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Modeling the Acid-Base Properties of Montmorillonite Edge Surfaces

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14 **Abstract**

15 The surface reactivity of clay minerals remains challenging to characterize because of a duality of
16 adsorption surfaces and mechanisms that does not exist in the case of simple oxide surfaces: clay
17 minerals edge surfaces have a variable proton surface charge arising from hydroxyl functional
18 groups, whereas basal surfaces have a permanent negative charge arising from isomorphous
19 substitutions. Hence, the relationship between surface charge and surface potential on edge
20 surfaces cannot be described using the Gouy-Chapman relation, because of a spillover of
21 negative electrostatic potential from the basal surface onto the edge surface. While surface
22 complexation models can be modified to account for these features, a predictive fit of
23 experimental data was not possible until recently, because of uncertainty regarding the densities
24 and intrinsic pK_a values of edge functional groups. Here, we reexamine this problem in light of
25 new knowledge on intrinsic pK_a values obtained over the last decade using *ab initio* molecular
26 dynamics simulations, and we propose a new formalism to describe edge functional groups. Our
27 simulation results yield good predictions of the best available experimental acid-base titration
28 data.

29 **1. Introduction**

30 Clay minerals are natural fine-grained particles, ubiquitous in terrestrial weathering
31 environments, that strongly influence the permeability, mechanics, and pore water chemistry of
32 soils, sediments, and rocks in which they are found^{1,2}. In particular, these minerals control the
33 performance of natural and engineered clay barriers used in the isolation of landfills and
34 contaminated sites and proposed for use in the geological storage of high-level radioactive waste
35^{3,4}. A widely examined feature of clay minerals that influences the performance of these barriers

36 is their cation-exchange capacity, the result of isomorphic substitutions in the structure ⁵. In
37 addition to this cation-exchange capacity, clay minerals, including montmorillonite (the most
38 studied swelling clay mineral) carry oxide-type functional groups on their edge surfaces. These
39 oxide-type functional groups, though present in much smaller quantity than the cation exchange
40 sites, dominate the adsorption of trace metals, oxyanions, and organic molecules ⁶⁻⁹, the
41 dissolution and growth kinetics of clay minerals ^{10,11}, and the colloidal mechanics of clay
42 particles ¹², at least in some conditions.

43 In the case of simple oxide minerals, surface reactivity is strongly influenced by their net proton
44 surface charge, which varies with pH through reactions of the following type, where >SOH_n is a
45 generic surface site ¹³:



46 The reaction described by Eq. (1) gives rise to a variable net proton surface charge density (σ_{H})
47 that depends on pH and ionic strength (I , dimensionless¹⁴). In the case of simple oxide minerals,
48 the last few decades have seen steady advances in the characterization of their proton surface
49 chemistry through a combination of experiments (in particular, acid-base titration and
50 electrophoretic mobility measurements), surface complexation model (SCM) calculations, and
51 bond-valence theory predictions of the intrinsic acidity constants of surface functional groups ¹⁵⁻
52 ¹⁹. In the case of the oxide-type functional groups on the montmorillonite edge surfaces, however,
53 σ_{H} remains poorly understood, as shown by the wide range of reported values of the point of zero
54 net proton charge (p.z.n.p.c., the pH value where $\sigma_{\text{H}} = 0$) and by the variety of models that have
55 been used to describe σ_{H} ^{9,20}. As described below, the difficulty in characterizing σ_{H} on
56 montmorillonite relates to the high permanent structural charge of the solid ($\sigma_0 \approx -1 \text{ mmol}_c \cdot \text{g}^{-1}$)

57 and to the presence of two different surfaces (edge and basal surfaces) with very different
58 properties. These properties have no equivalent in simple oxide minerals, but are widespread
59 features of lamellar structures including vernadite, a phyllosilicate that controls the fate of
60 trace metals in certain oxidized soils and sediments^{21,22}, green rust, a layered double hydroxide
61 that influences the mobility of iron and anions in reduced soils²³, and synthetic phases widely
62 used in materials chemistry, such as synthetic layered double hydroxides²⁴.

63 The challenges associated with characterizing the proton surface reactivity of montmorillonite
64 were summarized a decade ago by Bourg et al.²⁰. A first challenge is that montmorillonite
65 particles undergo significant dissolution during acid-base titration measurements. This can be
66 rendered near-negligible in the pH range from about 4.5 to 9.5 through a careful choice of clay
67 pretreatment, storage, and titration procedures²⁵⁻²⁹ (see below). Unfortunately, most
68 montmorillonite acid-base titration datasets do not fit the best practices established by Duc et al.
69²⁵⁻²⁸. A second challenge is that acid-base titration measurements do not directly measure the net
70 proton surface charge density σ_H but rather $\delta\sigma_H$, the *change* in net proton surface charge density
71 relative to its initial value $\sigma_{H,init}$ ($\delta\sigma_H = \sigma_H - \sigma_{H,init}$). Conversion of $\delta\sigma_H$ to σ_H values requires
72 knowledge of $\sigma_{H,init}$ or of the p.z.n.p.c. at the conditions of interest³⁰. For simple oxide surfaces,
73 this is achieved by measuring the sum of the adsorbed ion charge densities q_i of all species except
74 H^+ and OH^- (Δq) and applying the charge balance relation³⁰:

$$\sigma_0 + \sigma_H + \Delta q = 0 \quad (2)$$

75 For montmorillonite, experimental uncertainties make it impossible to accurately determine σ_H
76 using Eq. (2), because σ_H is small compared to σ_0 and Δq ^{20,29}. Alternatively, the p.z.n.p.c. of
77 oxide surfaces is sometimes determined by assuming that it coincides with the point of zero salt

78 effect (p.z.s.e., the pH value at which acid-base titration curves carried out at different ionic
79 strengths intersect) or with the isoelectric point (i.e.p., the pH value where the electrophoretic
80 mobility equals zero)³¹. These alternative methods, however, are neither strictly rigorous^{20,30} nor
81 applicable to montmorillonite, for which a p.z.s.e. or i.e.p. are not observed^{26,32-34}. Finally, the
82 p.z.n.p.c. of montmorillonite is sometimes assumed to correspond to the pH value obtained by
83 adding incremental amounts of dry solid to a solution³⁵, but this so-called “mass titration”
84 technique, just like a standard acid-base titration, is sensitive to the initial protonation state of the
85 solid³⁶.

86 A third challenge arises when attempting to develop a SCM for montmorillonite. An important
87 assumption of SCMs is that the ratio of activity coefficients of different surface species is a
88 function of the surface electrostatic potential ψ . For the reaction described by Eq. (1), the
89 relationship is almost always expressed with a quasi-thermodynamic equilibrium equation of the
90 form:

$$K_a = \frac{[> \text{SOH}_{n-1}](\text{H}^+)}{[> \text{SOH}_n]} \exp\left(\frac{-F\psi}{RT}\right) \quad (3)$$

91 where K_a is an intrinsic equilibrium constant, (H^+) is the thermodynamic activity of H^+ , square
92 brackets denote mole fractions, ψ is the surface electrostatic potential, F is the Faraday constant
93 ($96\,485 \text{ C mol}^{-1}$), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is temperature (in K).
94 Closure of any SCM requires a model of ψ as a function of surface charge, ionic strength, and
95 other conditions. For this, most studies rely on the Gouy-Chapman relation, a mean-field theory
96 prediction based on the Poisson-Boltzmann equation (PBE) of the relationship between surface
97 charge density and surface potential on an infinite planar surface in contact with an ideal
98 electrolyte solution^{31,37}. Montmorillonite consists of flake-shaped, 1-nm-thick layers such that

99 the narrow edge surface cannot be *a priori* treated as an infinite planar surface^{9,20}. Solutions to
100 the Poisson-Boltzmann equation for various possible arrangements of the montmorillonite layers
101 indicate that the value of ψ at montmorillonite edges (ψ_{edge}) is influenced by the charge density
102 of both edge and basal surfaces in a manner that depends on ionic strength and on the stacking
103 arrangement of montmorillonite layers^{9,20,38}. Finally, a fourth challenge is that montmorillonite
104 edge surfaces carry a variety of functional groups associated with tetrahedral Si and octahedral Al
105 atoms ($>\text{SiOH}$, $>\text{AlOH}$, $>\text{Al}_2\text{OH}$, $>\text{AlSiOH}$) as well as additional groups that arise from
106 isomorphic substitutions of Si by Al and of Al by Mg, Fe^{II} , or Fe^{III} . In the absence of independent
107 predictions of the densities and intrinsic acidity constants of each surface functional group, model
108 fits to experimental acid-base titration data are necessarily non-unique²⁰.

