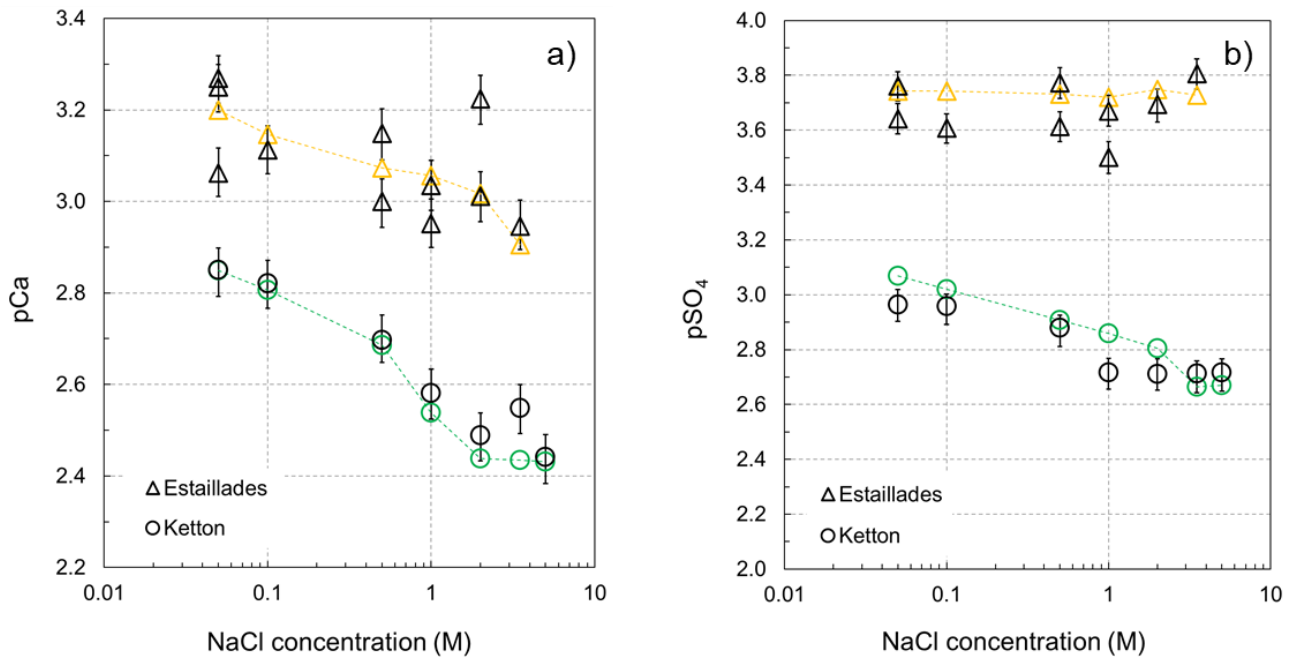
371 However, a considerably higher concentration of SO₄²⁻ was also reported in experiments with Ketton
 372 (Figure 9b in Al Mahrouqi et al. [12]), and more negative zeta potential compared with that of
 373 Estailades sample was attributed to it. The authors demonstrated that the zeta potential was not
 374 very sensitive to SO₄²⁻ 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 SO₄²⁻ 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 Ca^{2+} ions acting as bridges to SO_4^{2-} ions [38–40] thus enhancing sulfate adsorption
 378 when elevated concentration of Ca^{2+} is found in bulk solution. Such bridging ability of Ca^{2+} implies
 379 that higher concentration of Ca^{2+} (and/or Mg^{2+}) combined with higher concentration of 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 SO_4^{2-} could only originate from undetected
 382 minerals such as anhydrite (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 Ca^{2+} and/or Mg^{2+} as it
 384 was indeed reported by Al-Mahrouqi et al. [12]. Therefore, we assumed that the reactivity of calcite
 385 to 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 Ca^{2+} – 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 $-2.10 \leq \log K_{R10} \leq$
 394 3.30 , b) without the constraint $-2.10 \leq \log K_{R10}$. Black symbols denote the experimental results from
 395 AlMahrouqi et al. [12].

396 The calculated concentration of Ca^{2+} and SO_4^{2-} (note, that input pH and concentration of 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 pSO₄ (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**.

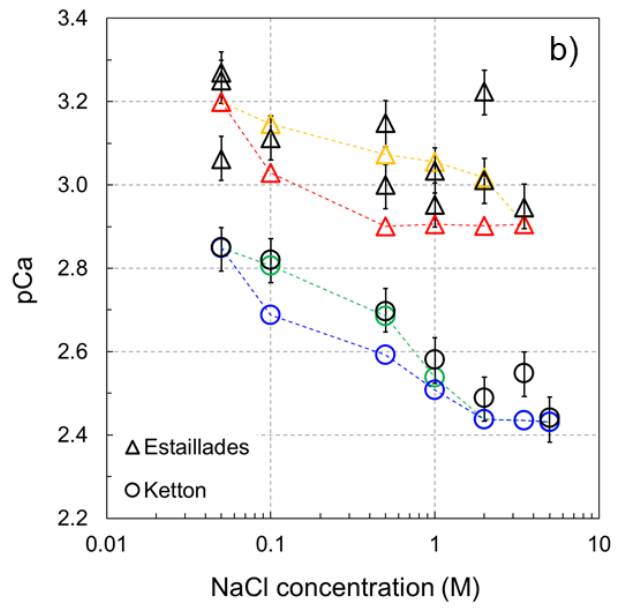
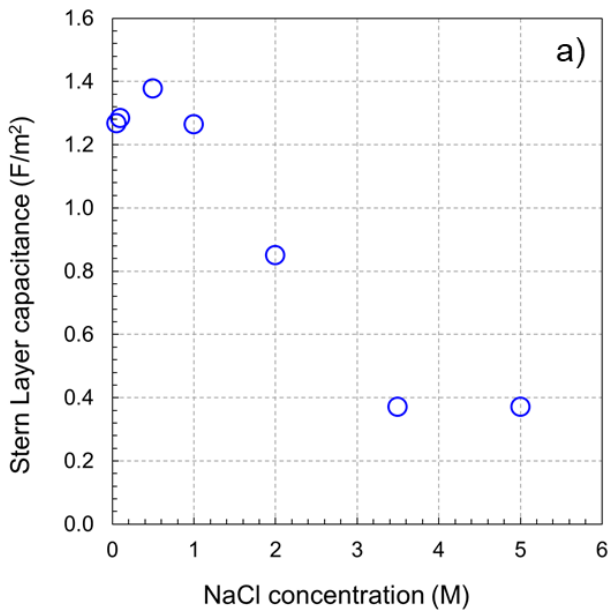
406

407 After increasing the LogK^{opt} 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 1st
 414 optimization step (**Eq. 3**), the 2nd step optimization was implemented for each rock sample and each
 415 concentration of NaCl solution using the following variables:

- 416 • The concentration of Ca²⁺ and SO₄²⁻ 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⁻²
 419 and 1.4 F·m⁻² (see more detailed discussion in section 2.2.5).

