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1 **Intrinsic hydrophobicity of smectite basal surfaces quantitatively probed by molecular**
2 **dynamics simulations**

3
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20 **KEY WORDS:** clay-water interface, hydrophobicity, adsorbed water, smectite, molecular
21 dynamics simulations

22 **ABSTRACT**

23 The siloxane surface of uncharged clays is known to be hydrophobic, which is
24 supported by strong experimental and theoretical evidence. For the siloxane surface of
25 charged clays, like smectites, the picture is not as clear. We are aiming to clarify this issue by
26 molecular simulations in which smectite surface hydrophobicity is quantified through the
27 separate contribution of the surface itself, and the contribution due to the presence of charge-
28 balancing cations on the surface. In order to explore systematically the effects of the total
29 smectite charge and its distribution in the structure, a series of molecular dynamics (MD)
30 simulations was performed for several models of dioctahedral smectites and compared with
31 the results for uncharged pyrophyllite.

32 The largest difference between the simulation results for smectite models with
33 naturally present surface counterions and the models where these ions were artificially
34 removed from the surface, while maintaining the same total charge balance of the model, is in
35 the shape of the water coverage. In the former case, full surface wetting is observed and a
36 relatively flat water film is forming on the surface. Its irregularity and thickness is connected
37 with number of ions on the surface. However, in all cases of smectite surfaces artificially
38 devoid of ions, a water droplet is always formed and the wetting is incomplete. The contact
39 angles of the water droplets on charged montmorillonites are very similar to that on uncharged
40 pyrophyllite surface and range roughly between 110° and 90° . These angles are also affected
41 by the distribution of the octahedral and tetrahedral substitutions in the structure and by their
42 ratio. In the case of purely tetrahedral substitutions the contact angle on the bare smectite
43 surface can be as low as $\sim 60^\circ$, but still far from complete wetting.

44 The angular distributions of the H_2O dipole vectors as a function of distance from the
45 smectite surface show two preferred surface-oriented types of water molecules when
46 counterions are present, and the total surface is highly hydrophilic. However, for surfaces

47 devoid of ions, a population with dipole angles close to $\sim 90^\circ$ is dominating, and the smectite
48 surfaces can be considered hydrophobic. It can be thus concluded that, independent of the
49 structural charge, bare smectite surfaces by themselves are either hydrophobic or only
50 moderately hydrophilic. Their experimentally observed highly hydrophilic character is almost
51 entirely due to the charge balancing cations present on the surface.

52

53 1. INTRODUCTION

54 Hydrophobicity of a surface is manifested by repelling water molecules. In practice,
55 this is due to the surface attractive forces towards H₂O molecules being much weaker than the
56 attractive forces between H₂O molecules themselves. Therefore, water forms a droplet on
57 such a surface. Generally, if the surface is hydrophobic, it has higher affinity towards oil
58 phase. This effect plays crucial role in the case of clay minerals, as these are major
59 constituents of rock formations associated with natural hydrocarbon reservoirs. A large
60 number of recent molecular simulation studies have demonstrated and confirmed that affinity
61 of aluminosilicate surfaces to hydrophilic or hydrophobic molecules strongly affects their
62 sorption (e.g., Tenney and Cygan, 2014; Smirnov, 2017a; Myshakin and Cygan, 2018;
63 Greathouse et al., 2018; Liu et al., 2019; Willemsen et al., 2019).

64 Clay minerals can possess neutral layer charge or have a net negative structural charge
65 that is balanced by the interlayer and/or surface cations. There is a strong experimental and
66 theoretical evidence of hydrophobic character of the siloxane surface of uncharged clays (e.g.,
67 Bridgeman and Skipper, 1997; Arab et al., 2003; Tunega et al., 2004; Churakov, 2006; Šolc et
68 al., 2011). In the case of trioctahedral structures (talc), the degree of hydrophobicity can vary
69 depending on the relative humidity (Michot et al., 1994; Rotenberg et al., 2011) or external
70 pressure on the system (Wang et al., 2004; 2005a). Thermal treatment (>900 °C) can also
71 significantly affect the hydrophobicity of talc, due to the disordering of silica tetrahedron
72 structures and formation of amorphous silica phases (Yi et al., 2019).

73 For siloxane surfaces of charged clays, like smectites, the picture is not as clear. Based
74 on aromatic hydrocarbon adsorption experiments, Jaynes and Boyd (1991) have classified the
75 smectite surface as mostly hydrophobic. Relative weakness of the hydrogen bonds donated by
76 the interlayer H₂O molecules to the clay basal surface, compared to a typical strength of H₂O-
77 H₂O bonds in bulk liquid water can be considered as molecular-scale indication of the relative

78 hydrophobicity of smectite siloxane surfaces (Kuligiewicz et al., 2015; Szczerba et al., 2016).
79 On the other hand, Sobolev et al. (2010) have used neutron scattering technique to determine
80 that the surfaces of smectite clays with tetrahedral substitutions are hydrophilic. The
81 importance of specific location of the structural charge within the clay layer for the existence
82 of hydrophobic and hydrophilic patches on the surfaces of clay particles has also been
83 confirmed in earlier Monte Carlo computer simulations (Sposito et al., 1999).

84 Important properties related to the surface hydrophobicity of 2:1 clay minerals are the
85 surface energy and the total structural charge of the clay layer (Liu et al., 2007; Shen et al.,
86 2017; Hartkamp et al., 2018). To measure the charge of the layers, a new O-D method,
87 employing IR spectroscopic measurements, has been recently developed (Kuligiewicz et al.,
88 2015; Kuligiewicz et al., 2018). Edge hydroxyl groups can be distinguished from H₂O
89 molecules at basal surfaces after deuteration also by means of vibrational spectroscopy
90 (Harvey et al., 2019). Studies on electroosmotic flow through hydrophobic nanochannels have
91 shown the dependence of the flow on the surface charge density (Silkina et al., 2019).

92 Wettability of minerals can be directly related to hydrophobicity. It has been shown
93 that introduction of anions or cations on the smectite surface plays a key role in adsorption of
94 water molecules by these minerals (Dzas et al., 2013; Dzas et al., 2015; Zhang et al., 2016;
95 Zhou et al., 2019). Attention should be also paid to the topography of the smectite surface,
96 which can significantly affect the surface wettability (Ou et al., 2018; Xi et al., 2017). It
97 should be also noted that a smectite surface can be defined in two different ways: as bare
98 siloxane surface of the crystal or as a surface covered with charge balancing cations.
99 Wettability can be more directly discussed using the second definition of the surface. On the
100 other hand, it seems more appropriate to use the first definition for the analysis of the balance
101 of hydrogen bonding H₂O-surface and H₂O-H₂O.

102 Considering other types of aluminosilicate surfaces, *ab initio* studies of kaolinite have

103 shown different nature of tetrahedral (siloxane surface) and octahedral (hydroxylated) sheets,
104 that are hydrophobic and hydrophilic, respectively (Tunega et al., 2002). Skeletal
105 aluminosilicates, i.e. zeolites, have an affinity for hydrophobic molecules, although the
106 hydroxyl groups on the outer surface act as hydrophilic adsorption sites (Smirnov, 2017b).

107 The present study aims to develop these considerations further by adding new
108 quantitative arguments based on a specially designed series of molecular simulations.
109 Theoretical calculations offer the unique ability to separate the effects of various
110 compositional and structural features of model systems on the observed properties, and this
111 methodology is employed here to quantitatively evaluate the hydrophobicity of smectite
112 surfaces from which all charge balancing cations have been removed.

113 There are various methods for assessing surface hydrophobicity based on molecular
114 simulations. For example, one can calculate the potential of mean force for the transfer of a
115 water molecule from the bulk liquid phase to the surface or from the gas phase to the surface.
116 Another method, more directly comparable with experimental observations, is the calculation
117 of the contact angle a water nanodroplet can form on the surface (Giovambattista et al., 2007;
118 Zheng and Zaoui, 2016; Khalkhall et al., 2017). Here this method is used to gain new insights
119 into the surface distribution of water molecules, and to quantitatively assess the destructive
120 effect of clay surfaces on the hydrogen bonding network of water via the calculation of the
121 orientational distributions of H₂O molecules depending on the distance from the surface.

122

123 **2. MODELS AND METHODS**

124 ***2.1. Smectite structures***

125 In order to explore systematically the effects of smectite composition on the
126 hydrophobicity of their surfaces, several models of dioctahedral smectites were constructed
127 for molecular dynamics (MD) simulations. They differed by total layer charges between 0.1

128 and 0.6¹ and by octahedral (montmorillonitic), tetrahedral (beidellitic), and mixed charge
129 localization. Simulations for an uncharged model of pyrophyllite were also performed for
130 comparison. The model structures were built on the basis of the pyrophyllite crystal structure
131 (Lee and Guggenheim, 1981), with isomorphic substitutions introduced at specific atomic
132 sites. The Mg/Al ordering in the octahedral sheets was set by maximizing the distance
133 between Mg atoms, following the work of Ortega-Castro *et al.* (2010). The distribution of
134 Al/Si substitutions followed the Löwenstein (1954) rule, i.e. excluding direct Al–O–Al
135 linkages in the tetrahedral sheets.

136 A smectite model with 12×7×2 unit cells in the *a*, *b*, and *c* crystallographic directions
137 was constructed (for pyrophyllite only one unit cell in the *c* direction was used). The final
138 simulation cell dimensions were 62.169 Å × 62.969 Å × 150 Å. The *z* dimension of the cell
139 was intentionally set at a very high value in order to assure that a large free water droplet
140 could be formed on the surface. At the edge of the periodic simulation box in the *z* direction a
141 graphene layer composed of repulsive carbon atoms was placed to prevent the transfer of H₂O
142 molecules to the other side of the smectite layer. The number of H₂O molecules introduced at
143 both sides of the structure was equal to 700 or 350 and initially formed a cuboid just above
144 the 2:1 layers. The Packmol computer program (Martínez *et al.*, 2009) was used to uniformly
145 distribute the H₂O molecules inside the cuboid. All model structures used in the study are
146 summarized in Table 1.

147

148

=== **Table 1** ===

149

150

151 For each smectite model with a particular structural charge, two cases were considered:

¹ The numerical values of the charge throughout this paper are presented in the units of elementary charge $|e|$ per half of the crystallographic unit cell, PHUC.

- 152 1) With charge-compensating Na^+ ions located on both external surfaces and K^+ ions in the
153 interlayers. The total number of potassium and sodium ions was set to be equal.
154 Additionally, for the montmorillonite model with the highest layer charge of 0.6, the
155 external number of Na^+ ions was set to correspond to the charge of 0.4.
- 156 2) Without any ions on the external surfaces and only with K^+ ions located between the clay
157 2:1 layers as the charge-compensating cations for the entire structure. This artificially
158 imposed distribution of the ions allowed us to separate the effect of the surface cations on
159 the distribution and orientation of the interfacial H_2O molecules and to quantitatively
160 analyze these molecular distributions as resulting primarily due to the H_2O interaction
161 with the charged smectite surfaces themselves. In the case of the highly charged models
162 (0.6), some interlayer K^+ ions had to be replaced by Ca^{2+} in order to keep the total charge
163 of the simulation cell neutral.