109 Bourg et al.²⁰ showed that the first three challenges outlined above could be resolved using
110 information available a decade ago. The second challenge was resolved by using an SCM to
111 predict both $\sigma_{\text{H,init}}$ (from reported conditions of clay pre-treatment) and σ_{H} . The first challenge
112 required identifying experimental datasets that followed that best practices established by Duc et
113 al.²⁶⁻²⁸ and that used montmorillonite samples pre-treated by repeated washing in a solution of
114 well-known pH and ionic strength (as required to predict $\sigma_{\text{H,init}}$); the available database included
115 only two datasets, those of Baeyens and Bradbury³⁹ and Duc et al.²⁷. The third challenge was
116 resolved by solving a two-dimensional version of the PBE near the edge surface of an isolated
117 montmorillonite particle. The fourth challenge, however, could not be satisfactorily resolved,
118 because of large disagreements between different bond-valence model predictions of the intrinsic
119 $\text{p}K_{\text{a}}$ values of edge surface sites^{40,41} and, also, because of insufficient knowledge of the densities
120 of different edge surface sites⁴¹. Eventually, Bourg et al.²⁰ concluded that experimental data on

121 the acid-base chemistry of montmorillonite edge surfaces could not be predicted from first
122 principles using existing knowledge.

123 The last decade has seen a significant number of new studies of the acid-base surface chemistry
124 of montmorillonite. Several new potentiometric titration studies have been carried out ⁴²⁻⁴⁷ as
125 well as one study that attempted to determine the i.e.p. of montmorillonite edge surfaces ⁴⁸.
126 Several studies have provided new estimates of the edge specific surface area of montmorillonite
127 particles ^{10,49}. Models of ψ_{edge} have been refined using new Poisson-Boltzmann calculations ⁹ and
128 Grand Canonical Monte Carlo (GCMC) simulations ⁵⁰. Finally, *ab initio* MD simulations have
129 been used to predict the intrinsic $\text{p}K_{\text{a}}$ values of montmorillonite edge surface sites ⁵¹⁻⁵⁷. Here, we
130 revisit the conclusions of Bourg et al. ²⁰ in light of these advances. First, we show that new
131 knowledge obtained during the last decade provides a more coherent picture of the proton surface
132 chemistry of montmorillonite. Then, we develop a state-of-the-art SCM for montmorillonite edge
133 surfaces, and we note possibilities for future improvements. This new SCM is mainly based on a
134 combination of the existing 2D Poisson-Boltzmann calculations, which are representative of clay
135 edges geometry, with the development of a revised thermodynamic concept for the description of
136 the edge sites, and with the use of $\text{p}K_{\text{a}}$ values that have been obtained from *ab initio* MD
137 simulations.

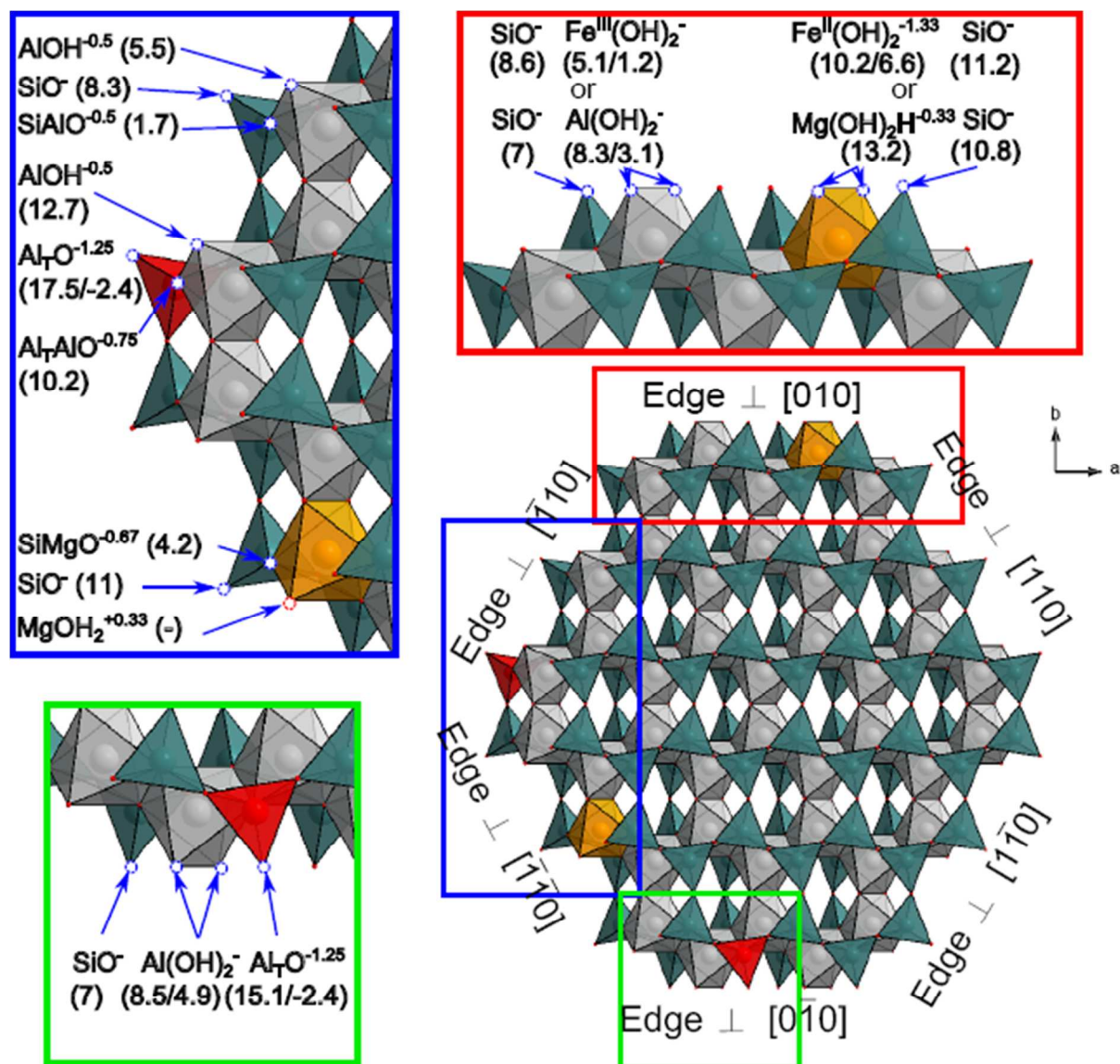
138 **2. Constraints on the proton surface chemistry of montmorillonite edges**

139 **2.1. Montmorillonite edge structure**

140 Current knowledge of the densities of different types of montmorillonite edge functional groups
141 remains limited by uncertainty regarding edge crystallographic orientations. Crystal growth
142 theory calculations, surface Coulomb energy considerations, atomistic simulations, and *in situ*

143 observation of dissolution kinetics using atomic force microscopy suggest the that most stable
144 edge surfaces are perpendicular to [010] and [110] (or, equivalently, $[\bar{1}10]$)⁵⁸⁻⁶³, where the Miller
145 indices are assigned according to Churakov⁶⁰ (Figure 1). The two edge surfaces are sometimes
146 referred to as the B and AC edges, respectively, following the seminal study by White and
147 Zelazny⁶³. Recent molecular dynamics (MD) and *ab initio* MD simulations of hydrated clay
148 edges suggest that the surface normal to [110] may be significantly more stable than the surface
149 normal to [010] in the presence of liquid water^{61,62,64}.

150 Montmorillonite edge surfaces are routinely assumed to have the same stoichiometry and
151 structure as the bulk crystal, with minor bond-length relaxation to accommodate over- or under-
152 coordinated surface O atoms⁴⁰. Recent MD and *ab initio* MD simulation results reveal a more
153 complex picture, the most well-established finding being that cations in the octahedral layer can
154 adopt a five-fold coordination^{55,61,65,66}.