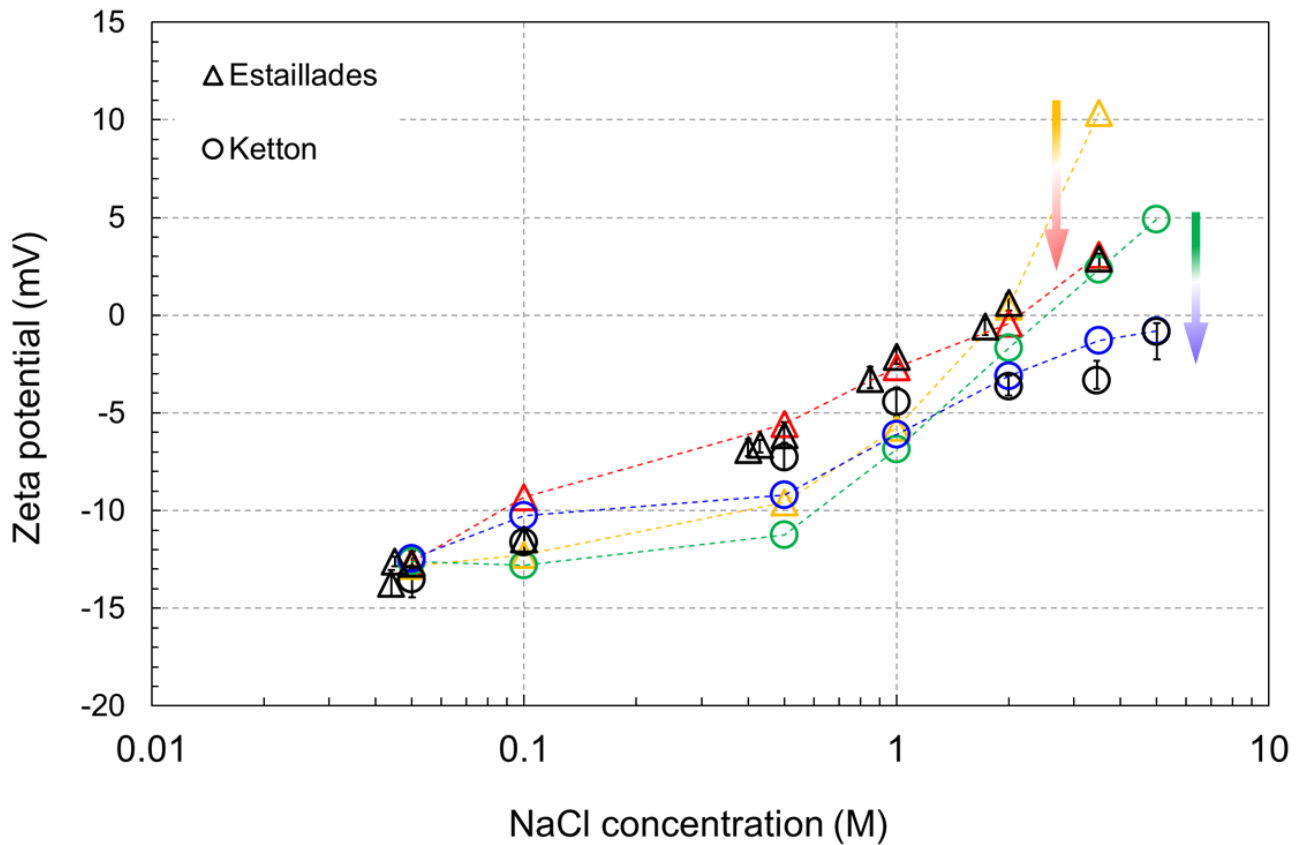
420 The resulting from the 2nd optimization step pH and concentration of SO₄²⁻ and Mg²⁺ remained the
 421 same compared with the results of the 1st optimization step. However, to obtain a better match to the
 422 experimentally measured zeta potential required a non-monotonic change of the optimized Stern
 423 layer capacitance (**Figure 5a**) and increased concentration of Ca²⁺ (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 β -plane, x , and
 442 decreasing relative permittivity of the Stern layer, ε_r , with increasing NaCl concentration; ii) constant
 443 relative permittivity and increasing with salinity x ; iii) increasing with salinity x and decreasing ε_r ; or
 444 iv) decreasing x and ε_r with increasing salinity so that the rate of decrease of ε_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 ε_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 ε_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 ε_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.

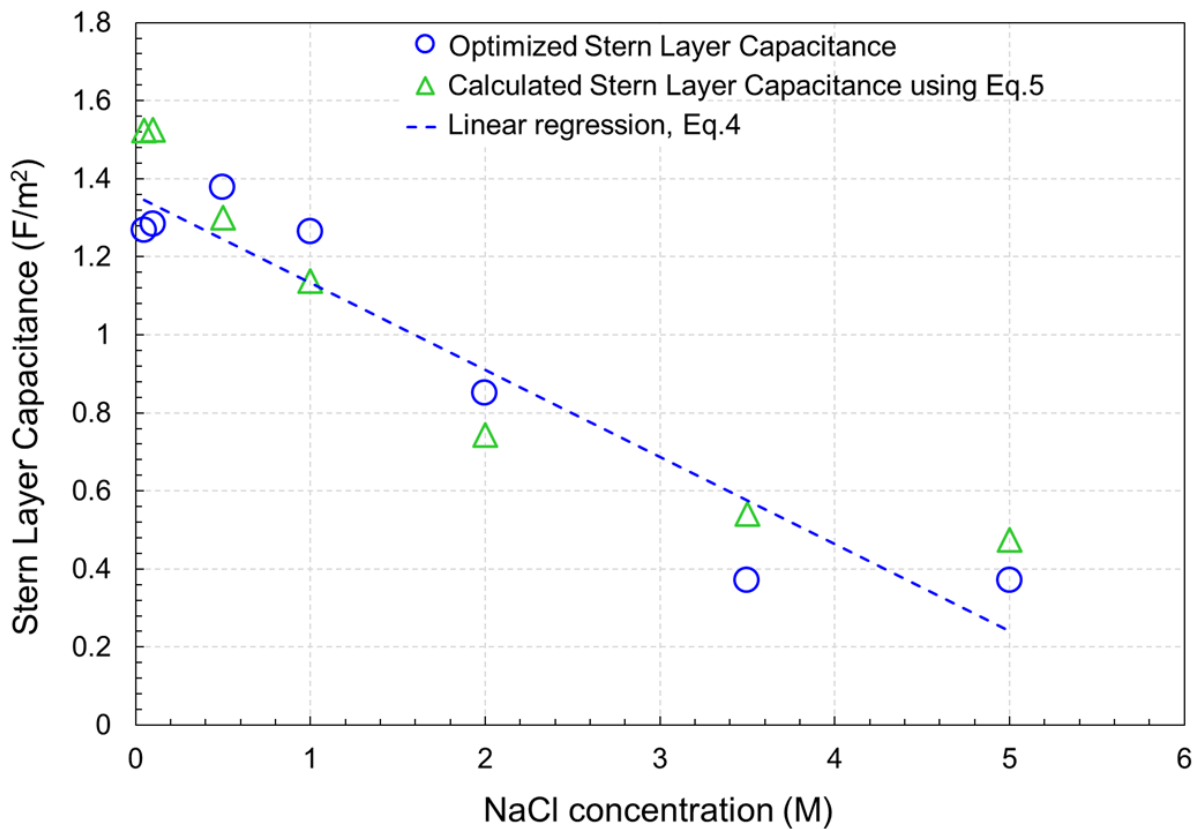
463 For simplicity we used a linear regression through optimized values of C_{SL} as shown in **Figure 7**:

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

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 β -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 ε_z is the relative permittivity of the bulk electrolyte (at a given ionic strength and temperature),
 468 ε_s is the relative permittivity near the mineral surface (~6 [48]), $d\phi$ is the electrical potential difference
 469 (V) between 0-plane with β -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 ε_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 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 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 Ca^{2+} in the solution is computed by
 494 PHREEQC and cross-compared with the experimental data. Otherwise, the measured
 495 concentration of 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**).

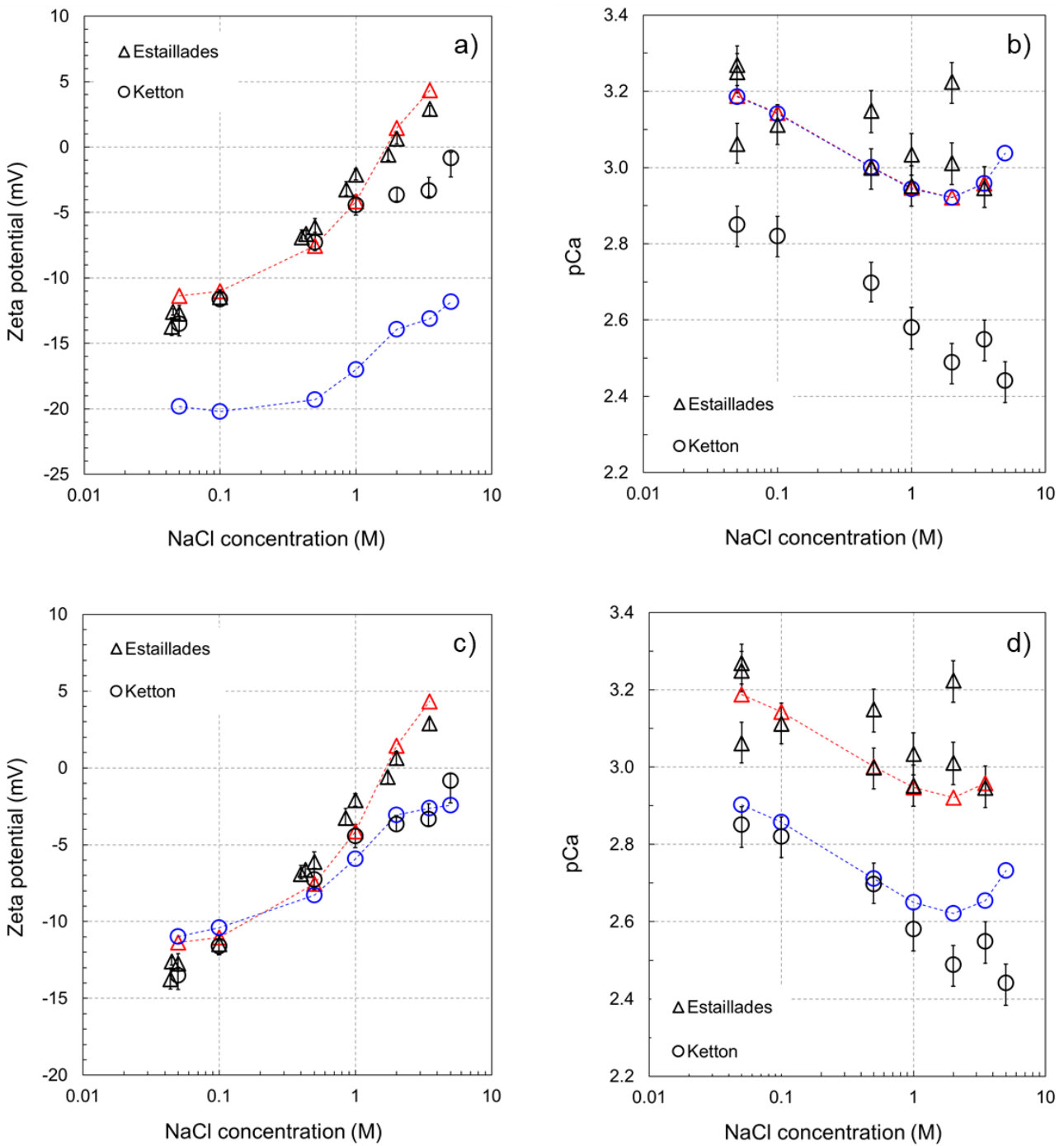
- 498 • For a given ionic strength, calculate the Stern layer capacitance using the linear regression
499 equation (**Eq. 4**) and allow PHREEQC to compute the zeta potential. To validate the result
500 cross-compare the simulated pH and concentrations of all ions against the measured values.
501

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 Na^+ , Cl^- ,
511 Mg^{2+} , SO_4^{2-} as reported in the paper. The initial input concentration of Ca^{2+} was set to zero M, partial
512 CO_2 pressure is set to $10^{-3.44}$ atm (consistent with atmospheric 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 Ca^{2+} , and the results are shown in **Figures 8a** and **8b** (note, that
517 simulated pH and concentration of all ions except 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 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 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