164

165 ***2.2. Molecular dynamics simulations and their analysis***

166 Partial atomic charges and other interatomic interaction parameters of smectite layers
167 were described using the ClayFF force field (Cygan *et al.*, 2004) with structural OH groups
168 described by a more accurate Morse potential (Greathouse *et al.*, 2009). Ewald summation
169 (e.g., Allen and Tildesley, 2017) was used to calculate the long range corrections to the
170 electrostatic interactions and the cutoff distance was set to 10.0 Å. The H_2O molecules were
171 described with the SPC model (Beredensen *et al.*, 1981). All simulations were performed
172 using the LAMMPS molecular modeling software package (Plimpton, 1995). Each system
173 was initially brought to a local energy minimum for 10000 steps, followed by a 5 ns MD run
174 in the *NVT* statistical ensemble (at constant volume and a temperature of $T = 300$ K). Standard
175 periodic boundary conditions were applied (e.g., Allen and Tildesley, 2017), and the equations
176 of atomic motion were numerically integrated with a time step of 1 fs.

177 Initial test MD runs for the model structures revealed that for the systems with all ions located
178 in the interlayer between the 2:1 clay layers, some of SiO_4 tetrahedra experienced significant
179 deformations: Si-O basal distances remained the same, but the Si-O apical distance could
180 become too long, apparently due to the quasi-ionic character of the ClayFF parametrization
181 (Cygan et al., 2004). This led to the mechanical deformation of tetrahedral sheets comparing
182 to real crystallographic structures of the smectite 2:1 layers (see Supplementary materials,
183 Fig. S1). To prevent this from happening, the simulation structures were built based on the
184 pre-optimized (in the *NPT* ensemble for 0.5 ns, then in the *NVT* for 0.5 ns) pyrophyllite layer
185 and then energy minimized anew. For smectite structures certain atoms were substituted, as
186 necessary, and the layer was replicated and translated into the simulation supercell $12 \times 7 \times 2$, as
187 discussed above. During the production runs all the tetrahedral silicon and aluminum atoms
188 were then fixed at their positions. All other atoms of the smectite structure were not fixed –
189 i.e. they were free to move around their crystallographically determined positions according
190 to the modeling force field used. The equilibrium MD-simulated trajectories were
191 recorded every 1 ps during the last 3 ns of each run, and then used to calculate the contact
192 angles of the water droplets formed at the smectite surfaces, according to the following
193 procedure. At first, the center of mass was calculated for the droplets on both sides of the
194 smectite layers for each frame. The density of oxygen atoms of water molecules (O_w) was
195 then calculated and centered in x and y directions (parallel to the surface) based on the
196 position of the center of mass, which was taken as the reference point (0, 0). The distribution
197 of atoms in the droplet was calculated as a sum from both sides of the smectite layers.
198 Assuming the equivalence of the x - and y - directions along the surface, the number of O_w
199 atoms was then averaged over the ac and bc crystallographic planes in order to obtain a 2-
200 dimensional plot. After that, hemispherical plots were calculated as averages over positive
201 and flipped negative positions. A curve enveloping 10 – 15 % of the maximum density of

202 H₂O molecules in the droplet was drawn and fitted with a circle. Finally, the contact angle
203 was calculated as the tangent to the circle at the point where it crosses the horizontal line
204 corresponding to first layer of surface water molecules along the z -direction normal to the
205 surface. Error bars were calculated as a sum of two contributions. The first one is the standard
206 deviation (σ_1) of contact angles determined for intervals of 1 ns in the last 3 ns of the
207 simulations. These results correspond, therefore, to three fits of enveloping curves and are
208 presented as $2\sigma_1$. The second contribution to the error is $2\sigma_2$ of the contact angles calculated
209 for positions of the first water layer modified by $\pm 0.1 \text{ \AA}$.

210 The values of 10 – 15 % of the maximum density of H₂O molecules was optimized to
211 give the density of water inside the droplet close to the experimental value at 25°C: 0.997
212 g/cm³. The volume of the droplet was calculated as the volume of the spherical cap (or the
213 volume of sphere minus the volume of the spherical cap, for the contact angles higher than
214 90°). Generally, it should be noted that the exact value of the contact angle depends on the
215 choice of the envelope or distance from the surface at which the tangential line is drawn, but
216 qualitative findings are not affected by this choice within reasonably broad limits.

217

218

=== Fig. 1 ===

219

220 In order to test if the shape of the droplet (and thus the contact angle) has equilibrated,
221 the measured 10% enveloping curves were compared for every 1 ns interval from the
222 beginning of the simulation for pyrophyllite. The initial minimization and the first 0.1 ns of
223 the *NVT* run were not taken into account, as these should significantly deviate from
224 equilibrium. A comparison of the five separate envelopes thus obtained (see Supplementary
225 materials Fig. S2) shows that for all intervals the shape is practically identical, with the
226 exception of the very first 1 ns interval. The second 1-ns interval was also not included in the
227 final contact angle analyses in order to make absolutely sure that the results for the last 3 ns of

228 the simulations correspond to well equilibrated structures.

229 The MD structural data were also used to calculate the distributions of angles formed
230 by the dipole axes of the H₂O molecules in the droplet with the vector normal to the 2:1
231 surfaces (angle α in Fig. 2) as functions of the distance z from the surface. Time-averaged
232 positions of the surface bridging oxygen atoms (O_b) on the siloxane surface were taken here
233 as the origin ($z = 0$), similarly to the previous studies (Wang *et al.*, 2005b, 2009; Loganathan
234 and Kalinichev, 2013; Szczerba *et al.*, 2014, Ngouana Wakou and Kalinichev, 2014;
235 Greathouse *et al.*, 2015; Teich-McGoldrick *et al.*, 2015). The direction of the H₂O dipole was
236 defined as the vector from the central point between the two hydrogen atoms of the water
237 molecule to its oxygen atom. As the HOH angle was allowed to vary in the flexible H₂O
238 molecular model used, this methodology introduces a minor additional spread of the
239 calculated angles. The ranges of the α angles used in calculations were not set equal but were
240 set to cover the same surface of spherical segment (i.e. narrower ranges for α angles close to
241 90°, and wider close to 0° and 180°). All these properties were calculated by averaging over
242 the last 3 ns for each equilibrium MD trajectory.

243

244 === Fig. 2 ===

245

246 3. RESULTS AND DISCUSSION

247 3.1. Formation of water droplets on the model smectite surfaces

248 Dramatically different wetting patterns visually demonstrate the largest difference
249 between the simulation results for the smectite model surfaces where counterions were
250 present and the results for the same smectites where these ions were artificially displaced
251 from the surface into the interlayer (Fig. 3). In the presence of surface ions, a quite
252 homogeneous flat water film is forming indicating complete wetting of the smectite surface
253 (Fig. 3a). The more surface Na⁺ ions are present, the less rugged is the boundary interface

254 between the water film and the “vapour phase” above it (see Supplementary materials, Figs
255 S3-S6). In the case of smectites with relatively low charge (≤ 0.2), there are some areas on the
256 surface that are temporarily exposed and not covered with water. However, this effect is not
257 observed for higher layer charge models with the same number of surface water molecules.
258 On the other hand, with no ions present on the surface, its wetting becomes much less evident,
259 and a distinct water droplet is always formed (Fig. 3 right panel).

260

261

==== Fig. 3 ====

262

263 In all the studied cases the increased density of water molecules next to the surface is
264 clearly visible (Figs. 1, 4, 5, 6). This corresponds to the first layer of H₂O molecules on the
265 surface. A second layer of surface water molecules is also visible, while a third one is barely
266 distinguishable. Between the first two interfacial water layers, a layer of low density is
267 observed, which is also manifested in the curve on the envelope corresponding to 10% of the
268 maximum density of O_w molecules (Figs. 1, 4, 5, 6). These features, of course, correspond to
269 the maxima and minima of the atomic density profiles as functions of distance from the
270 surface (e.g., Wang et al., 2005b, 2009; Loganathan and Kalinichev, 2013).

271

272 ***3.2. Contact angles of the water droplets on montmorillonite and beidellite surfaces devoid*** 273 ***of ions***

274 On the montmorillonite surfaces devoid of ions, a water droplet of a hemi-spherical
275 shape is always formed. Calculations based on the time-averaged shapes of the droplets show
276 that the contact angles for montmorillonites are very similar or lower than the ones obtained
277 for pyrophyllite - 106° (Figs. 1 and 4). For montmorillonite with the charge of 0.5, two
278 simulations were performed, differing in the ways Mg atoms in the octahedral sheet were
279 ordered. Significantly higher contact angle was observed for the structure characterized by

280 highly ordered substitutions in the octahedral sheet – 106.6° (Fig. 4), while the structure with
281 the same layer charge but with disordered substitutions shows a much lower contact angle of
282 97.2° . This is probably an effect of decreased adhesion between water molecules and the
283 surface, which is related to the ordering of charges in the 2:1 layers. Because of this effect of
284 ordering, there can be no clear dependence of the contact angle on the layer charge for
285 different montmorillonites (Fig. 4). Summarizing, it is clear from the calculations, that the
286 contact angles of water droplets on the surfaces of montmorillonite over a pretty broad range
287 of structural charges (but devoid of ions located directly on the surface) are only slightly
288 lower than those for electrostatically neutral pyrophyllite – on average by about $5-10^\circ$.

289

290

=== Fig. 4 ===

291

292 The tetrahedral charge introduced in the 2:1 layers by Al/Si substitutions leads to a
293 noticeable decrease of the surface hydrophobicity. For beidellites the calculated contact angles
294 are significantly lower than for pyrophyllite (Fig. 5). These are also highly dependent on the
295 layer charge: i.e. the higher the charge the lower the angle. The only exception from this trend
296 is beidellite with the highest charge of 0.6, which shows a slightly higher contact angle than
297 for a beidellite structure with the of 0.5. This can also be due to an ordering effect similar to
298 the one observed for montmorillonites. Because of these lower contact angles all the
299 calculations for beidellites were performed with lower water content (350 H₂O vs. 700 for
300 montmorillonites, on each side of the layer). For higher water content, the shape of the
301 coverage is different: instead of a spherical droplet formation, the surface water coverage
302 spreads all the way to the edges of the simulation cell, and the calculation of the contact angle
303 becomes biased because of the limited size of the surface and the periodic boundary
304 conditions imposed on the system.

305

332 more deeply explain origin of this phenomenon, calculations of plots showing orientation of
333 water molecules on the surfaces were performed.