155

156 Figure 1. Edge surface sites of a model montmorillonite particle. Inserts with red and green
 157 borders describe sites on the B edge. The insert with a blue border describes sites on the AC
 158 edge. The clay mineral structure was taken from Viani et al.⁶⁷ and is representative of the
 159 structures considered in bond valence calculations and *ab initio* MD simulations. Grey octahedra:
 160 Al or Fe(III); orange octahedra: Mg or Fe(II); green tetrahedra: Si; red tetrahedra: Al. Isomorphic
 161 substitutions are only shown if they occur at the edge surface. The stoichiometries of the
 162 deprotonated sites are written on the figure along with numbers corresponding to the log K values

163 of the associated protonation reactions predicted by *ab initio* MD calculations (see Section 2.4; an
164 absence of value means that the site does not protonate/deprotonate in the pH range 1 to 14).

165

166 2.2. Edge specific surface area

167 An important parameter in studies of montmorillonite edge reactivity is the edge specific surface
168 area, $a_{s,edge}$. Unfortunately, the N₂ gas adsorption method with the Brunauer-Emmett-Teller
169 technique (N₂-BET) quantifies only the external surface area of crystals (stacks of
170 montmorillonite layers) after drying, which provides no information on $a_{s,edge}$ ⁶⁸. The ethylene
171 glycol monoethyl ether (EGME) adsorption method quantifies the total specific surface area of
172 montmorillonite layers, a_s , dominated by the basal surfaces⁶⁹. In principle, $a_{s,edge}$ equals the
173 difference between the measured a_s value and the theoretical basal specific surface area $a_{s,basal}$ [\approx
174 750 to 780 m² g⁻¹⁷⁰]. Unfortunately, EGME-derived a_s values show a significant dependence on
175 experimental conditions⁶⁸ that precludes a precise calculation of $a_{s,edge}$.

176 Direct measurements of $a_{s,edge}$ for montmorillonite have been achieved using two approaches.
177 The first consists in evaluating edge specific surface area by statistical analysis of particle
178 morphology from atomic force microscopy (AFM) or transmission electron microscopy (TEM)
179 images⁷¹⁻⁷³. Alternatively, the derivative isotherms summation (DIS) method distinguishes
180 different clay surfaces in a single gas adsorption measurement based on differences in adsorption
181 energy⁶⁸. Comparison of microscopic imaging and DIS results yields satisfactory agreement
182 (Table S-1), with a possible slight overestimation of edge surface area by the DIS method⁷⁴.

183 2.3. Edge surface electrostatic potential

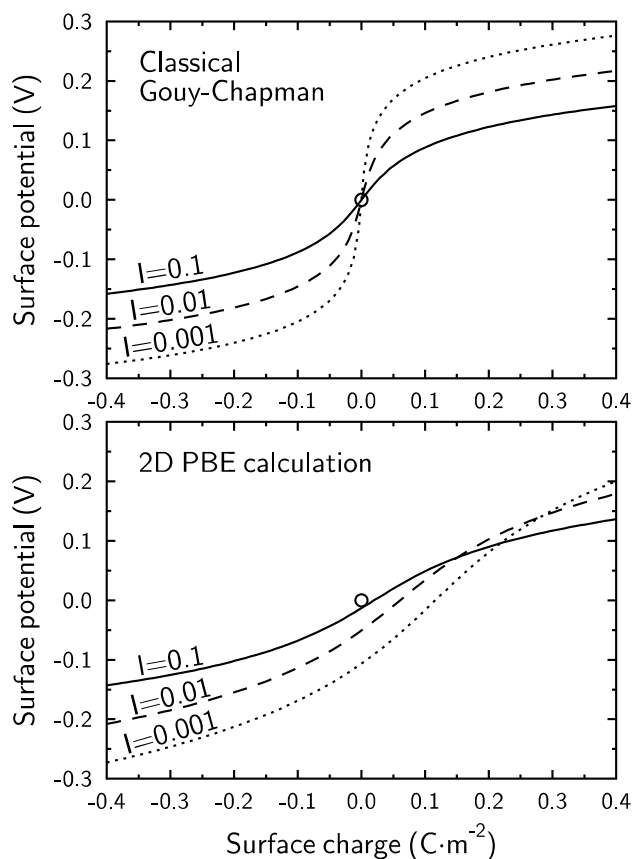
184 As noted above, SCMs of proton adsorption on montmorillonite require a model of the edge
 185 surface electrostatic potential, ψ_{edge} . Most modeling studies have assumed that clay edges do not
 186 develop a significant electrostatic potential ($\psi_{\text{edge}} = 0$)^{41,75-79} or that ψ_{edge} follows the Gouy-
 187 Chapman relation for an infinite planar surface^{33,35,43,80-91}. The few studies that solved the PBE
 188 near clay edges for realistic geometries, however, showed that ψ_{edge} differs strongly from zero
 189 and from the Gouy-Chapman model prediction and is sensitive to the stacking arrangement of the
 190 clay layers^{38,92-94}. Bourg et al.²⁰ solved a two-dimensional form of the PBE near the edge
 191 surface of an isolated montmorillonite layer (consistent with exfoliated layers in Na-
 192 montmorillonite suspensions at ionic strengths lower than $I \sim 0.2$) and found that ψ_{edge} was
 193 reasonably described by:

$$\frac{F\psi_{\text{edge}}}{RT} = A_1 \operatorname{asinh}\left(A_2(Q_{\text{edge}} + A_3)\right) \quad (4)$$

194 where Q_{edge} ($\text{C}\cdot\text{m}^{-2}$) is the charge at the edge and A_1 (unitless), A_2 ($\text{m}^{-2}\cdot\text{C}$) and A_3 ($\text{C}\cdot\text{m}^{-2}$) are
 195 parameters that were fitted with the ψ_{edge} values obtained from the full resolution of the 2D PB
 196 equation. For montmorillonite at 25 °C, Tournassat et al.⁹ refined the values of these parameters
 197 to: $A_1 = 1.4 - 1.2 \log I$, $A_2 = 11 + \log I$, and $A_3 = -0.02 \times (-\log I)^{1.60}$. This equation can be
 198 compared with the classical Gouy-Chapman model for infinite planar surfaces¹³:

$$\frac{F\psi}{RT} = 2 \operatorname{asinh}(B \cdot \sigma) \text{ with } B = \frac{1}{\sqrt{8\epsilon\epsilon_0 RT \cdot 1000 \cdot I}} \quad (5)$$

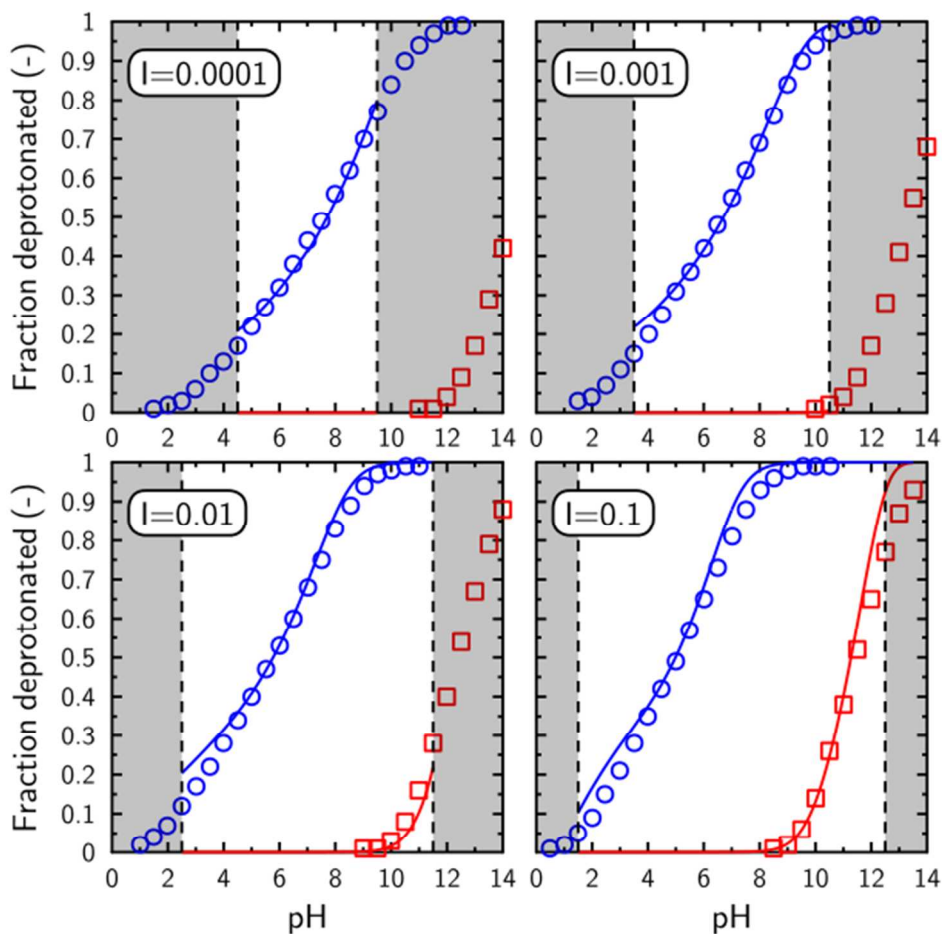
199 where σ is the surface charge density (in m^{-2}). A key prediction of Eq. 4 is that ψ_{edge} is negative
200 when the edge surface charge is zero (Figure 2) because of a spillover of negative electrostatic
201 potential from the basal surfaces^{92,94}.