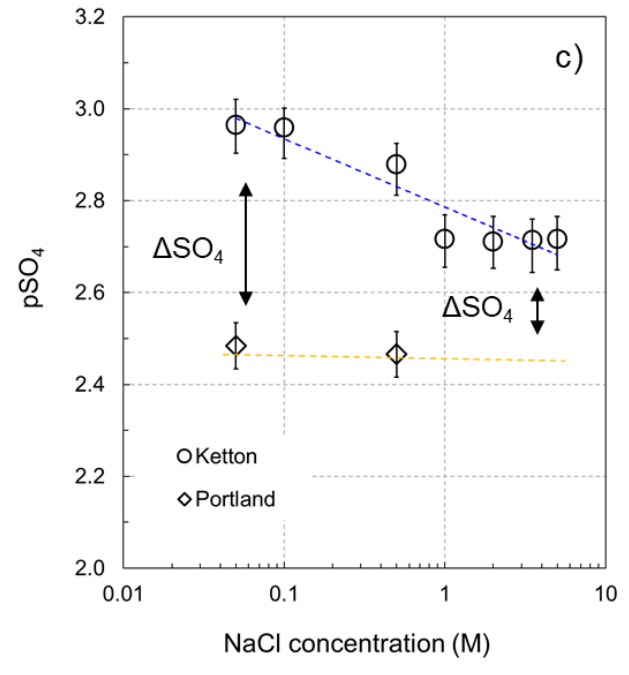
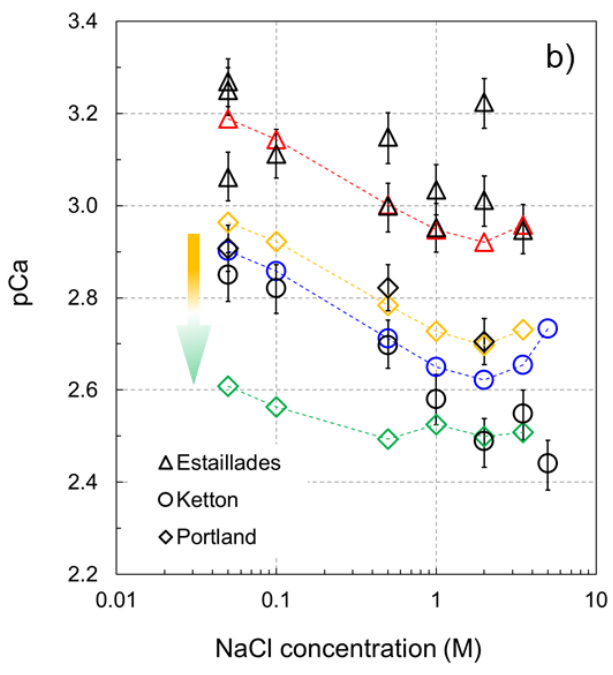
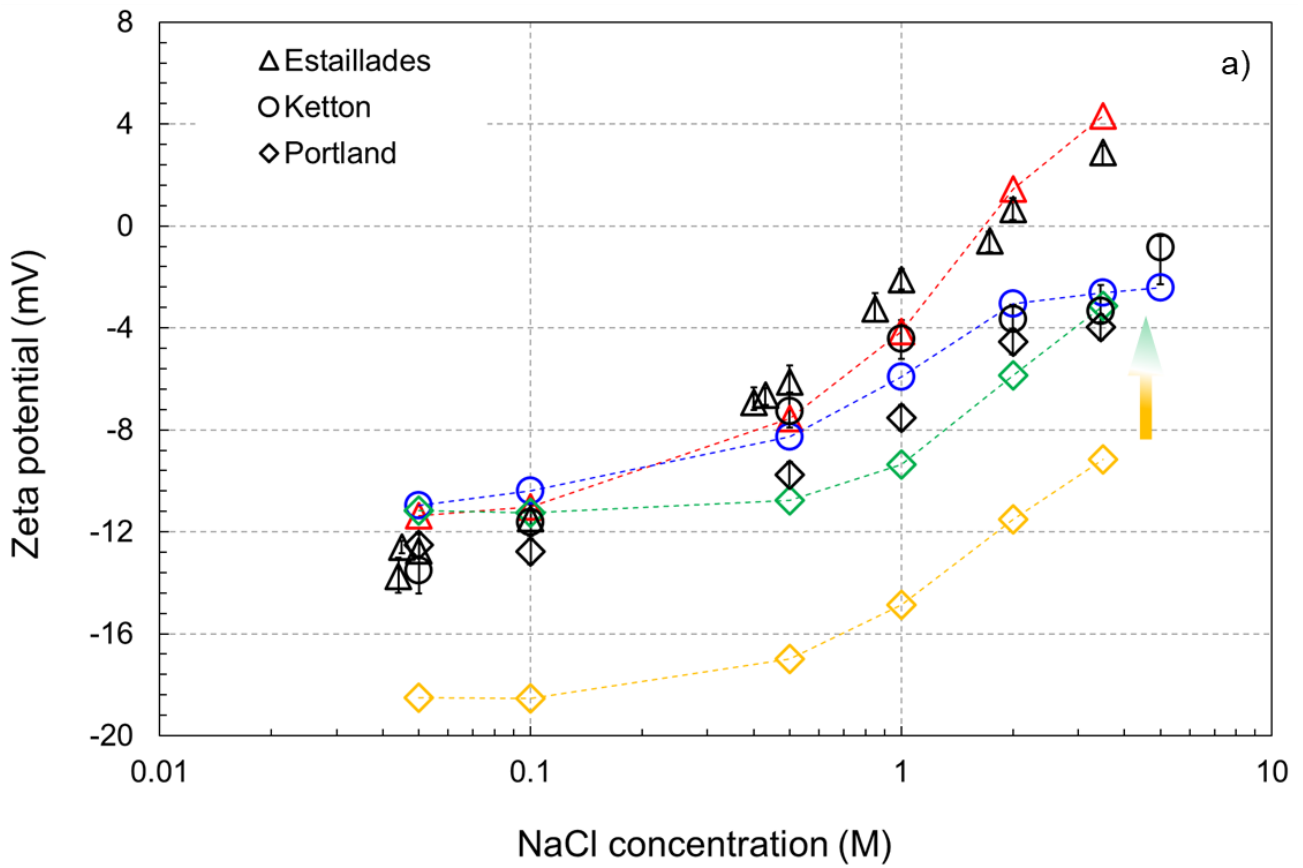
525 **Figure 8.** Experimentally measured (black symbols) and simulated zeta potential (a, c) and pCa (b, d) at
 526 equilibrium conditions for Estailades and Ketton samples saturated with NaCl solutions. The modelled results
 527 were obtained assuming identical *saturation index* for both rock samples 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 Ca^{2+} dissolved from the Portland sample we implemented
 533 a similar procedure by comparing the computed and measured equilibrium concentration of 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 Ca^{2+} concentration corresponded to the *saturation index* of 0.6. However, a significantly