334

335 ***3.4. H₂O molecular orientations at the smectite surfaces in the presence of counterions***

336 For simulations of smectite models with surface ions, the contour maps of the angular
337 distributions of the interlayer H₂O dipole vectors with respect to the direction normal to the
338 surface and as a function of the distance z from the surface allow to distinguish two surface-
339 oriented types of H₂O molecules: monodentate and bidentate. In the bidentate orientation, a
340 water molecule donates two weak hydrogen bonds to the surface oxygens, while in the
341 monodentate orientation it can donate only one H-bond to the surface. In the two-dimensional
342 plots of the angular distributions (Fig. 7), the bidentate population is located somewhat closer
343 to the surface at $z \sim 2.0 \text{ \AA}$ and is characterized by the angles $\alpha \sim 0-20^\circ$. At the same time, the
344 monodentate population is observed at distances $z \sim 2.6 \text{ \AA}$ and is characterized by a broader
345 distribution of angles between 30° and 80° with a maximum at $\alpha \sim 50^\circ$. The presence of
346 monodentate H₂O molecules is ubiquitous, while the bidentate H₂O population is observed
347 mainly for smectites with higher layer charge. This is consistent with earlier results for
348 muscovite (Wang *et al.*, 2005b, 2009; Loganathan and Kalinichev, 2013) and for smectites
349 (Szczerba *et al.*, 2016).

350 As the number of water molecules on the surface was the same for all the simulated
351 structures, it is also visible in Fig. 7 that the thickness of the water film shows dependence on
352 the number of ions: the more the ions are on the surface, the thinner and more densely packed
353 is the interfacial water film. For example: in the case of Mtm02 the envelope corresponding to
354 90% of the total number of O_w atoms (second envelope line) extends to distances about 9.2 \AA
355 from the surface, while for Mtm05 this value is only about 6.2 \AA (Fig. 7). In the case of
356 beidellites the trends are practically the same. The main difference is in the distribution of the

357 surface ions, which tends to be much closer to the surface, than in the case of montmorillonite
358 structures.

359

360 === Fig. 7 ===

361

362 All previous simulations assumed that the layer charge is fully balanced by the
363 interlayer and surface cations. In the structure Mtm06_surface_04 the layer charge was 0.6,
364 while the number of surface ions was lower and corresponded to 0.4. For this structure the
365 distribution of angles and cation density are corresponding to those of Mtm04 model and the
366 number of H₂O molecules in bidentate population is clearly lower than for Mtm05 (Fig. 7).
367 This result demonstrates how significantly and directly the orientation of interfacial H₂O
368 molecules and the distribution of cations on montmorillonite surfaces depend on the total
369 number of ions present, and not on the absolute layer charge. The thickness of the interfacial
370 water film is also directly dependent on the number of ions and not on the layer charge: the
371 maximum of the envelope corresponding to 90% of the total number of O_w atoms extends to
372 distances about 6.5 Å for both Mtm06_surface_04 and Mtm04 smectite models.

373

374 ***3.5. H₂O molecular orientations at the smectite surfaces devoid of counterions***

375 The angular distributions of the interlayer H₂O dipole vectors with respect to the
376 direction normal to the smectite surfaces devoid of ions (Fig. 8) are dramatically different
377 from those in the presence of ions (Fig. 7). For all montmorillonite models, the distributions
378 look practically identical: no difference between smectites with higher or lower charges are
379 observed. The distributions are centered around $z \sim 3.0$ Å and $\alpha \sim 90^\circ$. This larger distance
380 from the surface indicates that the lack of ions leads to an increased hydrophobicity of the
381 surface, or, in other words, to a decreased H₂O affinity towards the surface. There is also no

382 distinct contribution from neither bidentate nor monodentate H₂O orientations, contrary to
383 what was observed for montmorillonites with counterions on the surface.

384 In the case of beidellite surfaces an additional non-negligible contribution from H₂O
385 molecules at $z \sim 2.6 \text{ \AA}$ and $\alpha \sim 50^\circ$ is also visible (Fig. 8). Relative intensity of this maximum
386 is increasing with increasing number of tetrahedral substitutions, while its position is not
387 dependent on the layer charge. This additional sub-population is clearly responsible for
388 increasing H₂O affinity towards the beidellitic surface, thus also for decreasing contact angle
389 of the water droplet (Fig. 5).

390

391 **=== Fig. 8 ===**

392

393 In order to get further insight into the origin of this additional sub-population,
394 distributions of H₂O molecular orientations for the structure with and without ions were
395 compared. For example, in the case of Beid05, monodentate and bidentate populations are
396 clearly visible (Fig. 9, left panel). However, for the Beid05_no_surf_ions model, there is no
397 bidentate population, but there is a “hydrophobic” population instead, with both hydrogens of
398 H₂O oriented away from the surface. Distances from the surface and angles α are practically
399 identical between this additional sub-population for Beid05_no_surf_ions model and the
400 monodentate population of the Beid05 model. This indicates that it is specifically the
401 population of monodentate water molecules which is responsible for decrease of
402 hydrophobicity of beidellitic smectites.

403

404 **=== Fig. 9 ===**

405

406 Relation of the positions of H₂O molecules contributing to this monodentate sub-
407 population to the positions of Al/Si substitutions in tetrahedral sheet indicates that it is

408 concentrated only around charge deficient Al^{3+} sites (Fig. 10). In contrast, the water molecules
409 contributing to the population of “hydrophobic” orientations tend to be located mainly above
410 the centers of SiO_4 tetrahedra and also above the hexagonal cavities on the siloxane surface.
411 There is practically no “hydrophobic” water molecules above AlO_4 tetrahedra.

412

413 === Fig. 10 ===

414

415 ***3.6. Factors affecting hydrophobicity of smectite surfaces***

416 The simulation results show that the hydrophobicity (or hydrophilicity) of smectite
417 surfaces is controlled primarily by the presence of ions that balance the negative charge of the
418 2:1 layer. The hydrophobicity of bare smectite surfaces themselves, without the counterions
419 present, closely resembles that of hydrophobic pyrophyllite. However, if the structural charge
420 originates from the tetrahedral sheet (i.e., closer to the aqueous interface), the surfaces are
421 more hydrophilic and the contact angle is below 90° . Nevertheless, it is still significantly
422 above 0° , indicating that the situation is still far from complete wetting which is observed for
423 smectite surfaces in the presence of charge balancing cations.

424 This effect is clearly related to the fact that the ions, due to electrostatic interactions,
425 tend to be located as close as possible to the charged surface. There is, however, an opposite
426 force limiting the ions ability to approach smectite surfaces too closely, which is the hydration
427 enthalpy, that can be highly negative (e.g., -99.9 kcal/mol for Na^+). Therefore, the ions
428 attract H_2O molecules, and quite strongly hold them in their hydration spheres, which
429 prevents their direct contact with the charged surface. The orientation of water molecules
430 around ions is then rearranged and H_2O can form hydrogen bonds with the surface. These H-
431 bonds are, however, relatively weak compared to H-bonds in bulk liquid water (e.g., Szczerba
432 et. al., 2016).

433 It is the number of surface cations that most significantly affects the orientation of
434 interfacial water molecules, which is clearly manifested in the comparison of the simulation
435 results between the Mtm04 and Mtm06_surface_04 smectite models. Even with the
436 montmorillonitic charge being higher by 50% in the latter case, if the number of surface
437 cations is the same, the orientational distribution of interfacial H₂O molecules and the
438 distribution of ions as function of distance from the surface remains practically identical (Fig.
439 7). In nature however, the number of surface ions is of course directly related to the smectite
440 layer charge, so these two effects cannot be observed separately, except in such model
441 simulations.

442

443 ***3.7. Charge polarization in natural samples.***

444 Of course, smectites with negatively charged layers, but without adsorbed cations are
445 impossible to find in nature. However, in the case of illitic particles, that are formed by the
446 process of smectite illitization, the model can possibly be, to some extent, similar to the one
447 presented in this manuscript.

448 In the case of illite-smectite (I/S) particles, Środoń et al. (2009) found that smectitic
449 charge is independent on the percent of smectite in I/S and is close to 0.41, while illitic
450 interlayer has also stable charge of 0.95. More recently, a constant value of smectitic surface
451 charge of I/S (0.47 ± 0.03) was confirmed independently, using IR spectroscopy, by
452 Kuligiewicz et al., (2018). Theoretically, if there can be more effective binding of potassium
453 ions in the “illitic” interlayers, the measured “smectitic” charge should thus be effectively
454 smaller. This is clearly shown in Fig. 7 for Mtm06 with the layer charge of 0.6, but with the
455 surface charge of 0.4. The distributions of cations and water molecules are practically
456 identical to the case of Mtm04, with the layer charge of 0.4. This effect can possibly be
457 responsible, to some extent, for constant values of the “smectitic” surface charges of I/S,

458 being unaffected by percentage of smectite layers in I/S, and also for the variation of
459 “smectitic” charge with illite crystal size fraction (Kuligiewicz et al., 2018).

460

461 **CONCLUSIONS**

462 (1) Molecular dynamics simulations show that if montmorillonite surface could be
463 devoid of ions, it would be practically as hydrophobic as that of pyrophyllite. For negatively
464 charged montmorillonite surfaces, if no charge balancing cations are present, a water droplet
465 would be formed with contact angles just slightly lower ($\sim 15^\circ$ at most) than that for
466 completely neutral pyrophyllite.

467 (2) Bare beidellitic surfaces have lower hydrophobicity than similarly charged
468 montmorillonitic surfaces, and their contact angles can be as low as 60° .

469 (3) The highly hydrophilic character of smectite surfaces observed in experiments is,
470 therefore, almost entirely due to the presence of charge balancing cations on the surface.

471 (4) The orientation of H_2O molecules nearest to the surface vary significantly between
472 a typical smectite surface and the same surface from which all counterions are removed
473 (moved to the interlayer while keeping the same amount of charge). In the presence of
474 counterions, there are two distinct H_2O populations nearest to the surface: with one and two
475 molecular O–H bonds oriented towards the surface, thus forming with it one (monodentate) or
476 two (bidentate) H-bonds. However, on the surface without ions, the dominant angles formed
477 by the H_2O dipole and the vector normal to the 2:1 surface are close to 90° . On beidellite
478 surfaces additional monodentate H_2O population is also observed.

479 (5) The simulation results clearly demonstrate that the notion of hydrophobicity or
480 hydrophilicity of the smectite surface depends, essentially, on the decision how the surface is
481 defined. If we consider the smectite surfaces by themselves, devoid of the counterions, the
482 bare 2:1 surface is hydrophobic or only moderately hydrophilic. However, if the counterions

483 are considered as integral part of the surface, then the smectite surfaces are highly
484 hydrophilic, which is, of course, what is observed in nature. These findings could be helpful
485 for better quantitative understanding of the role of surface cations on the adsorption and
486 transport of hydrocarbons in clay mineral nanopores (e.g., Greathouse et al., 2018; Liu et al.,
487 2019).

488

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495

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642

643 **FIGURE CAPTIONS**

644

645 **Fig. 1.** Methodology of the contact angle calculation.

646 **Fig. 2.** Definition of the α angle.