202
203 Figure 2. Comparison of the relationships between surface charge (horizontal axis) and surface
204 electrostatic potential (vertical axis) predicted by the classical Gouy-Chapman model for a flat
205 oxide surface (top) and by the PBE calculations of Bourg et al.²⁰ for the edge surface of an
206 isolated montmorillonite layer (bottom) at three ionic strengths. The circles mark the condition of
207 zero charge and zero potential on each graph.

208 A potential limitation to the accuracy of the PBE is that it uses the mean-field theory
209 approximation, i.e., it neglects specific ion-ion and ion-surface site interactions. On infinite flat

210 surfaces, the PBE is nevertheless known to adequately predict the structure of the electrical
211 double layer except at high salinities or in the presence of multivalent counterions^{37,95,96}. In the
212 case of montmorillonite, an opportunity to verify the validity of Eq. (4) is provided by GCMC
213 simulations of the acid-base chemistry of individual clay particles where water was treated as a
214 uniform dielectric continuum⁵⁰. To this end, we implemented Eq. (4) in PHREEQC⁹⁷ (the
215 modification of the source code is made available in the supporting information file; a executable
216 file can be sent upon request) and predicted the protonation of surface sites using the same site
217 densities and pK_a values as Delhomme et al.⁵⁰ (PHREEQC scripts and database are available in
218 the supporting information file). An excellent agreement was found between the two predictions
219 (Figure 3), suggesting that Eq. (4) is valid over the entire range of experimental conditions where
220 montmorillonite particles are made of single layers. This condition is met in experiments carried
221 out with montmorillonite particles dispersed in a NaCl or NaClO₄ background electrolyte at ionic
222 strengths lower than $I \sim 0.2$ ⁹⁸⁻¹⁰¹.



223

224 Figure 3. Comparison of the GCMC simulations of Delhorme et al.⁵⁰ (circles and squares) with
225 an SCM that used Eq. (4) (solid lines) at three different ionic strengths in NaCl salt background.
226 Both models used the same site densities and intrinsic pK_a values. Activity coefficients of solute
227 species in the SCM were modeled using the extended Debye-Hückel formalism. Blue symbols
228 and lines refer to aluminol sites having a pK_a of 3.75 and a site density of 4.5 nm^{-2} ; red symbols
229 and lines refer to silanol sites having a pK_a of 8.0 and a site density of 5.2 nm^{-2} . Shaded areas
230 correspond to conditions that cannot exist, i.e., domains where the specified ionic strength is
231 exceeded because of high H^+ or OH^- concentrations.

232 2.4. Intrinsic pK_a values of edge surface sites

233 Until recently, theoretical estimates of the intrinsic pK_a values of edge surface sites were based on
234 bond-valence theories. The resulting predicted pK_a values were highly sensitive to model
235 assumptions^{40,41} and did not provide accurate predictions of experimental montmorillonite
236 titration data²⁰. In the last decade, *ab initio* MD simulations have proved capable of accurately
237 predicting the intrinsic pK_a values of simple oxide surface functional groups¹⁰²⁻¹⁰⁴, including
238 oxide-type functional groups on montmorillonite edge surfaces⁵¹⁻⁵⁷. In particular, a series of
239 papers by Liu et al.⁵¹⁻⁵⁵ explored the influence of edge crystallographic orientation and the
240 presence of octahedral and tetrahedral substitutions on the intrinsic pK_a values of edge surface
241 groups. Their predictions are summarized in Figure 1. It is noteworthy that similar sites on the
242 surfaces perpendicular to the [010] and [110] crystallographic directions have different reactivity
243 according to the *ab initio* MD calculations. For example, silanol sites ($>SiOH$) have pK_a values of
244 7.0 on the [010] edge vs. 8.3 on the [110] edge when no octahedral substitution is present. These
245 values are significantly different from the values predicted by bond valence methods^{40,41} and
246 used by Bourg et al.²⁰ (Table S-2).

247 2.5. Experimental data

248 Duc et al.²⁶⁻²⁸ carried out a comprehensive examination of montmorillonite acid-base titration
249 methodologies and identified a series of best practices. These included careful montmorillonite
250 pre-treatment and storage procedures (use of a series of acid washes at $pH \approx 4$, exchangeable
251 cation homogenization at ionic strength $I \approx 1$, and rinsing steps; storage in liquid water at low
252 temperature for relatively short durations, or storage of freeze-dried samples as an acceptable
253 alternative). For the titration experiments themselves, they noted the importance of using an inert
254 atmosphere and limiting the experiments to the pH range $\approx 4.5-9.5$. They found that a continuous

255 titration method was acceptable if equilibration times between additions of acid or base were
256 short (< 10 min) and if hysteresis was quantified; alternatively, a discontinuous batch titration
257 method was acceptable if the atoms released by clay dissolution (Si, Al, Mg, Fe) were analyzed
258 (both in solution and on the clay cation-exchange sites) to account for pH buffering by side
259 reactions. In the alkaline domain, however, correction of the raw batch titration data for measured
260 side reactions failed to reproduce the continuous titration curves. The authors concluded on the
261 superiority of fast, continuous methods for quantifying the dissociable surface charge of clays.
262 Among the many reported studies of montmorillonite titration^{12,27–29,33–35,39,80,84,86,88–90,105}, Bourg
263 et al.²⁰ determined that only three studies^{27,28,39} followed this set of best practices. One of these
264 studies used the batch titration technique³⁹, and its results at alkaline pH values are therefore of
265 unclear reliability. Of the acid-base titration studies published over the last decade^{42–47}, none
266 followed the entire established set of best practices while also reporting the pH and ionic strength
267 of the solutions used during clay pre-treatment. The present study, therefore, focuses on the
268 dataset from Duc et al.²⁷ as the best available set of montmorillonite acid-base titration results.

269 An interesting indirect quantification of edge surface charge was pursued by Pecini and Avena⁴⁸,
270 who measured the i.e.p. of montmorillonite loaded with cationic dyes with a strong affinity for
271 the basal surface. Under the assumption that the dyes completely screen the basal surface charge
272 but do not interact with the edge surfaces (such that the measured i.e.p. reflects edge surface
273 properties) and within the well-established theoretical limitations associated with relating an i.e.p.
274 to a point of zero charge³⁰, the results of Pecini and Avena⁴⁸ suggest that the point of zero
275 charge of clay edge surfaces (the pH value where $\sigma_{0,\text{edge}} + \sigma_{\text{H}} = 0$, where $\sigma_{0,\text{edge}}$ corresponds to the
276 permanent structural charge density “expressed” on the edge surface) is in the pH range 3.8–5.5,
277 in qualitative agreement with a previous measurement of the i.e.p. of thermally treated Cu-

278 montmorillonite for which the structural layer charge was reduced to almost zero, whereby the
279 authors estimated that the edge surfaces are negatively charged at $\text{pH} > 3.5$ ¹⁰⁶.