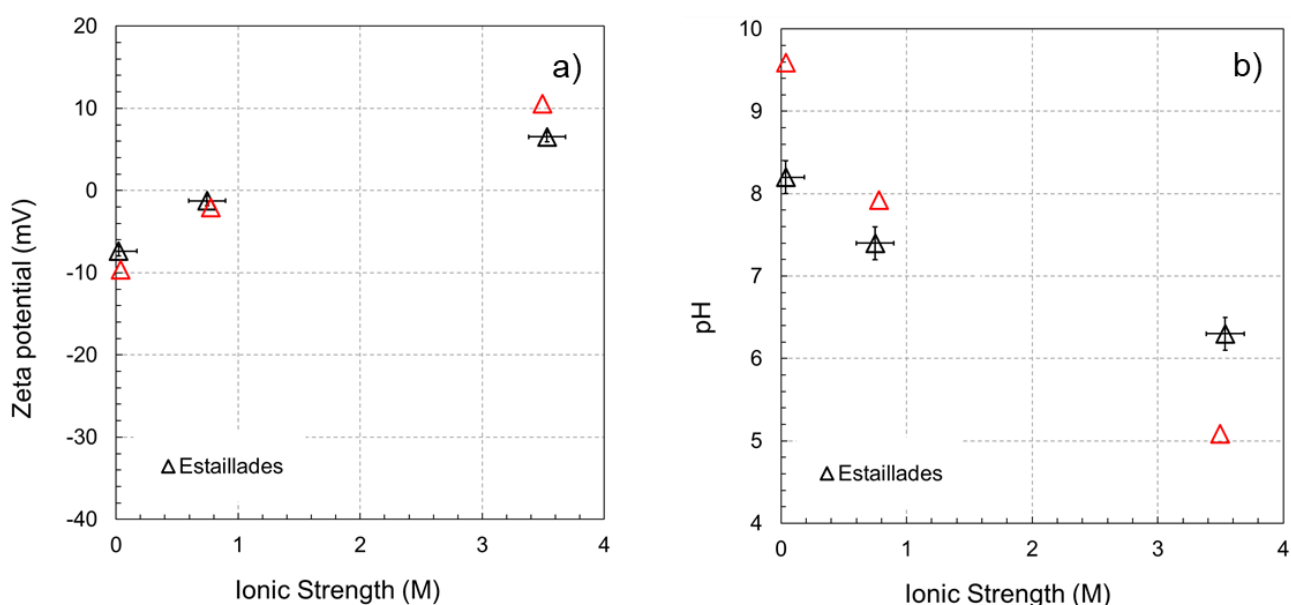
537 higher, compared with either Estailades or Ketton, concentration of SO_4^{2-} was reported for
538 equilibrated solutions in contact with Portland (compare diamonds with squares in Figure 10b of Al
539 Mahrouqi et al. [12]), while the reported concentration of Mg^{2+} in all rock samples was the same (pMg
540 = 4.19). Since SO_4^{2-} in the equilibrated solution could only originate from dissolution of sulfate
541 containing minerals (anhydrite or epsomite), the equilibrium concentration of SO_4^{2-} would not be
542 expected to exceed that of the total concentration of Ca^{2+} and 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 Ca^{2+} was inaccurate and contained an experimental uncertainty, which resulted in
545 underestimated concentration of the cation. Therefore, we artificially added 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 Ca^{2+} to the
550 solution artificially. Keeping the *saturation index* equal to 0.6, the total computed concentration of
551 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 Ca^{2+} to the
554 solution).



555
 556 **Figure 9.** Measured and modelled zeta potential (a), pCa (b) and SO_4^{2-} (c) of three natural rock samples. The
 557 amount of artificially added Ca^{2+} to the model of Portland equals the reported difference in concentration of
 558 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 Ca^{2+} . The results of the model with
 560 artificially added 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 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].

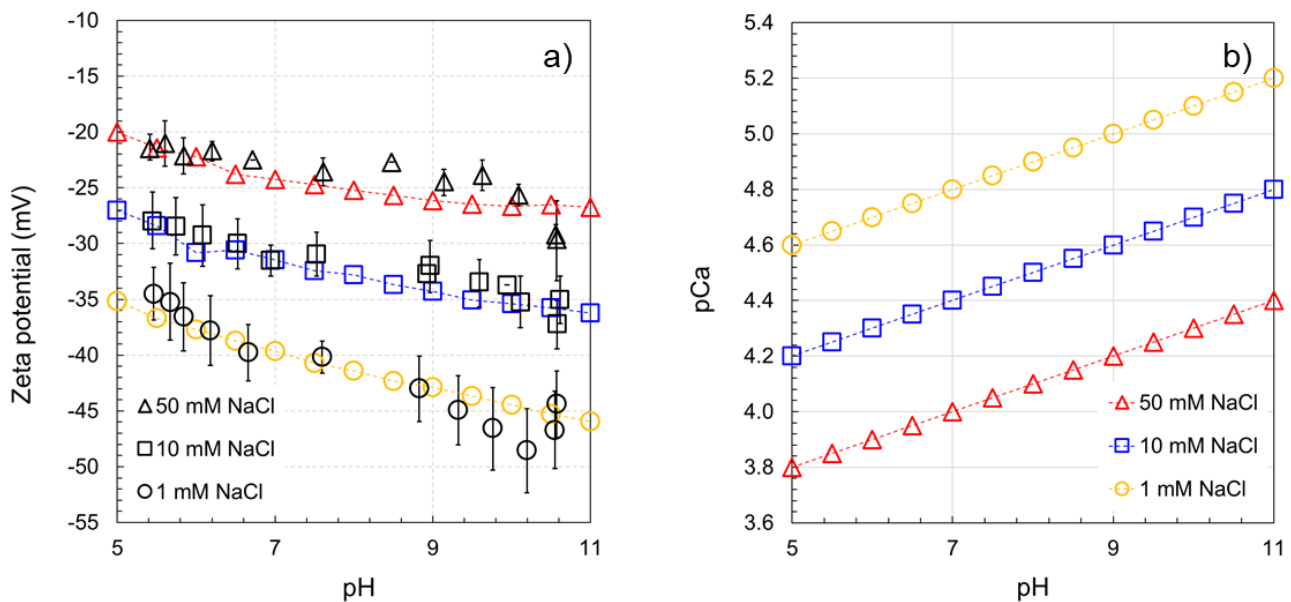
582
 583 It is worth mentioning, that equilibrium pH computed by our model in all tested aqueous solutions
 584 and rock samples matched the experimentally measured values apart from the results presented in
 585 **Figure 10**, where the simulated equilibrium pH was higher than experimental for 20dSW 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 5×10^{-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 Ca^{2+} to the modelled solution. The concentration of dissolved 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) Ca^{2+} should depend on pH (lower pH would lead to higher concentration of
609 dissolved Ca^{2+} , consistent with higher dissolution rate reported by Anabaraonye et al. [51]).
610 Furthermore, the pH dependence of 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 Ca^{2+} concentration should also depend on NaCl concentration
614 (higher NaCl concentration would lead to higher concentration of dissolved 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 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 Ca^{2+} concentration for each tested NaCl solution on the pH scale
621 (**Figure 11b**) and applying linear variation of pCa between these end-points, our model successfully
622 predicted the measured zeta potential (**Figure 11a**). Moreover, our model predicts that 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 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 CO_2 . Despite the
626 fact that the computed from calcite dissolution or artificially added 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 Ca^{2+} and $\text{C}(4)$ in the solution, both of which should increase with
631 decreasing pH. If such pH dependence of 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 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 SO_4^{2-} should not exceed the combined concentration of Ca^{2+} and 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 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 β -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 CO₂ 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 CO₂-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 Ca²⁺, Mg²⁺, SO₄²⁻ 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 SO_4^{2-} and Mg^{2+} that leach from dolomite
703 and anhydrite inclusions, while the equilibrium concentration of 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* 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 SO_4^{2-}
710 concentration exceeds that of Ca^{2+} and 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 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.