647 **Fig. 3.** Comparison of final snapshots obtained for montmorillonite with the same structural charge of 0.3, but
648 with the Na^+ ions present on the surface (left) or replaced with K^+ and hidden in the interlayer between the 2:1
649 layers of smectite (right).

650 **Fig. 4.** Distribution of oxygen atoms in the water droplets (O_w) formed by 700 H_2O molecules on the basal
651 surfaces of montmorillonite devoid of the counterions. The envelope corresponds to 90% of the total number of
652 O_w atoms. The contact angle for each structure is marked with corresponding tangent straight line. The
653 distributions of Mg/Al substitutions in the octahedral sheet of montmorillonites is shown in the insets.

654 **Fig. 5.** Distribution of oxygen atoms in the water droplets (O_w) formed by 350 H_2O molecules and the contact
655 angles on beidellite surfaces devoid of the ions.

656 **Fig. 6.** Distribution of oxygen atoms in water droplets (O_w) formed by 350 H_2O molecules and contact angles on
657 mixed montmorillonite-beidellite surfaces devoid of the ions.

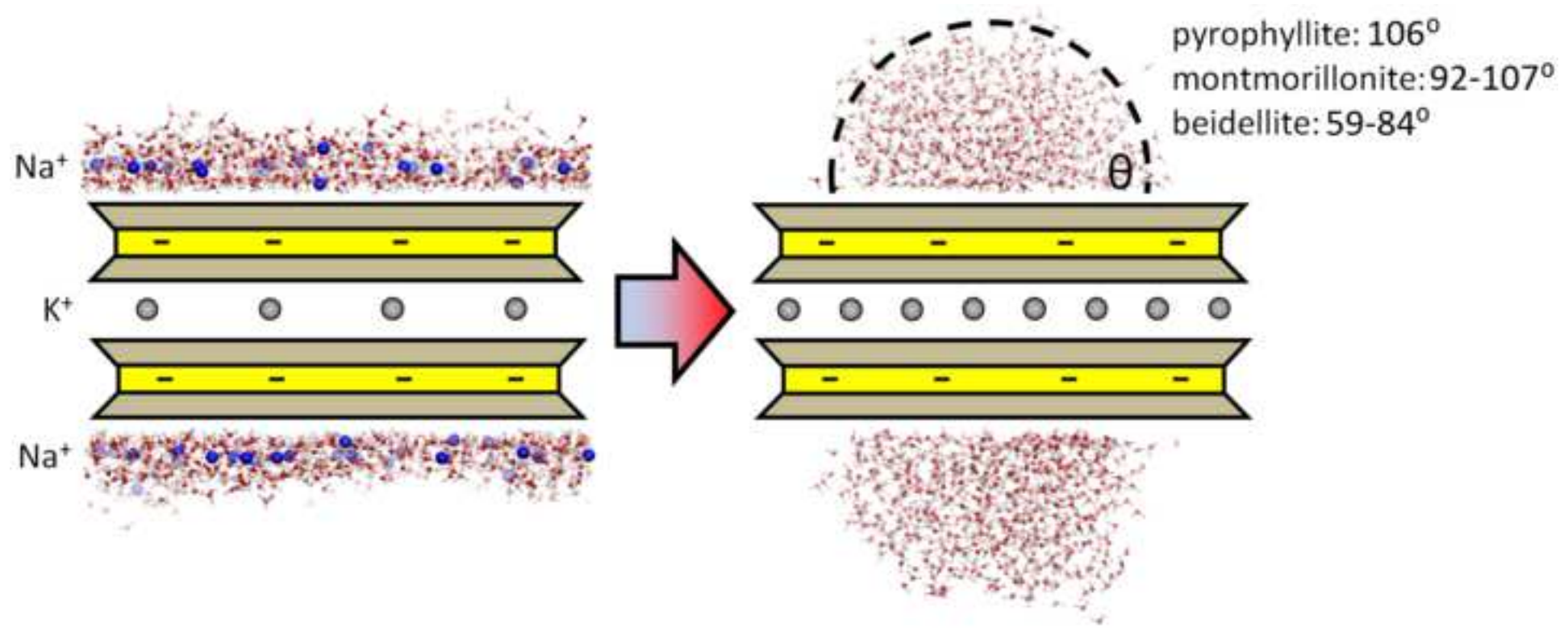
658 **Fig. 7.** Distributions of the H_2O dipole vector orientations (α , left axes) as function of the distance from the
659 surface (z) for various smectite surfaces in the presence of counterions. The blue curves and the left axes show
660 the cation density profiles. 700 H_2O molecules on each side of the smectite structure was assumed.

661 **Fig. 8.** Distributions of the H_2O dipole vector orientations (α) as function of the distance from the surface (z) for
662 various smectite surfaces devoid of counterions. 700 H_2O molecules on each side of the smectite structure was
663 assumed.

664 **Fig. 9.** Distributions of the H_2O dipole vector orientations (α) as function of the distance from the surface (z) for
665 Beid05 structures with and without the counterions on the surface. The positions of all maxima are marked.
666 Close correspondence of the monodentate sub-populations for both structures are clearly visible.

667 **Fig. 10.** Distribution of oxygens of H_2O molecules for two sub-populations on the surface of
668 Beid02_no_surf_ions. The specific ranges of distance z and angle α are indicated in parentheses. Black triangles
669 correspond to the positions of Al/Si substitutions and light grey triangles – Si^{4+} positions of the tetrahedral sheet.
670 Only part of the surface was covered with water forming droplet.

671



- (1) Montmorillonite surface devoid of ions is hydrophobic.
- (2) Beidellite surface devoid of ions is moderately hydrophilic.
- (3) Highly hydrophilic smectite surfaces are due to the presence of cations.
- (4) In the presence of cations, there are two distinct H₂O populations on the surface.
- (5) On the surface devoid of ions, there is dominant “hydrophobic” H₂O population.

Table 1. Smectite model structures used in the study.

Model	Layer charge (PHUC)	No external surface ions	of No of interlayer ions	Number of water molecules in droplet
Pyrophyllite	0.0	0	0	700
Mtm02	0.2	34 (Na ⁺)	34 (K ⁺)	700
Mtm03	0.3	50 (Na ⁺)	50 (K ⁺)	700
Mtm04	0.4	68 (Na ⁺)	68 (K ⁺)	700
Mtm05	0.5	84 (Na ⁺)	84 (K ⁺)	700
Mtm05_order	0.5 (ordered)	84 (Na ⁺)	84 (K ⁺)	700
Mtm06_surface_04	0.6	66 (Na ⁺)	134 (K ⁺)	700
Mtm02_no_surf_ions	0.2	0	68 (K ⁺)	700
Mtm03_no_surf_ions	0.3	0	100 (K ⁺)	700
Mtm04_no_surf_ions	0.4	0	134 (K ⁺)	700
Mtm05_no_surf_ions	0.5	0	168 (K ⁺)	700
Mtm05_order_no_surf_ions	0.5 (ordered)	0	168 (K ⁺)	700
Mtm06_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	700
Beid01	0.1	18 (Na ⁺)	18 (K ⁺)	350 (700) ^a
Beid02	0.2	34 (Na ⁺)	34 (K ⁺)	350 (700) ^a
Beid03	0.3	50 (Na ⁺)	50 (K ⁺)	350 (700) ^a
Beid04	0.4	68 (Na ⁺)	68 (K ⁺)	350 (700) ^a
Beid05	0.5	84 (Na ⁺)	84 (K ⁺)	350 (700) ^a
Beid01_no_surf_ions	0.1	0	36 (K ⁺)	350
Beid02_no_surf_ions	0.2	0	68 (K ⁺)	350
Beid03_no_surf_ions	0.3	0	100 (K ⁺)	350
Beid04_no_surf_ions	0.4	0	134 (K ⁺)	350
Beid05_no_surf_ions	0.5	0	168 (K ⁺)	350
Beid06_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Beid05_Mtm01_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Beid04_Mtm02_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Beid03_Mtm03_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Beid02_Mtm04_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Beid01_Mtm05_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350
Mtm06_no_surf_ions	0.6	0	136 (K ⁺) 32 (Ca ²⁺)	350

^a the structures with 700 H₂O molecules were not used in the contact angle calculations, but only in the calculations of the orientational distribution of H₂O molecules depending on their distance from the surface.

Figure 1
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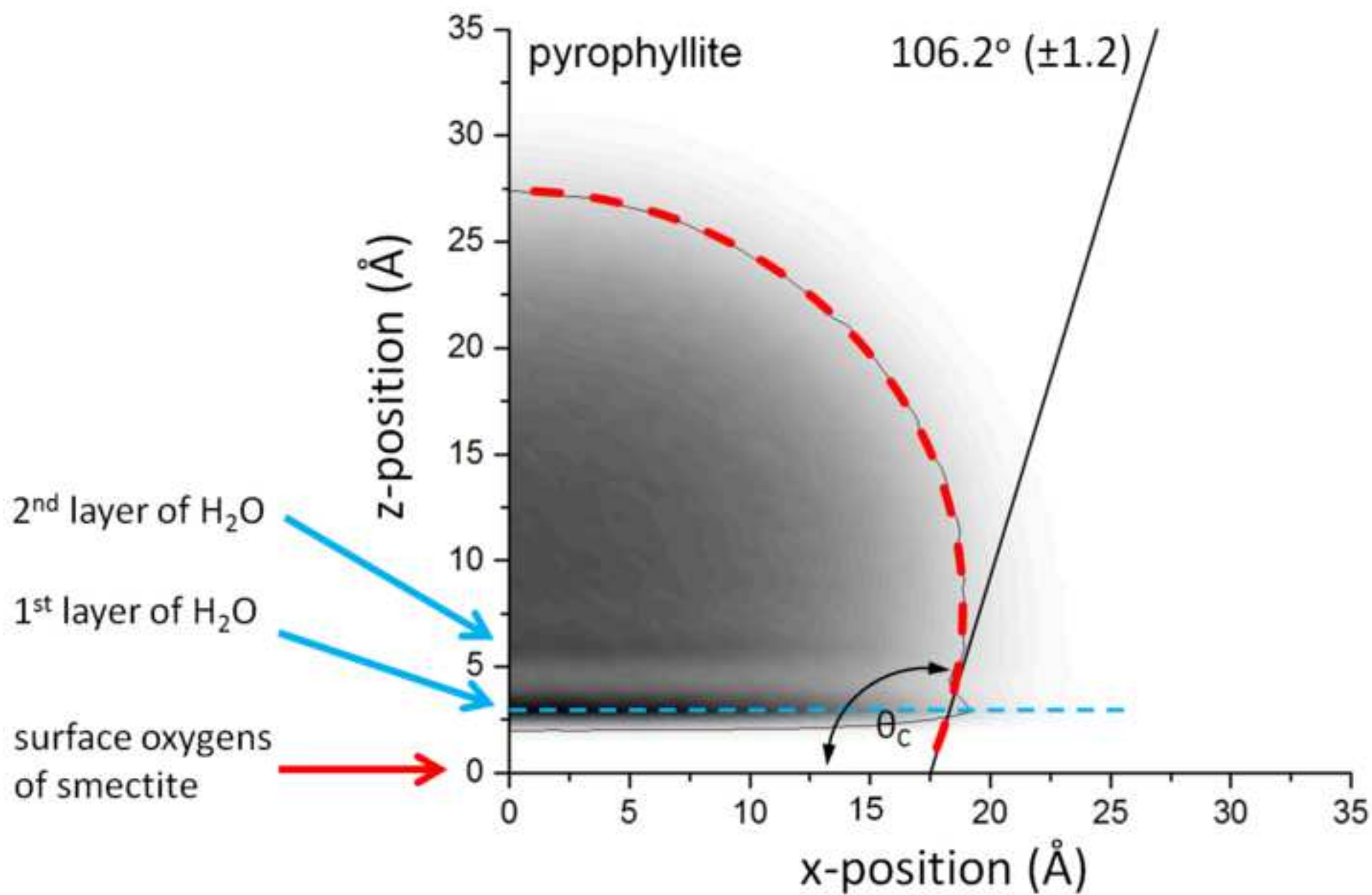