280 **3. Towards a predictive SCM for montmorillonite edge surfaces**

281 **3.1. Reactivity of edge surface functional groups**

282 To determine whether the new knowledge summarized above allows a predictive simulation of
283 the acid-base chemistry of montmorillonite, we developed a generic SCM for the [010] and [110]
284 edge surfaces in our modified version of PHREEQC that applies Eq. (4) for the calculation of
285 ψ_{edge} . Edge surface functional groups were modeled as groups of one octahedral and two
286 tetrahedral cations together with their associated OH groups. The overall charge of a group was
287 calculated from bond valence principle applied to the terminal oxygen atoms of the edge sites.
288 For example, a fully-deprotonated functional group with no isomorphic substitution on the [010]
289 edge corresponds to the grouping of two Si-O^- sites and one Al-(OH)_2^- site and is denoted $>\text{Si-Al-}$
290 SiO_4^{-3} (leaving the unreactive H out of the formula). It can be protonated four times with intrinsic
291 pK_a values of 8.3, 7, 7, and 3.1 as predicted by *ab initio* MD simulation (section 2.4 and Figure
292 1). This representation deviates from the classical description used in SCMs, where each surface
293 hydroxyl is modeled as a distinct functional group with a single pK_a value¹⁰⁷. The advantages of
294 the present representation are that the calculation of the number of sites affected by neighboring
295 substitutions is straightforward and that future implementation of metal adsorption through the
296 formation of multi-dentate surface complexes is made easier with regards to the calculation of
297 surface site activities^{9,108}. Simple cases were used to verify that the grouping of surface sites had
298 little effect on model predictions (Fig. SI-1 in supporting information; PHREEQC script files are
299 also available in order to test further the effect of grouping sites). The fractions of edge functional

300 groups that include octahedral or tetrahedral substitutions were calculated from the structural
 301 formula of montmorillonite with the assumption that edge chemistry reflects that of the bulk
 302 mineral. Because of the absence of *ab initio* MD simulation predictions of the reactivity of Fe-
 303 substituted sites on the [110] edge surface, sites with Fe(III) for Al substitutions on this surface
 304 were assigned the same properties as sites without substitutions, while sites with Fe(II) for Al
 305 substitutions were assigned the same properties as sites with Mg for Al substitutions. Surface site
 306 densities were estimated from crystallographic considerations and from reported clay unit cell
 307 formulae: each site group, SiAlSi, AlAlSi, SiMgSi, SiFe^{III}Si, and SiFe^{II}Si had a density of $2.06 \times$
 308 $x_i \text{ nm}^{-2}$, where $x_{>\text{Si-Mg-Si}} = \left(\frac{\text{Mg}}{\text{Al}+\text{Mg}+\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}}} \right)_{\text{oct}}$, $x_{>\text{Si-Fe}^{\text{III}}\text{-Si}} = \left(\frac{\text{Fe}^{\text{III}}}{\text{Al}+\text{Mg}+\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}}} \right)_{\text{oct}}$
 309 , $x_{>\text{Si-Fe}^{\text{II}}\text{-Si}} = \left(\frac{\text{Fe}^{\text{II}}}{\text{Al}+\text{Mg}+\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}}} \right)_{\text{oct}}$, $x_{>\text{Al-Al-Si}} = 2 \times \left(\frac{\text{Al}}{\text{Si}+\text{Al}} \right)_{\text{tet}}$, and $x_{>\text{Si-Al-Si}} = 1 -$
 310 $x_{>\text{Si-Mg-Si}} - x_{>\text{Al-Al-Si}} - x_{>\text{Si-Fe}^{\text{III}}\text{-Si}} - x_{>\text{Si-Fe}^{\text{II}}\text{-Si}}$. This calculation implicitly neglects the
 311 possible existence of edge sites with both octahedral and tetrahedral substitutions or with two
 312 tetrahedral substitutions, for which predicted pK_a values are not available.

313 3.2. Impact of clay permanent structural charge

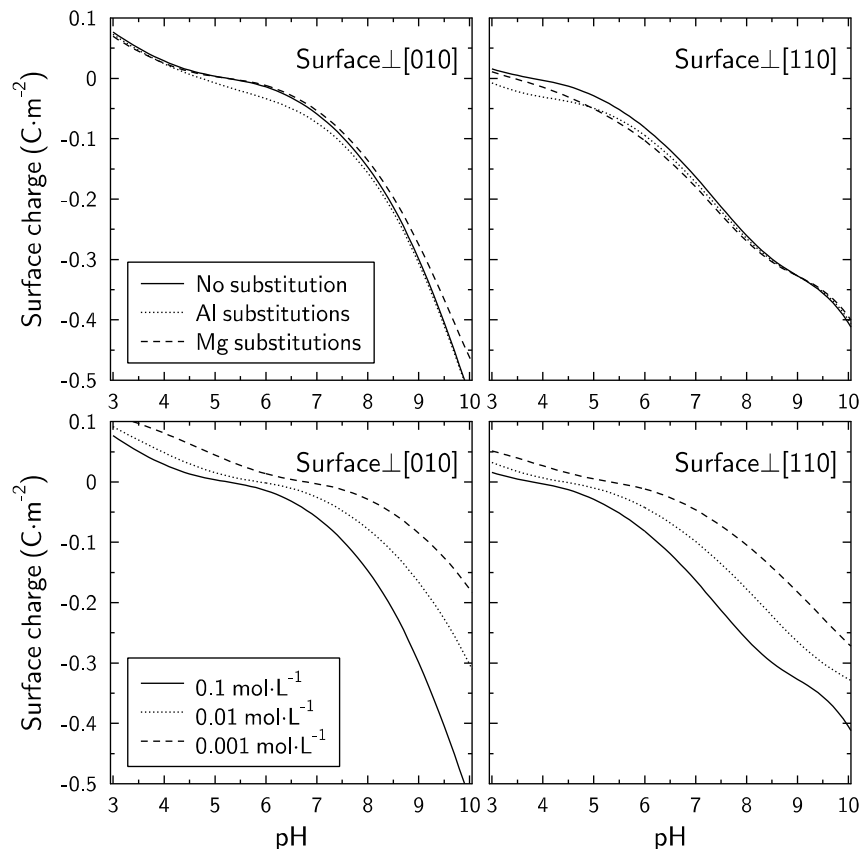
314 Proton adsorption by Na-H cation exchange on basal surfaces was taken into account by using a
 315 constant selectivity coefficient of 3.2 ($\log K = 0.5$) in near agreement with previously published
 316 values^{41,109}. The permanent structural charge was set to $0.9 \text{ mol}_c \cdot \text{kg}^{-1}$, yielding an overall charge
 317 density of $\sigma_0 = -0.12 \text{ C} \cdot \text{m}^{-2}$ for the clay layers. As noted above, the edge surface charge equals
 318 $\sigma_{0,\text{edge}} + \sigma_{\text{H}} = 0$, where $\sigma_{0,\text{edge}}$ is the edge surface charge density resulting from nearby isomorphous
 319 substitutions. Bourg et al.²⁰ assumed that $\sigma_{0,\text{edge}} = \sigma_0$ for simplicity. Here, we modeled edge
 320 surface charge arising from near-edge isomorphous substitutions in an even simpler way: we added
 321 -1 to the valence of edge functional groups that include an isomorphous substitution of Al for Si or

322 of Mg or Fe(II) for Al. For example, a fully-deprotonated edge functional group with no
323 isomorphous substitutions ($>\text{Si-Al-SiO}_4^{-3}$), upon substitution of Mg for Al, becomes ($>\text{Si-Mg-SiO}_4^{-4}$).
324 ⁴).

325 **3.3. Predicted acid-base properties of edge surfaces**

326 According to the predictive model described above, montmorillonite edge surface charge has
327 little dependence on the type and extent of layer structural substitutions, but it depends
328 significantly on crystallographic orientation between the [010] and [110] edge surfaces (Figure 4,
329 top). In the presence of $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaCl, the [010] surface is positively charged at $\text{pH} < 5$,
330 whereas the [110] surface is positively charged only at $\text{pH} < 3.5$, consistent with the experimental
331 findings of Thomas et al.¹⁰⁶ and Pecini and Avena⁴⁸. The relative proportion of [010] and [110]
332 edge surface orientations on montmorillonite is unfortunately unknown, which leaves one
333 unavoidable free parameter in the presently developed SCM.