715 Acknowledgments

716 Miftah Hidayat was supported by the Aberdeen-Curtin PhD studentship. David Vega-Maza is funded
717 by the Spanish Ministry of Science, Innovation and Universities (“Beatriz Galindo Senior” fellowship
718 BEAGAL18/00259). The research work of Philippe Leroy was conducted within the framework of the
719 O-ZNS project which is part of PIVOTS project (financial support provided by the Région Centre-Val
720 de Loire and the French Ministry of Higher Education and Research).

721 **References**

- 722 [1] R.E. Hester, R.M. Harrison, eds, Carbon Capture: Sequestration and Storage, The Royal
723 Society of Chemistry, 2009. <https://doi.org/10.1039/9781847559715>.
- 724 [2] M.T. Graham, D.J. MacAllister, J. Vinogradov, M.D. Jackson, A.P. Butler, Self-Potential as a
725 Predictor of Seawater Intrusion in Coastal Groundwater Boreholes, *Water Resour. Res.* 54
726 (2018) 6055–6071. <https://doi.org/10.1029/2018WR022972>.
- 727 [3] D.J. MacAllister, M.D. Jackson, A.P. Butler, J. Vinogradov, Remote Detection of Saline
728 Intrusion in a Coastal Aquifer Using Borehole Measurements of Self-Potential, *Water*
729 *Resour. Res.* 54 (2018) 1669–1687. <https://doi.org/10.1002/2017WR021034>.
- 730 [4] J.H. Saunders, M.D. Jackson, M.Y. Gulamali, J. Vinogradov, C.C. Pain, Streaming
731 potentials at hydrocarbon reservoir conditions, *Geophysics.* 77 (2012) E77–E90.
732 <https://doi.org/10.1190/geo2011-0068.1>.
- 733 [5] F. Carrasco, P. Mutjé, M.A. Pelach, Control of retention in paper-making by colloid titration
734 and zeta potential techniques, *Wood Sci. Technol.* 32 (1998) 145–155.
735 <https://doi.org/10.1007/BF00702595>.
- 736 [6] F. Heberling, D. Bosbach, J.-D. Eckhardt, U. Fischer, J. Glowacky, M. Haist, U. Kramar, S.
737 Loos, H.S. Müller, T. Neumann, C. Pust, T. Schäfer, J. Stelling, M. Ukrainczyk, V. Vinograd,
738 M. Vučak, B. Winkler, Reactivity of the calcite–water-interface, from molecular scale
739 processes to geochemical engineering, *Appl. Geochemistry.* 45 (2014) 158–190.
740 <https://doi.org/10.1016/j.apgeochem.2014.03.006>.
- 741 [7] R.J. Hunter, *Zeta potential in colloid science: principles and applications*, Academic press,
742 New York, 1981.
- 743 [8] R. Eriksson, J. Merta, J.B. Rosenholm, The calcite/water interface: I. Surface charge in
744 indifferent electrolyte media and the influence of low-molecular-weight polyelectrolyte, *J.*
745 *Colloid Interface Sci.* 313 (2007) 184–193. <https://doi.org/10.1016/j.jcis.2007.04.034>.
- 746 [9] M.D. Jackson, A.P. Butler, J. Vinogradov, Measurements of spontaneous potential in chalk
747 with application to aquifer characterization in the southern UK, *Q. J. Eng. Geol. Hydrogeol.*
748 45 (2012) 457–471. <https://doi.org/10.1144/qjegh2011-021>.
- 749 [10] F. Heberling, T.P. Trainor, J. Lützenkirchen, P. Eng, M.A. Denecke, D. Bosbach, Structure
750 and reactivity of the calcite–water interface, *J. Colloid Interface Sci.* 354 (2011) 843–857.
751 <https://doi.org/10.1016/j.jcis.2010.10.047>.
- 752 [11] S. Li, P. Leroy, F. Heberling, N. Devau, D. Jougnot, C. Chiaberge, Influence of surface
753 conductivity on the apparent zeta potential of calcite, *J. Colloid Interface Sci.* 468 (2016)
754 262–275. <https://doi.org/10.1016/j.jcis.2016.01.075>.
- 755 [12] D. Al Mahrouqi, J. Vinogradov, M.D. Jackson, Zeta potential of artificial and natural calcite in
756 aqueous solution, *Adv. Colloid Interface Sci.* 240 (2017) 60–76.
757 <https://doi.org/10.1016/j.cis.2016.12.006>.
- 758 [13] T. Foxall, G.C. Peterson, H.M. Rendall, A.L. Smith, Charge determination at calcium
759 salt/aqueous solution interface, *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens.*
760 *Phases.* 75 (1979) 1034–1039. <https://doi.org/10.1039/F19797501034>.
- 761 [14] D.W. Thompson, P.G. Pownall, Surface electrical properties of calcite, *J. Colloid Interface*
762 *Sci.* 131 (1989) 74–82. [https://doi.org/10.1016/0021-9797\(89\)90147-1](https://doi.org/10.1016/0021-9797(89)90147-1).
- 763 [15] A. V Delgado, F. González-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, Measurement
764 and interpretation of electrokinetic phenomena, *J. Colloid Interface Sci.* 309 (2007) 194–
765 224. <https://doi.org/10.1016/j.jcis.2006.12.075>.
- 766 [16] M. Kosmulski, P. Dahlsten, High ionic strength electrokinetics of clay minerals, *Colloids*