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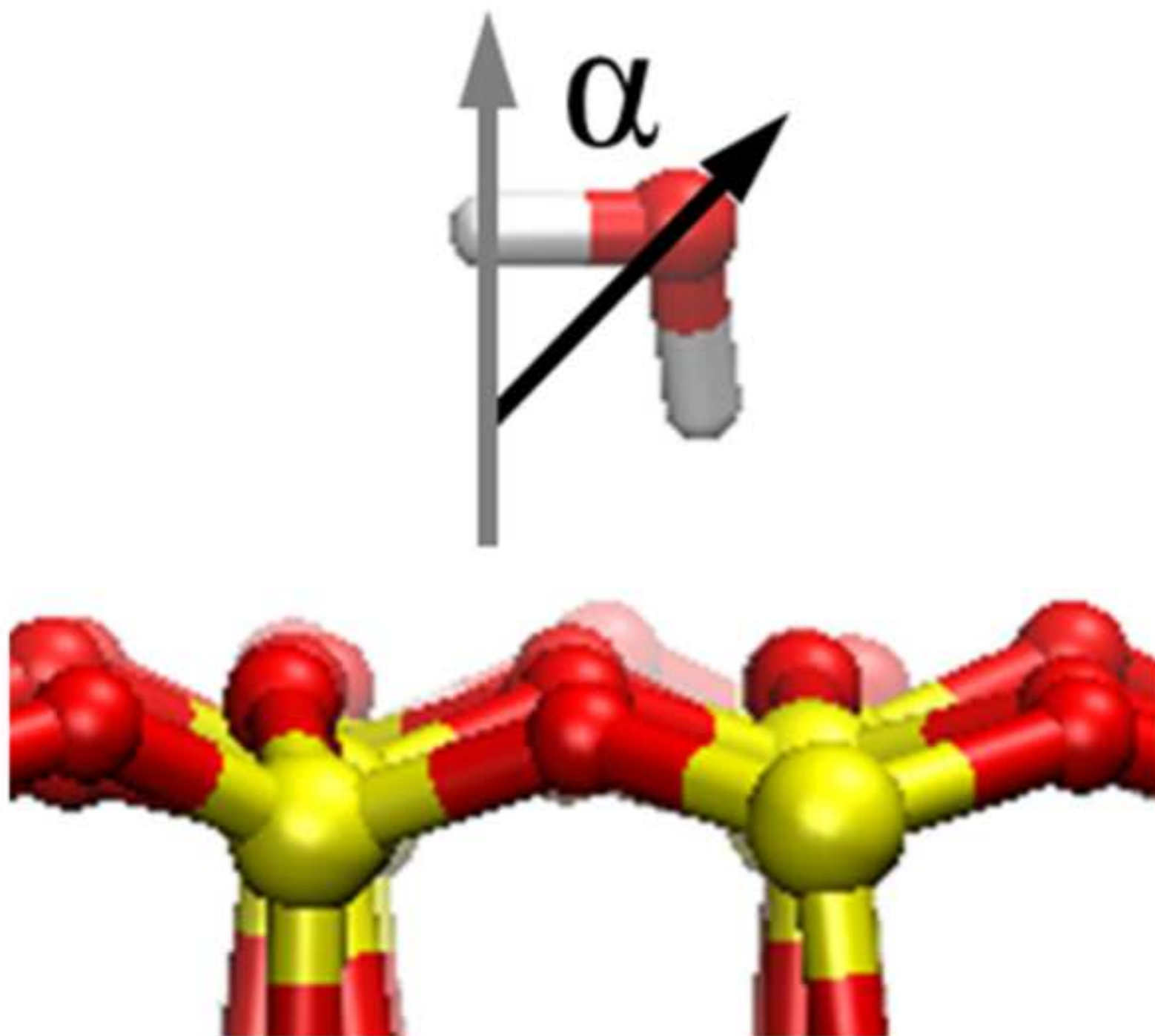


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Mtm03

Mtm03_no_surface_ions

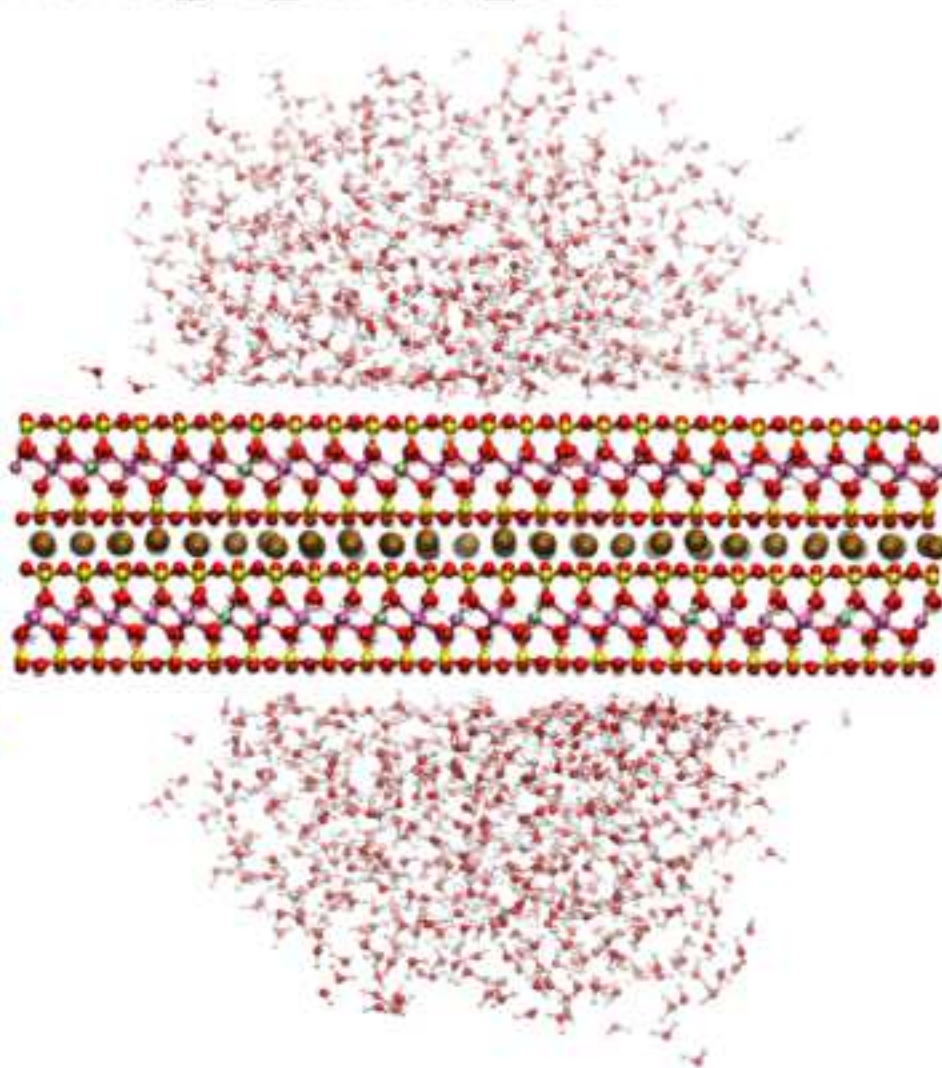
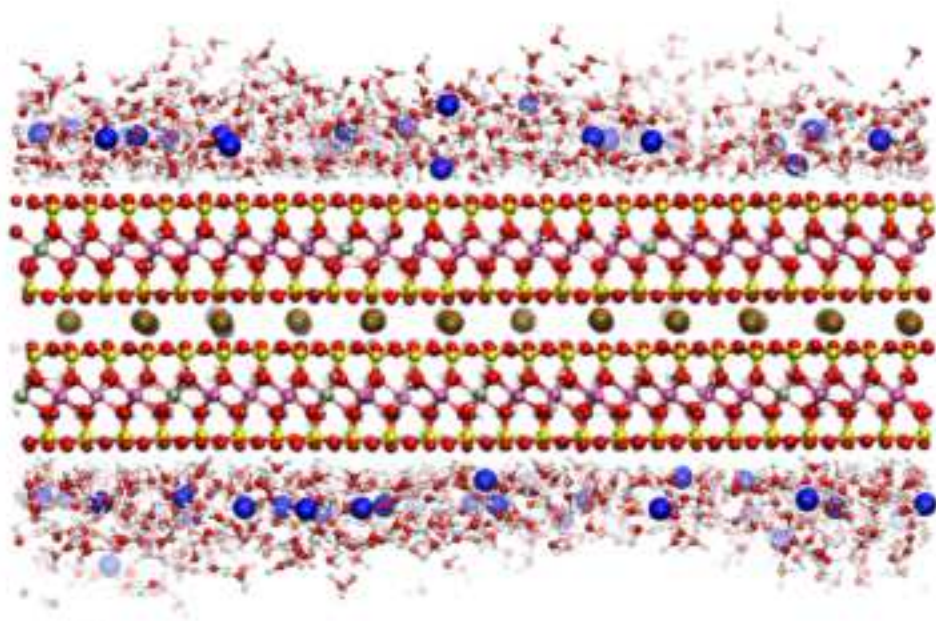