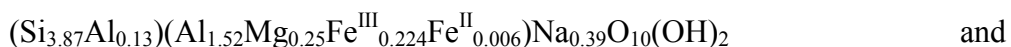
334 Changes in ionic strength are predicted to have a marked effect on surface charge but not on the
335 shape of the charge vs. pH curves, especially for the surface perpendicular to [110] (Figure 4,
336 bottom). A decrease in ionic strength results primarily in a translation of the surface charge curve
337 towards higher pH values, in agreement with experimental results.



338
 339 Figure 4. Top: Predicted edge surface charge as a function of pH for montmorillonite particles
 340 immersed in a $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaCl background electrolyte. “No”, “Al” and “Mg” substitutions refer
 341 to simulations carried out with $(x_{>\text{Si-Mg-Si}} = 0; x_{>\text{Al-Al-Si}} = 0)$, $(x_{>\text{Si-Mg-Si}} = 0; x_{>\text{Al-Al-Si}} =$
 342 $0.1)$ and $(x_{>\text{Si-Mg-Si}} = 0.2; x_{>\text{Al-Al-Si}} = 0)$ respectively. Bottom: Influence of NaCl
 343 concentration ($0.001, 0.01, \text{ and } 0.1 \text{ mol}\cdot\text{L}^{-1}$) on the predictions obtained if $x_{>\text{Si-Al-Si}} = 1$.

344 3.4. Comparison with potentiometric titration data

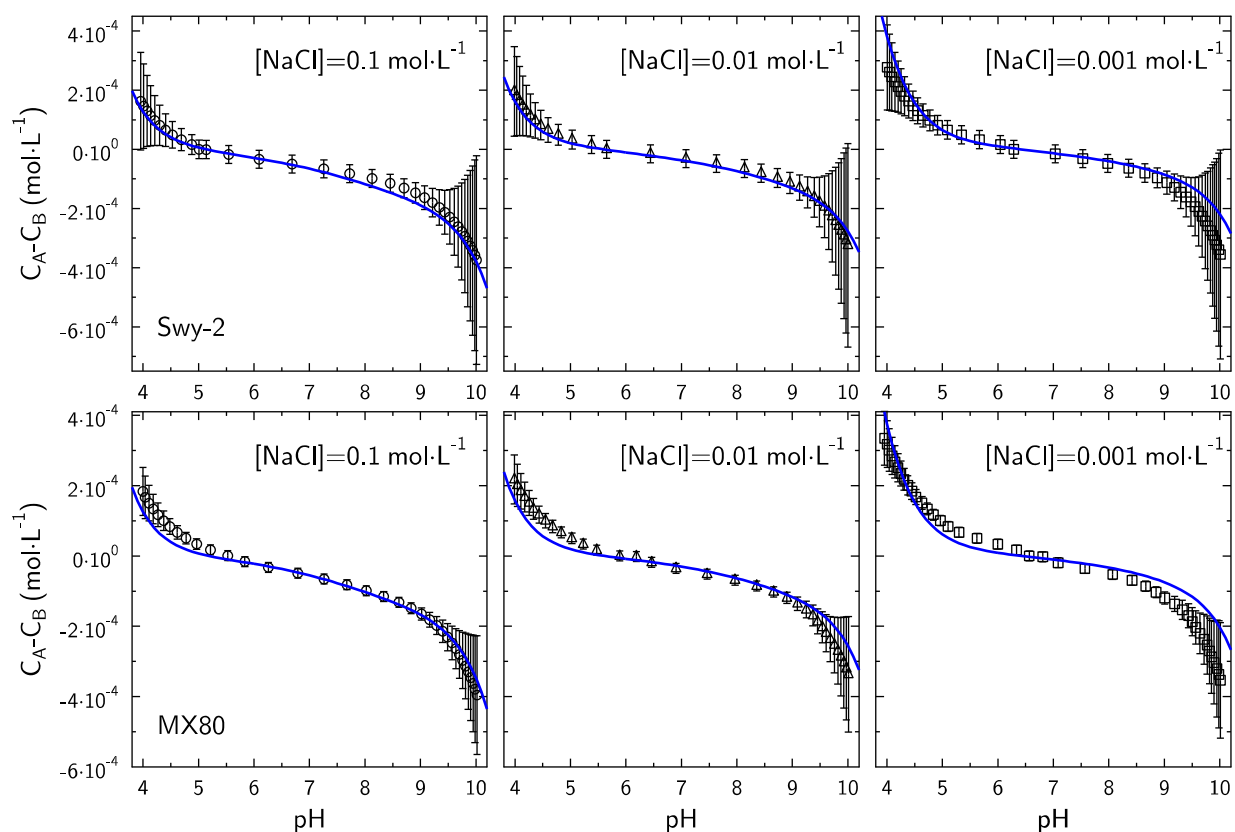
345 Model predictions were compared with the potentiometric titration results of Duc et al.²⁷ for the
 346 SWy-2 and MX80 reference montmorillonites (the dataset for SWy-2 was made available in
 347 Delhorme et al.⁵⁰). The structural formulae of SWy-2 and MX80 montmorillonites were reported
 348 as



349 $(\text{Si}_4)(\text{Al}_{1.57}\text{Mg}_{0.25}\text{Fe}^{\text{III}}_{0.09}\text{Fe}^{\text{II}}_{0.09})\text{Na}_{0.34}\text{O}_{10}(\text{OH})_2$, respectively ²⁷. Reported montmorillonite
350 structural formulae can vary as a function of sample preparation and calculation method ⁶⁵. This
351 variability adds a minor source of uncertainty to our model predictions according to Figure 4. The
352 $x_{>\text{Si-Mg-Si}}$, $x_{>\text{Si-Fe}^{\text{II}}\text{-Si}}$, $x_{>\text{Si-Fe}^{\text{III}}\text{-Si}}$ and $x_{>\text{Al-Al-Si}}$ values were set, respectively, to 0.125,
353 0.045, 0.045 and 0 for MX80 montmorillonite and to 0.125, 0.003, 0.112 and 0.13 for SWy-2
354 montmorillonite.

355 A good agreement was found between experimental and predicted potentiometric titration data
356 for SWy-2 montmorillonite if the specific edge surface area was set to $14 \text{ m}^2 \cdot \text{g}^{-1}$ and the relative
357 abundance of [010] and [110] edges was set to 1:1 (Figure 5). The modeled edge specific surface
358 area is in agreement with the value of $19.2 \text{ m}^2 \cdot \text{g}^{-1}$ measured on the sample used for the titration
359 experiment (Table S-1), because the DIS method tends to overestimate the surface area ⁷⁴. A
360 lesser agreement was found for the lowest ionic strength ($I=0.001$) at pH values greater than 8,
361 but the significance of this discrepancy is tempered by the increased experimental uncertainty at
362 $\text{pH} > 9$ ²⁰. For MX80 montmorillonite, the agreement between experimental and predicted
363 potentiometric titration curves was acceptable if the specific edge surface area was set to $12 \text{ m}^2 \cdot \text{g}^{-1}$
364 and the relative abundance of [010] and [110] edges was set to 1:1 (Figure 5) (the effect of
365 varying the relative abundance of [010] and [110] edges can be seen on Figure 4, and it can be
366 quantified by using the PHREEQC script files provided in the supporting information). The
367 modeled edge specific surface area was larger than the measured value (Table S-1, from 6 to 9
368 $\text{m}^2 \cdot \text{g}^{-1}$, depending on the considered study). However, the values reported in Table S-1 were not
369 measured for the same samples used in the titration experiments. For both titration datasets, the
370 pH values corresponding to $\delta\sigma_{\text{H}} = 0$ were correctly predicted at all investigated ionic strengths.
371 A better agreement with the experimental data likely could have been achieved by adjusting the

372 pK_a values of edge surface sites in the limit of the uncertainty reported in Liu et al.⁵¹⁻⁵⁵ (from
373 ± 0.6 to ± 1.6 depending on the site under consideration), but such a refinement was not deemed
374 justified in light of the uncertainties in the experimental data. Such exercise can be done using the
375 files made available in the supporting information.



376
377 Figure 5. Comparison of model predictions (lines) and potentiometric titration data (symbols^{27,50})
378 for MX80 montmorillonite (bottom) and Swy-2 montmorillonite (top). The specific edge surface
379 area was set to $12 \text{ m}^2 \cdot \text{g}^{-1}$ and $14 \text{ m}^2 \cdot \text{g}^{-1}$ for MX80 and Swy-2 montmorillonite respectively, and
380 the relative abundance of [010] and [110] edges was set at 0.5/0.5. Error bands were estimated as
381 in Bourg et al.²⁰.