- 767 Surfaces A Physicochem. Eng. Asp. 291 (2006) 212–218.
768 <https://doi.org/10.1016/j.colsurfa.2006.06.037>.
- 769 [17] A. Cherubini, B. Garcia, A. Cerepi, A. Revil, Influence of CO₂ on the Electrical Conductivity
770 and Streaming Potential of Carbonate Rocks, *J. Geophys. Res. Solid Earth*. 124 (2019)
771 10056–10073. <https://doi.org/10.1029/2018JB017057>.
- 772 [18] A. Cherubini, B. Garcia, A. Cerepi, A. Revil, Streaming Potential Coupling Coefficient and
773 Transport Properties of Unsaturated Carbonate Rocks, *Vadose Zo. J.* 17 (2018) 180030.
774 <https://doi.org/10.2136/vzj2018.02.0030>.
- 775 [19] A. Alroudhan, J. Vinogradov, M.D. Jackson, Zeta potential of intact natural limestone:
776 Impact of potential-determining ions Ca, Mg and SO₄, *Colloids Surfaces A Physicochem.*
777 *Eng. Asp.* 493 (2016) 83–98. <https://doi.org/10.1016/j.colsurfa.2015.11.068>.
- 778 [20] J.A. Davis, R.O. James, J.O. Leckie, Surface ionization and complexation at the oxide/water
779 interface: I. Computation of electrical double layer properties in simple electrolytes, *J.*
780 *Colloid Interface Sci.* 63 (1978) 480–499. [https://doi.org/10.1016/S0021-9797\(78\)80009-5](https://doi.org/10.1016/S0021-9797(78)80009-5).
- 781 [21] A. Revil, P.A. Pezard, P.W.J. Glover, Streaming potential in porous media: 1. Theory of the
782 zeta potential, *J. Geophys. Res. Solid Earth*. 104 (1999) 20021–20031.
783 <https://doi.org/10.1029/1999JB900089>.
- 784 [22] D.L. Parkhurst, C.A.J. Appelo, Description of Input and Examples for PHREEQC Version
785 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and
786 Inverse Geochemical Calculations, U.S. Geological Survey, 2013.
- 787 [23] M. Wolthers, L. Charlet, P. Van Cappellen, The surface chemistry of divalent metal
788 carbonate minerals; a critical assessment of surface charge and potential data using the
789 charge distribution multi-site ion complexation model, *Am. J. Sci.* 308 (2008) 905–941.
790 <https://doi.org/10.2475/08.2008.02>.
- 791 [24] A. Alizadeh, M. Wang, Flexibility of inactive electrokinetic layer at charged solid-liquid
792 interface in response to bulk ion concentration, *J. Colloid Interface Sci.* 534 (2019) 195–204.
793 <https://doi.org/10.1016/j.jcis.2018.09.010>.
- 794 [25] H. Ding, S.R. Rahman, Investigation of the Impact of Potential Determining Ions from
795 Surface Complexation Modeling, *Energy & Fuels*. 32 (2018) 9314–9321.
796 <https://doi.org/10.1021/acs.energyfuels.8b02131>.
- 797 [26] P. Van Cappellen, L. Charlet, W. Stumm, P. Wersin, A surface complexation model of the
798 carbonate mineral-aqueous solution interface, *Geochim. Cosmochim. Acta.* 57 (1993) 3505–
799 3518. [https://doi.org/10.1016/0016-7037\(93\)90135-J](https://doi.org/10.1016/0016-7037(93)90135-J).
- 800 [27] O.S. Pokrovsky, J. Schott, Surface Chemistry and Dissolution Kinetics of Divalent Metal
801 Carbonates, *Environ. Sci. Technol.* 36 (2002) 426–432. <https://doi.org/10.1021/es010925u>.
- 802 [28] O.S. Pokrovsky, J.A. Mielczarski, O. Barres, J. Schott, Surface Speciation Models of Calcite
803 and Dolomite/Aqueous Solution Interfaces and Their Spectroscopic Evaluation, *Langmuir*.
804 16 (2000) 2677–2688. <https://doi.org/10.1021/la980905e>.
- 805 [29] O.S. Pokrovsky, J. Schott, Kinetics and Mechanism of Dolomite Dissolution in Neutral to
806 Alkaline Solutions Revisited, *Am. J. Sci.* 301 (2001) 597 LP – 626.
807 <https://doi.org/10.2475/ajs.301.7.597>.
- 808 [30] T. Udoh, J. Vinogradov, Controlled Salinity-Biosurfactant Enhanced Oil Recovery at Ambient
809 and Reservoir Temperatures—An Experimental Study, *Energies*. 14 (2021).
810 <https://doi.org/10.3390/en14041077>.
- 811 [31] A. Villegas-Jiménez, A. Mucci, M.A. Whitehead, Theoretical Insights into the Hydrated (10.4)
812 Calcite Surface: Structure, Energetics, and Bonding Relationships, *Langmuir*. 25 (2009)
813 6813–6824. <https://doi.org/10.1021/la803652x>.