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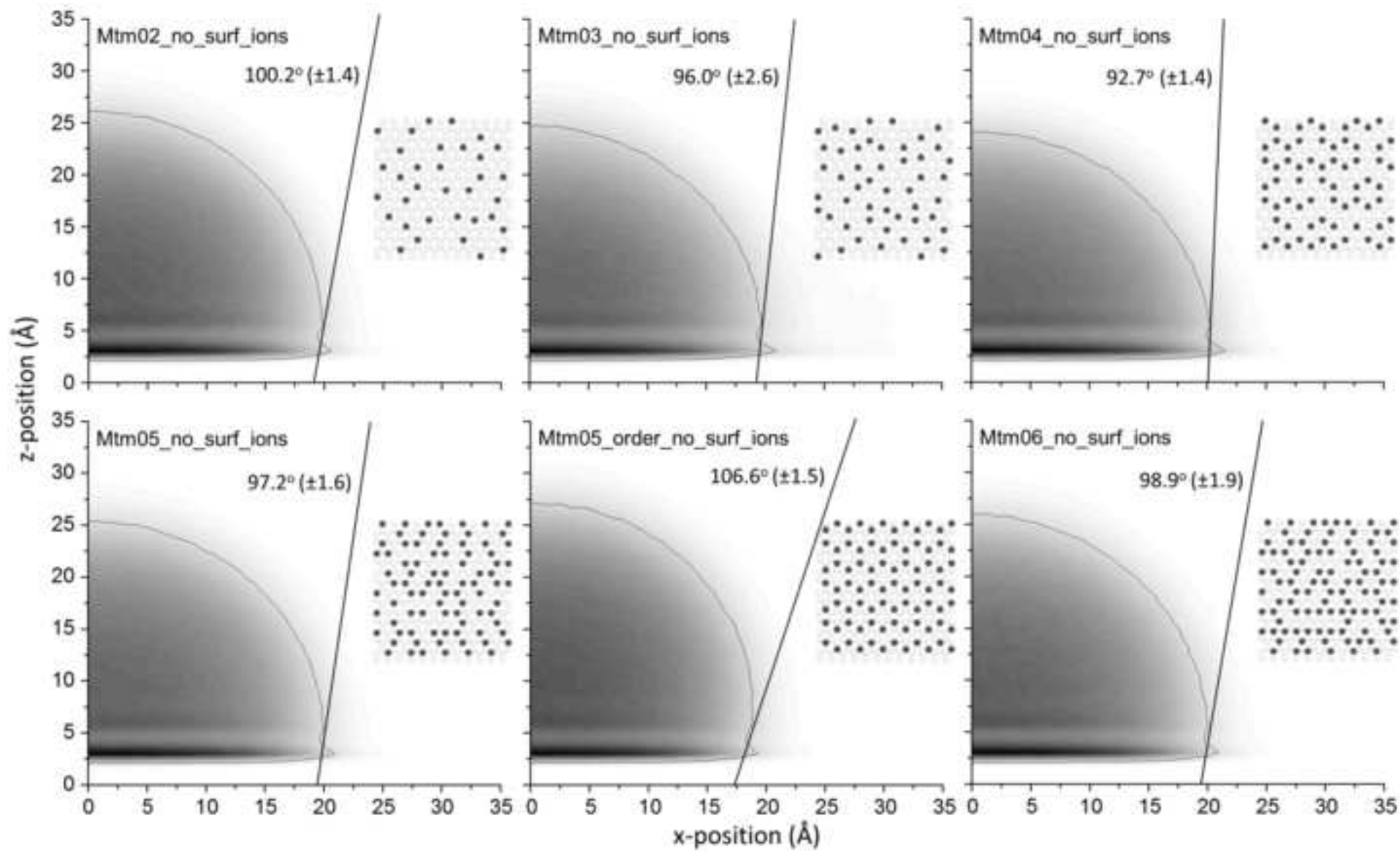


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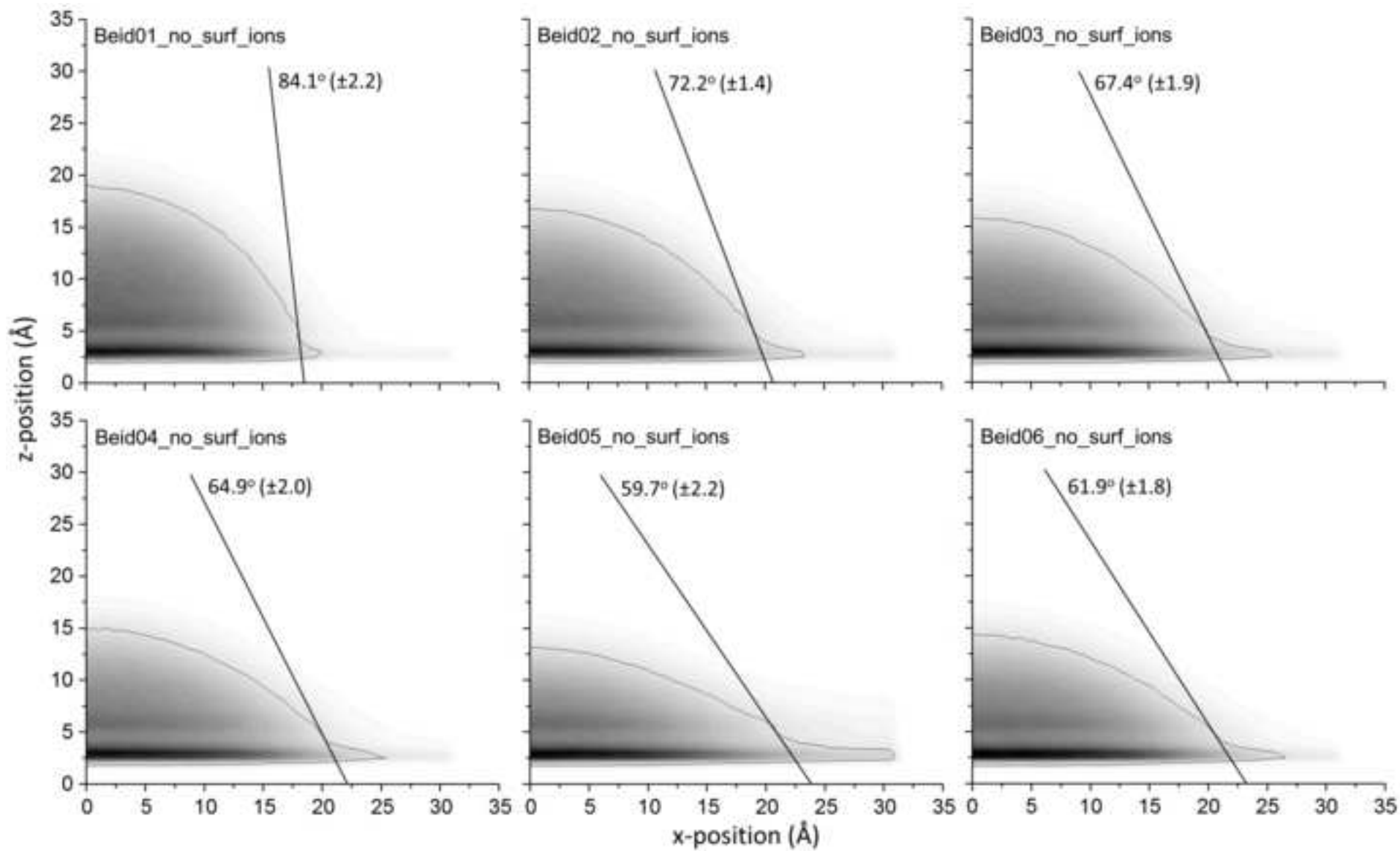


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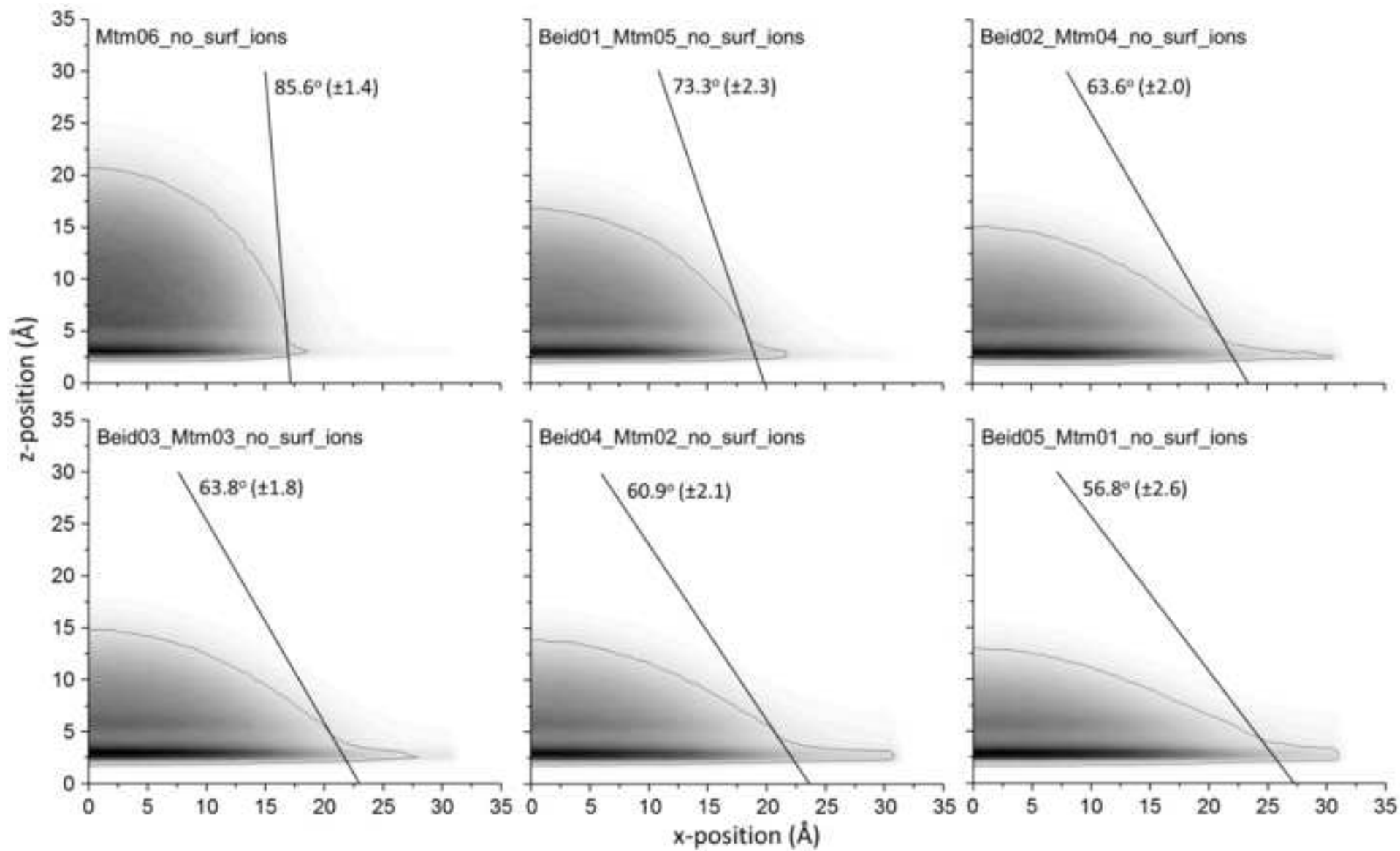