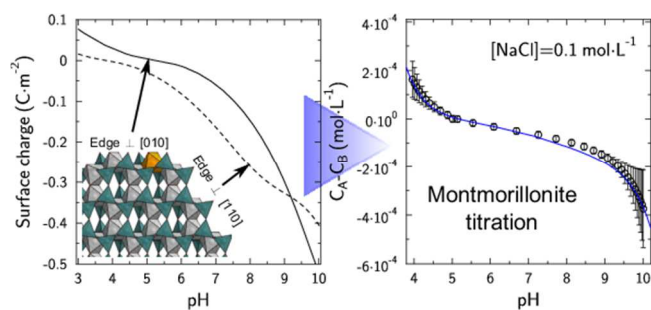
382 The present study relies on several simplifying assumptions or conditions that inherently limit the
383 range of applicability of the proposed model. First and foremost, the model was derived for the
384 case of simple indifferent 1:1 electrolytes such as NaCl at relatively dilute concentrations (≤ 0.1
385 M) where clay layer stacking is minimal and where the mean field approximation inherent in the
386 PBE is valid. Extension of the model to a broader set of conditions would require a new model of
387 ψ_{edge} derived for the appropriate aggregation structure of montmorillonite layers and for
388 deviations from the mean-field approximation. A significant challenge to such an extension is
389 that the best-quality experimental titration data are limited to the conditions modeled in the
390 present study.

391 Another important condition for the applicability of our proposed model is that the model's
392 description of edge surface sites must be accurate. At the most fundamental level, this condition
393 can be challenged on the grounds that most, if not all, theoretical calculations of montmorillonite
394 edge site properties were carried out based on a pyrophyllite-like model structure, which is *trans*-
395 vacant, whereas available data suggest that most montmorillonites have a *cis*-vacant structure
396 ^{110,111}. Structural OH groups have different positions in *cis*- and *trans*-vacant structures.
397 Additionally, *cis*-vacant structures are not centrosymmetric ¹¹¹, and the types of edge surface
398 configurations are thus more diverse than for *trans*-vacant structures. In particular, edge surface
399 site configurations are different for the edges perpendicular to the [010] and $[0\bar{1}0]$
400 crystallographic directions in a *cis*-vacant structure, whereas they are the same in a *trans*-vacant
401 structure (see Figure S-1 in supporting information).

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410 5. TOC



411

412

413 6. References

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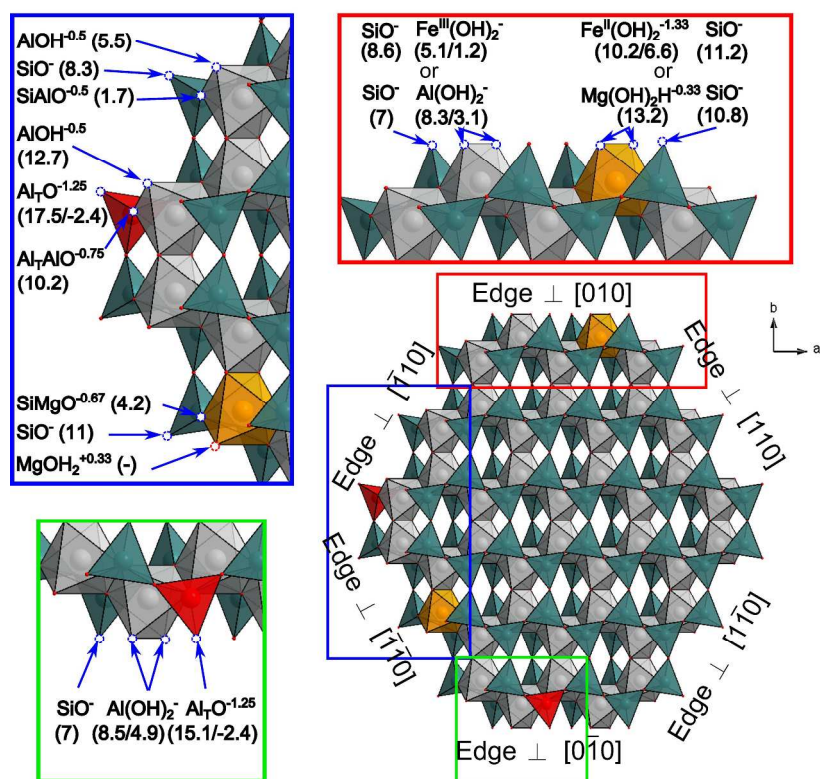


Figure 1

297x420mm (300 x 300 DPI)