- 814 [32] I. Kurganskaya, S. V Churakov, Carbonate Dissolution Mechanisms in the Presence of
815 Electrolytes Revealed by Grand Canonical and Kinetic Monte Carlo Modeling, *J. Phys.*
816 *Chem. C.* 122 (2018) 29285–29297. <https://doi.org/10.1021/acs.jpcc.8b08986>.
- 817 [33] J. Song, S. Rezaee, L. Zhang, Z. Zhang, M. Puerto, O.B. Wani, F. Vargas, S. Alhassan, S.L.
818 Biswal, G.J. Hirasaki, Characterizing the Influence of Organic Carboxylic Acids and
819 Inorganic Silica Impurities on the Surface Charge of Natural Carbonates Using an Extended
820 Surface Complexation Model, *Energy & Fuels.* 33 (2019) 957–967.
821 <https://doi.org/10.1021/acs.energyfuels.8b03896>.
- 822 [34] C. Qiao, R. Johns, L. Li, J. Xu, Modeling low salinity waterflooding in mineralogically
823 different carbonates, in: *SPE Annu. Tech. Conf. Exhib.*, Society of Petroleum Engineers
824 (SPE), Houston, Texas, USA, 2015. <https://doi.org/10.2118/175018-ms>.
- 825 [35] C. Qiao, L. Li, R.T. Johns, J. Xu, A Mechanistic Model for Wettability Alteration by
826 Chemically Tuned Waterflooding in Carbonate Reservoirs, *SPE J.* 20 (2015) 767–783.
827 <https://doi.org/10.2118/170966-PA>.
- 828 [36] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J.*
829 *Phys. Chem.* 77 (1973) 268–277. <https://doi.org/10.1021/j100621a026>.
- 830 [37] C.E. Harvie, N. Møller, J.H. Weare, The prediction of mineral solubilities in natural waters:
831 The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C,
832 *Geochim. Cosmochim. Acta.* 48 (1984) 723–751. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(84)90098-X)
833 [7037\(84\)90098-X](https://doi.org/10.1016/0016-7037(84)90098-X).
- 834 [38] L. Nachbaur, P.-C. Nkinamubanzi, A. Nonat, J.-C. Mutin, Electrokinetic Properties which
835 Control the Coagulation of Silicate Cement Suspensions during Early Age Hydration, *J.*
836 *Colloid Interface Sci.* 202 (1998) 261–268. <https://doi.org/10.1006/jcis.1998.5445>.
- 837 [39] T. Austad, S. Strand, T. Puntervold, Is wettability alteration of carbonates by seawater
838 caused by rock dissolution?, in: *Int. Symp. Soc. Core Anal.*, Noordwijk, 2009.
- 839 [40] Y. Elakneswaran, T. Nawa, K. Kurumisawa, Electrokinetic potential of hydrated cement in
840 relation to adsorption of chlorides, *Cem. Concr. Res.* 39 (2009) 340–344.
841 <https://doi.org/10.1016/j.cemconres.2009.01.006>.
- 842 [41] V.N. Afanas'ev, A.N. Ustinov, Hydration numbers and the state of water in hydration
843 spheres of magnesium chloride and magnesium sulfate solutions, *Russ. J. Inorg. Chem.* 57
844 (2012) 1107–1122. <https://doi.org/10.1134/S0036023612080025>.
- 845 [42] V.N. Afanasiev, A.N. Ustinov, I.Y. Vashurina, State of Hydration Shells of Sodium Chloride
846 in Aqueous Solutions in a Wide Concentration Range at 273.15–373.15 K, *J. Phys. Chem.*
847 *B.* 113 (2009) 212–223. <https://doi.org/10.1021/jp711542j>.
- 848 [43] M.A. Brown, A. Goel, Z. Abbas, Effect of Electrolyte Concentration on the Stern Layer
849 Thickness at a Charged Interface, *Angew. Chemie Int. Ed.* 55 (2016) 3790–3794.
850 <https://doi.org/10.1002/anie.201512025>.
- 851 [44] I.C. Bourg, G. Sposito, Molecular dynamics simulations of the electrical double layer on
852 smectite surfaces contacting concentrated mixed electrolyte (NaCl–CaCl₂) solutions, *J.*
853 *Colloid Interface Sci.* 360 (2011) 701–715. <https://doi.org/10.1016/j.jcis.2011.04.063>.
- 854 [45] I.-C. Yeh, M.L. Berkowitz, Dielectric constant of water at high electric fields: Molecular
855 dynamics study, *J. Chem. Phys.* 110 (1999) 7935–7942. <https://doi.org/10.1063/1.478698>.
- 856 [46] J. Kielland, Individual Activity Coefficients of Ions in Aqueous Solutions, *J. Am. Chem. Soc.*
857 59 (1937) 1675–1678. <https://doi.org/10.1021/ja01288a032>.
- 858 [47] B.E. Conway, Ionic hydration in chemistry and biophysics, Elsevier Scientific Publishing
859 Company, Amsterdam, Netherlands, 1981.
- 860 [48] T. Hiemstra, W.H. Van Riemsdijk, On the relationship between charge distribution, surface

- 861 hydration, and the structure of the interface of metal hydroxides, *J. Colloid Interface Sci.* 301
862 (2006) 1–18. <https://doi.org/10.1016/j.jcis.2006.05.008>.
- 863 [49] M.D. Jackson, D. Al-Mahrouqi, J. Vinogradov, Zeta potential in oil-water-carbonate systems
864 and its impact on oil recovery during controlled salinity water-flooding, *Sci. Rep.* 6 (2016) 1–
865 13. <https://doi.org/10.1038/srep37363>.
- 866 [50] J. Vinogradov, M.D. Jackson, M. Chamerois, Zeta potential in sandpacks: Effect of
867 temperature, electrolyte pH, ionic strength and divalent cations, *Colloids Surfaces A*
868 *Physicochem. Eng. Asp.* 553 (2018) 259–271.
869 <https://doi.org/10.1016/j.colsurfa.2018.05.048>.
- 870 [51] B.U. Anabaraonye, J.P. Crawshaw, J.P.M. Trusler, Brine chemistry effects in calcite
871 dissolution kinetics at reservoir conditions, *Chem. Geol.* 509 (2019) 92–102.
872 <https://doi.org/https://doi.org/10.1016/j.chemgeo.2019.01.014>.
- 873 [52] L. Chou, R.M. Garrels, R. Wollast, Comparative study of the kinetics and mechanisms of
874 dissolution of carbonate minerals, *Chem. Geol.* 78 (1989) 269–282.
875 [https://doi.org/10.1016/0009-2541\(89\)90063-6](https://doi.org/10.1016/0009-2541(89)90063-6).
- 876 [53] E. Ruiz-Agudo, C. V Putnis, C. Jiménez-López, C. Rodríguez-Navarro, An atomic force
877 microscopy study of calcite dissolution in saline solutions: The role of magnesium ions,
878 *Geochim. Cosmochim. Acta.* 73 (2009) 3201–3217.
879 <https://doi.org/10.1016/j.gca.2009.03.016>.
- 880 [54] S. Kuyucak, S.-H. Chung, Temperature dependence of conductivity in electrolyte solutions
881 and ionic channels of biological membranes, *Biophys. Chem.* 52 (1994) 15–24.
882 [https://doi.org/10.1016/0301-4622\(94\)00034-4](https://doi.org/10.1016/0301-4622(94)00034-4).
- 883 [55] D. Jougnot, D. Roubinet, L. Guarracino, A. Mainault, Modeling Streaming Potential in
884 Porous and Fractured Media, Description and Benefits of the Effective Excess Charge
885 Density Approach., in: A. Biswas, S.P. Sharma (Eds.), *Adv. Model. Interpret. Near Surf.*
886 *Geophys.*, Springer International Publishing, 2020: bll 61–96. https://doi.org/10.1007/978-3-030-28909-6_4.
- 888 [56] M.D. Jackson, M.Y. Gulamali, E. Leinov, J.H. Saunders, J. Vinogradov, Spontaneous
889 Potentials in Hydrocarbon Reservoirs During Waterflooding: Application to Water-Front
890 Monitoring, *SPE J.* 17 (2012) 53–69. <https://doi.org/10.2118/135146-PA>.
- 891 [57] X. Li, C. Peng, J.P. Crawshaw, G.C. Maitland, J.P.M. Trusler, The pH of CO₂-saturated
892 aqueous NaCl and NaHCO₃ solutions at temperatures between 308 K and 373 K at
893 pressures up to 15 MPa, *Fluid Phase Equilib.* 458 (2018) 253–263.
894 <https://doi.org/10.1016/j.fluid.2017.11.023>.
- 895 [58] T.K. Tokunaga, DLVO-Based Estimates of Adsorbed Water Film Thicknesses in Geologic
896 CO₂ Reservoirs, *Langmuir.* 28 (2012) 8001–8009. <https://doi.org/10.1021/la2044587>.
- 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 CO₂ pressure at equilibrium with atmospheric air equal to 10^{-3.44} 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 Ca²⁺
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 Ca²⁺ 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 Ca²⁺.
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 -----