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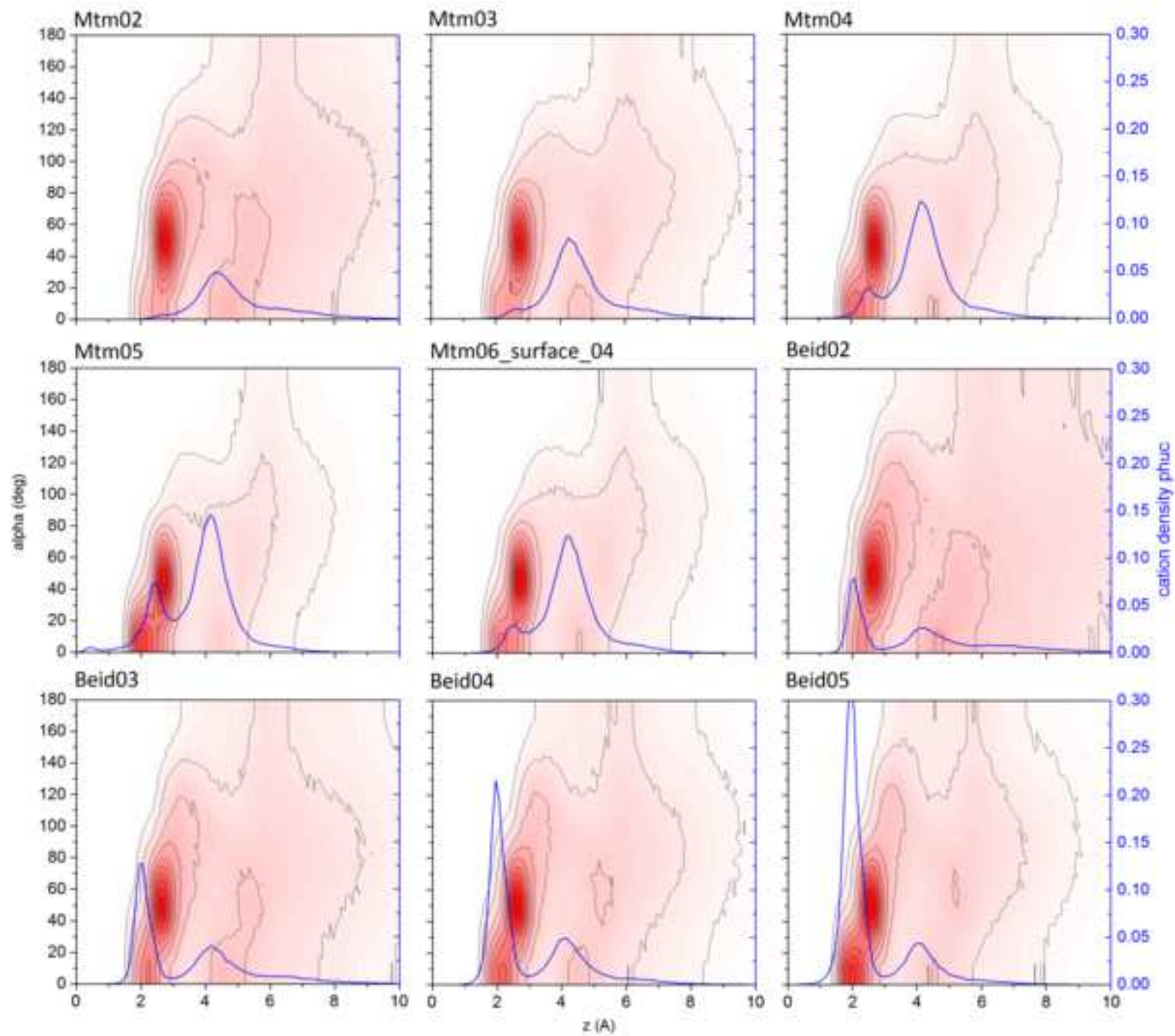


Figure 8
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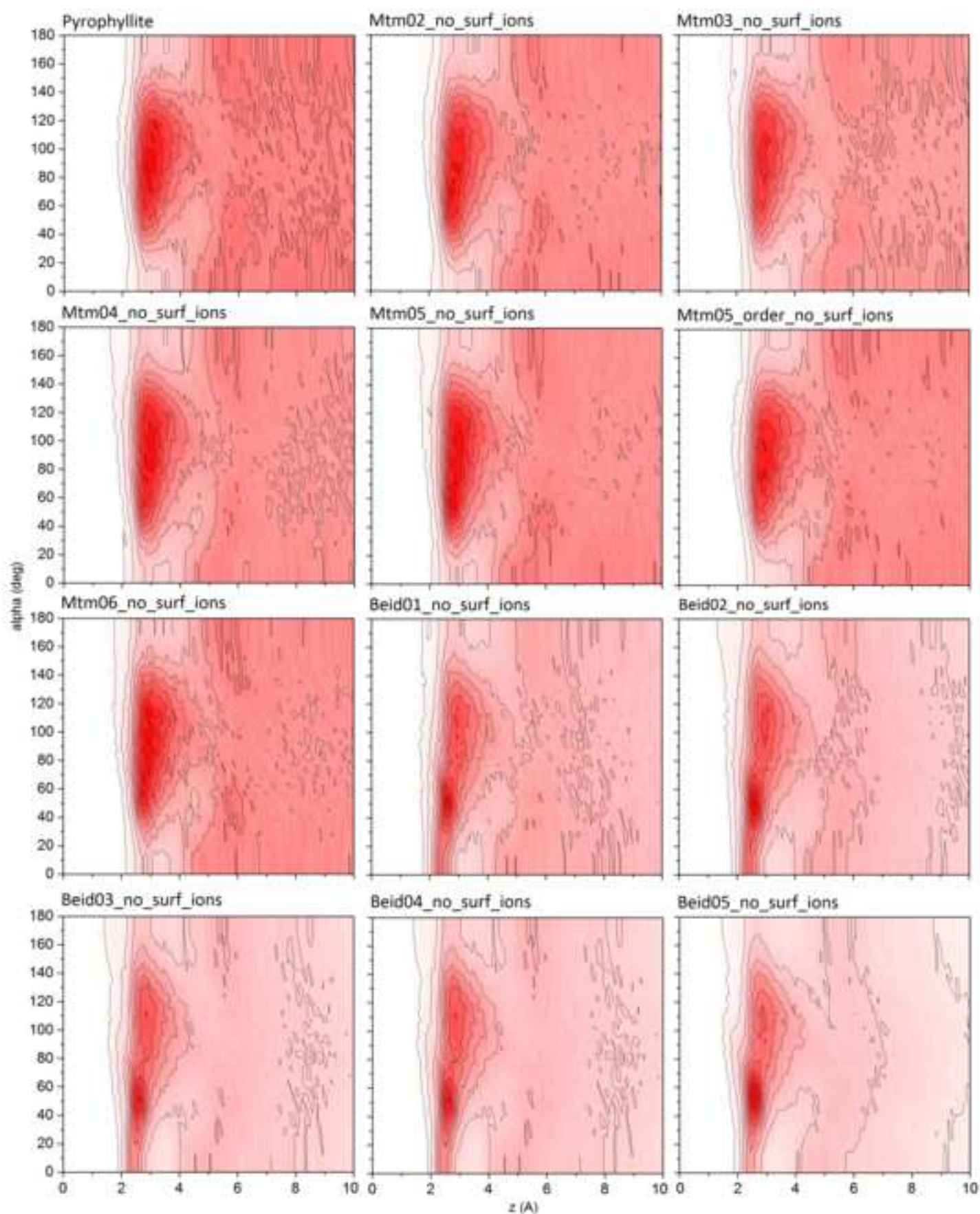


Figure 9
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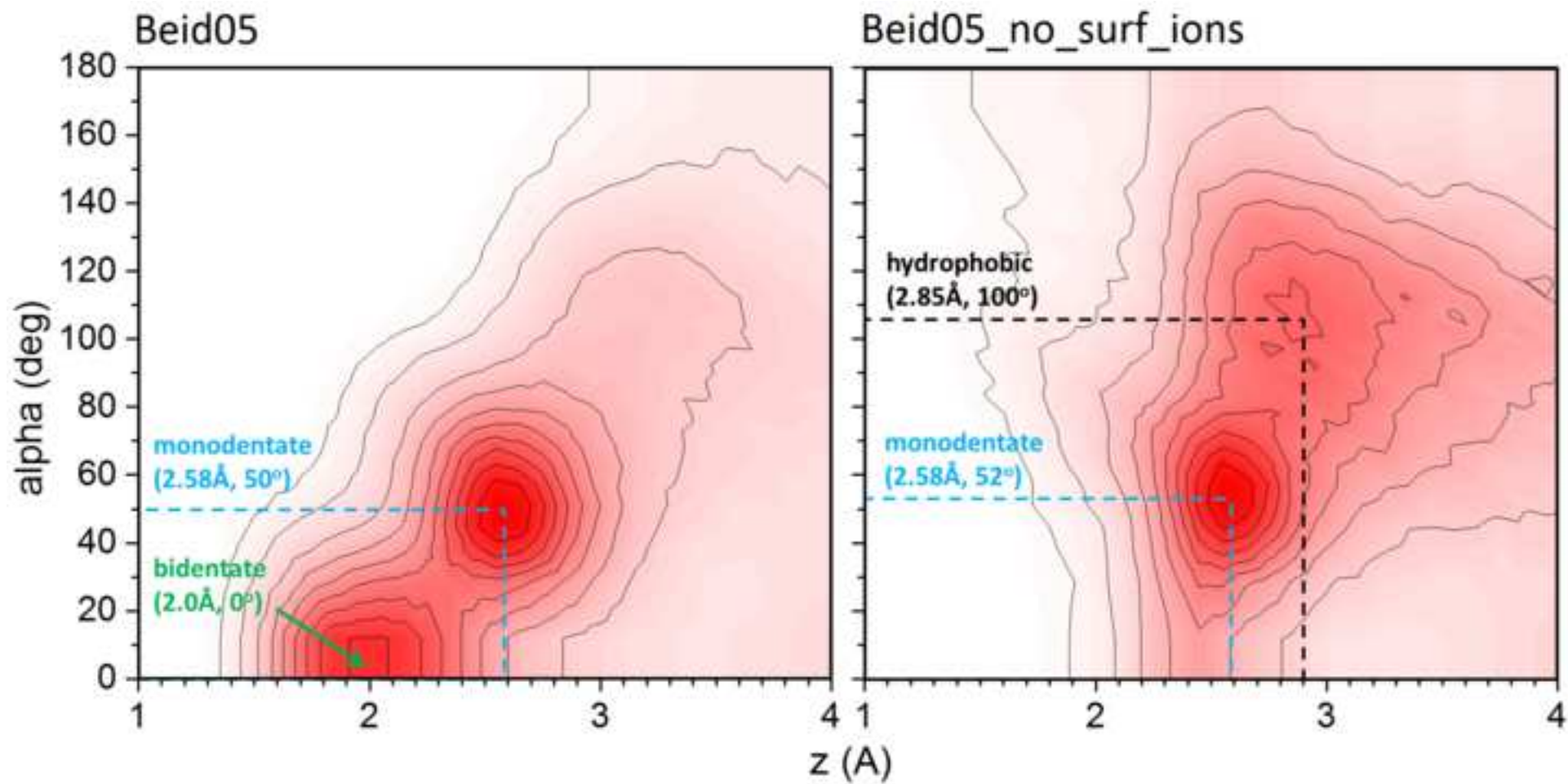
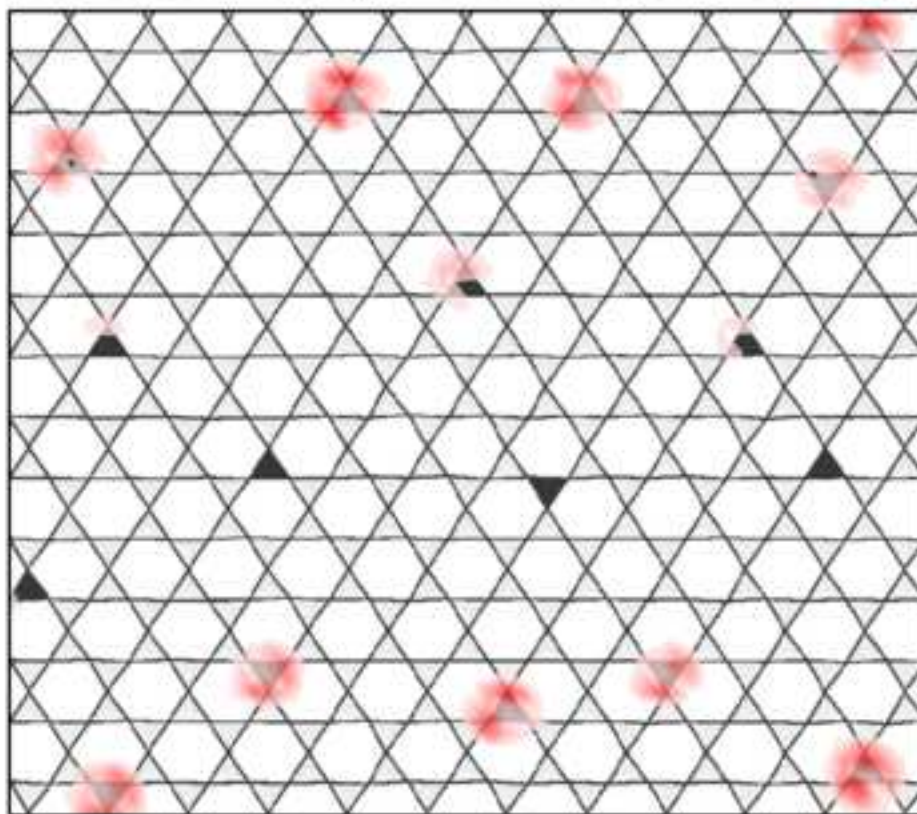