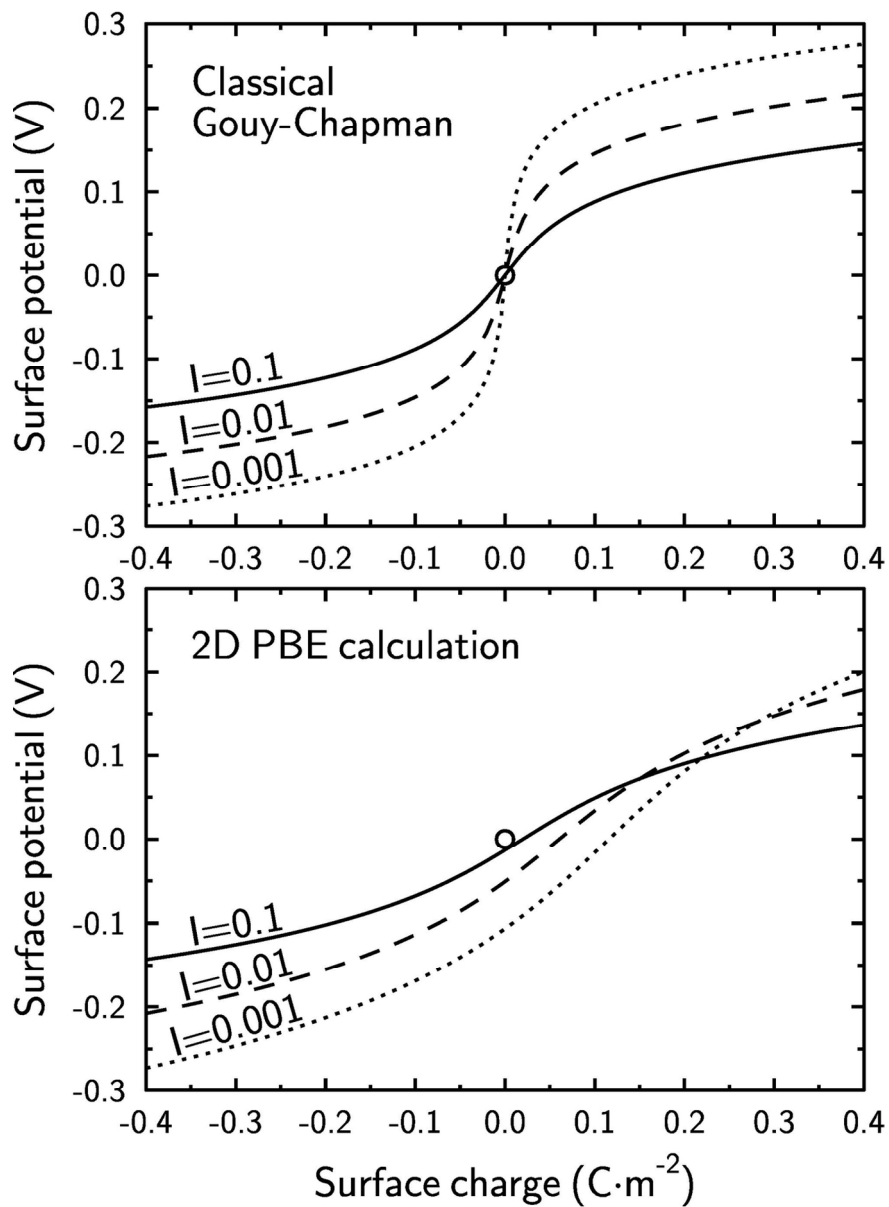


Figure 2

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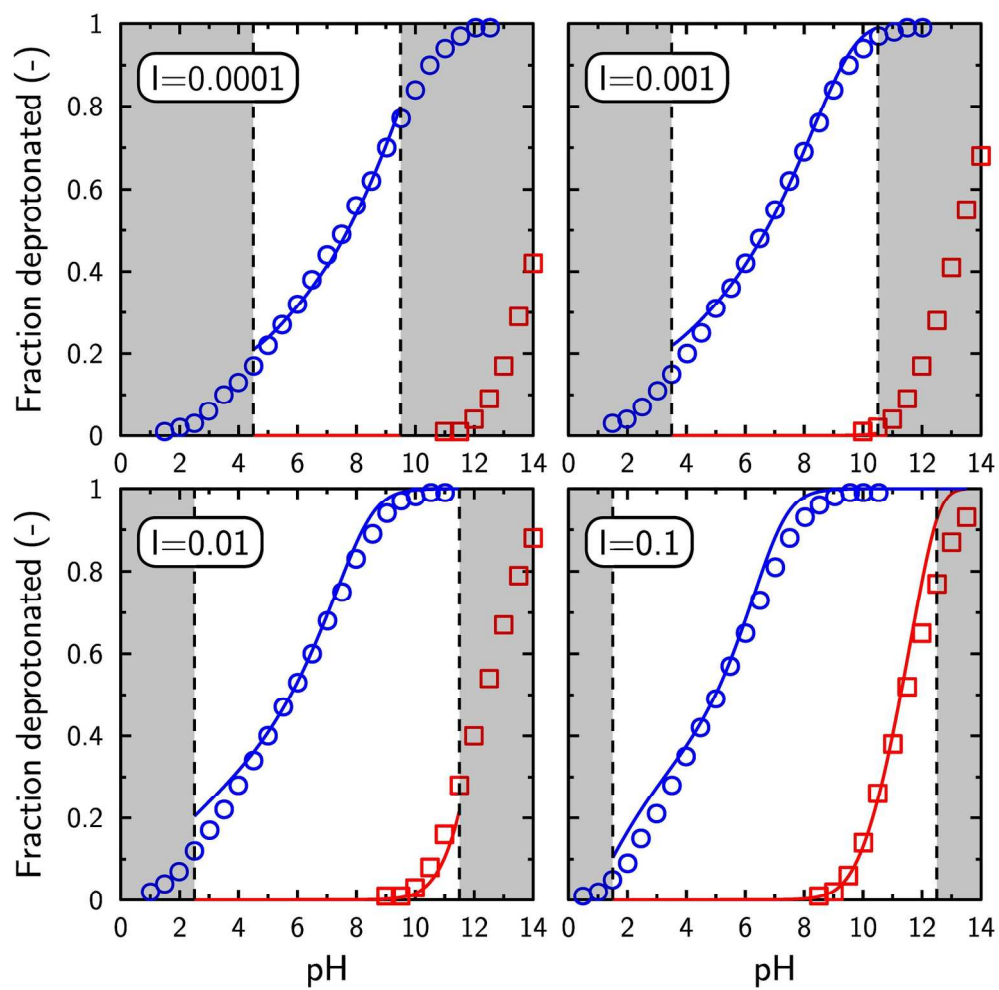


Figure 3

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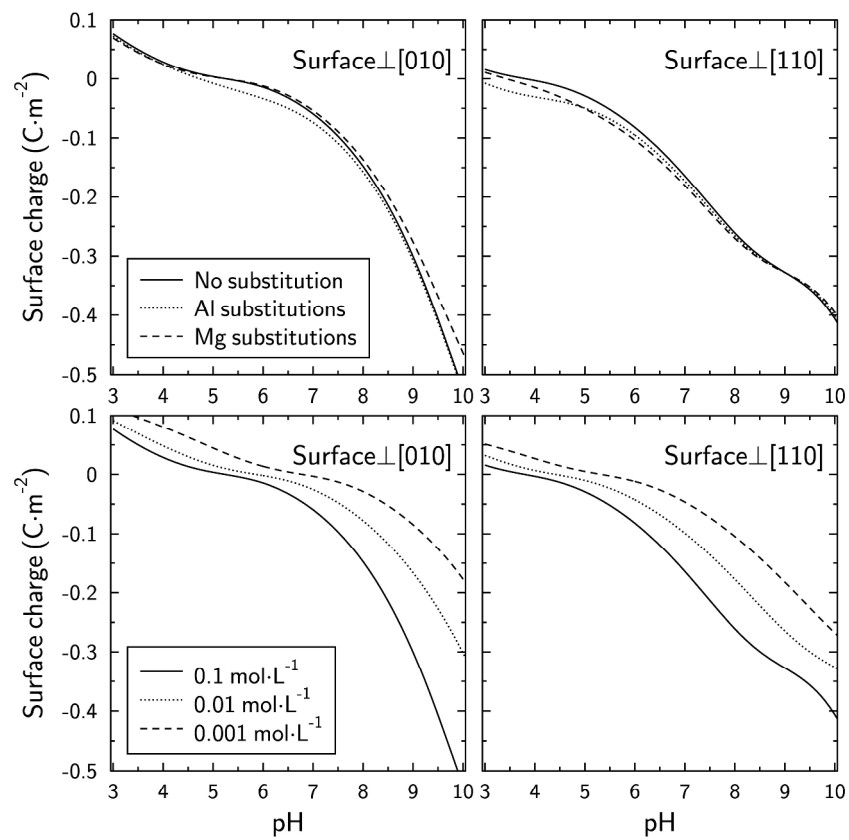


Figure 4

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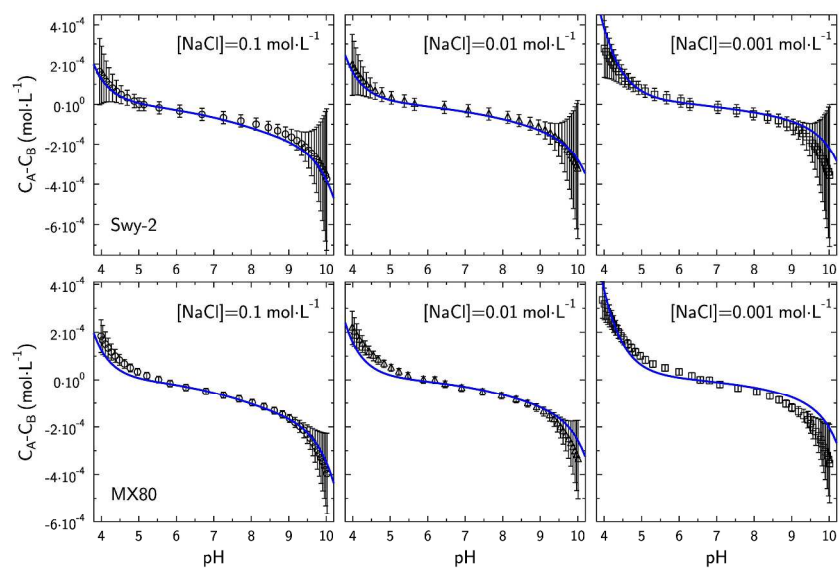
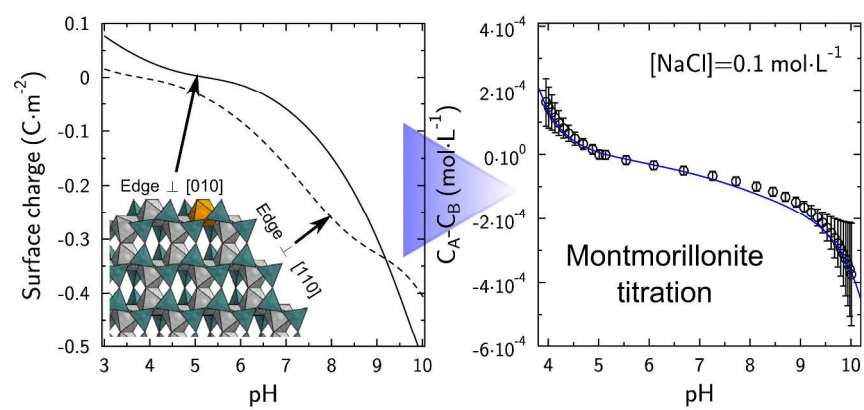


Figure 5

297x420mm (300 x 300 DPI)



TOC

297x420mm (300 x 300 DPI)