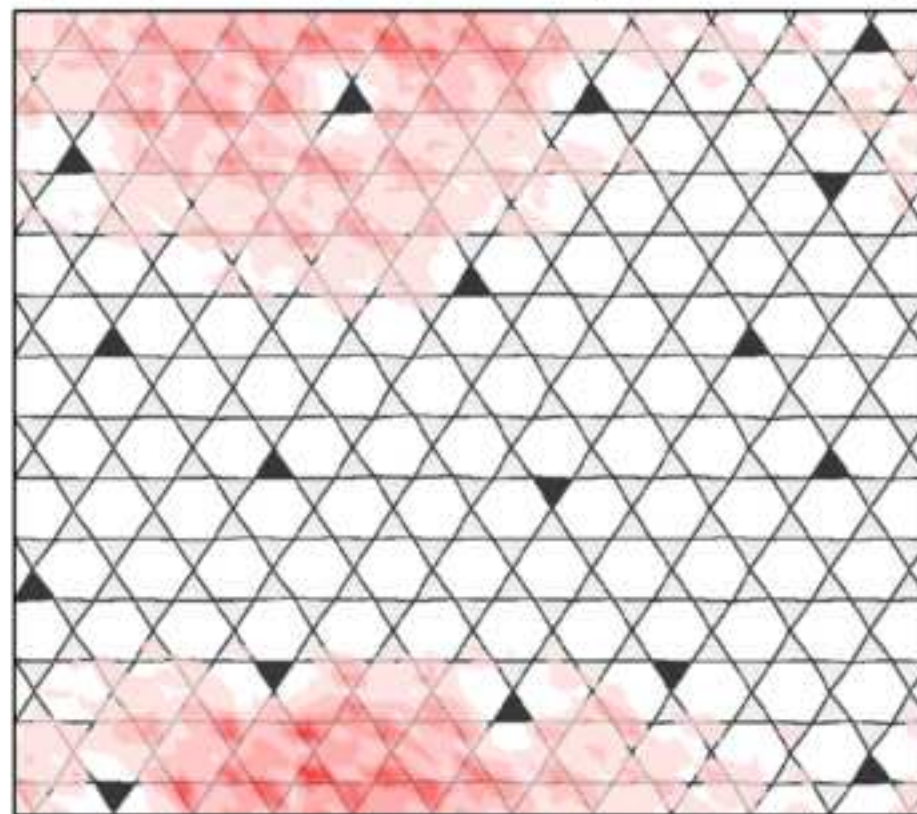
Figure 10

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monodentate ($z = 2.4-2.8$, $\alpha = 30-70$)



hydrophobic ($z = 2.7-3.2$, $\alpha = 80-140$)



Supplementary materials for
“Intrinsic hydrophobicity of smectite basal surfaces quantitatively probed by molecular
dynamics simulations”

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1. Deformations of SiO₄ tetrahedra in NPT simulations.

In the *NPT* simulations with all atoms allowed to move, in some parts of the surface for the systems with all ions located in the interlayer between the 2:1 clay layers, some of SiO₄ tetrahedra experienced significant deformations: Si-O basal distances remained the same, but the Si-O apical distance could become too long, apparently due to the quasi-ionic character of the ClayFF parametrization (Cygan et al., 2004). This lead to the mechanical deformation of tetrahedral sheets comparing to real crystallographic structures of the smectite 2:1 layers the Si-O basal distances are kept similar but the Si-O apical distance becomes too long (Figure S1). To prevent this from happening, the simulation structures were constructed based on the pre-optimized (in the *NPT* ensemble for 0.5 ns, then in the *NVT* for 0.5 ns) pyrophyllite layer and then energy minimized anew.

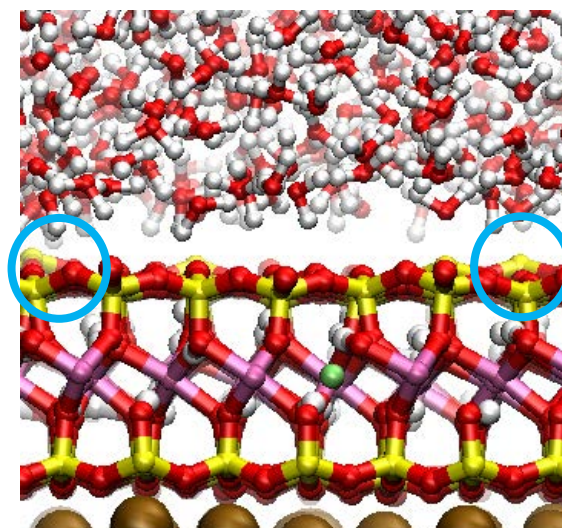


Figure S1. Deformation of SiO_4 tetrahedra leading to exposure of some Si atoms above their crystallographic positions (blue circles). MD simulation run in NPT -ensemble for the .Mtm05 structure.

2. Check for equilibration of the shape of the droplet

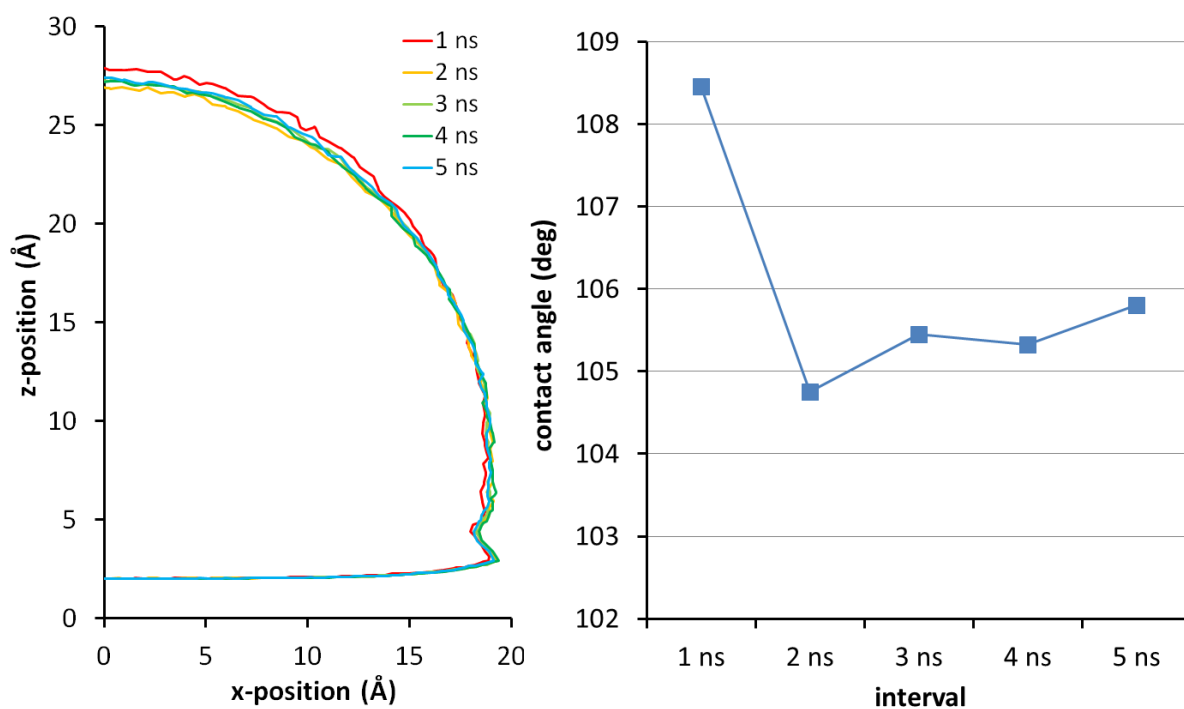


Figure S2. Enveloping curves calculated in 1 ns intervals for pyrophyllite along with corresponding contact angles.

3. Shape of the water film for smectites with Na⁺ ions on the surface.

Irregularity of monotonous, flat water film is correlated with the number of sodium ions on the surface: the more Na⁺ ions, the less rugged is the boundary between the water film and the surrounding “vapour phase” (Figs. S2-S5).

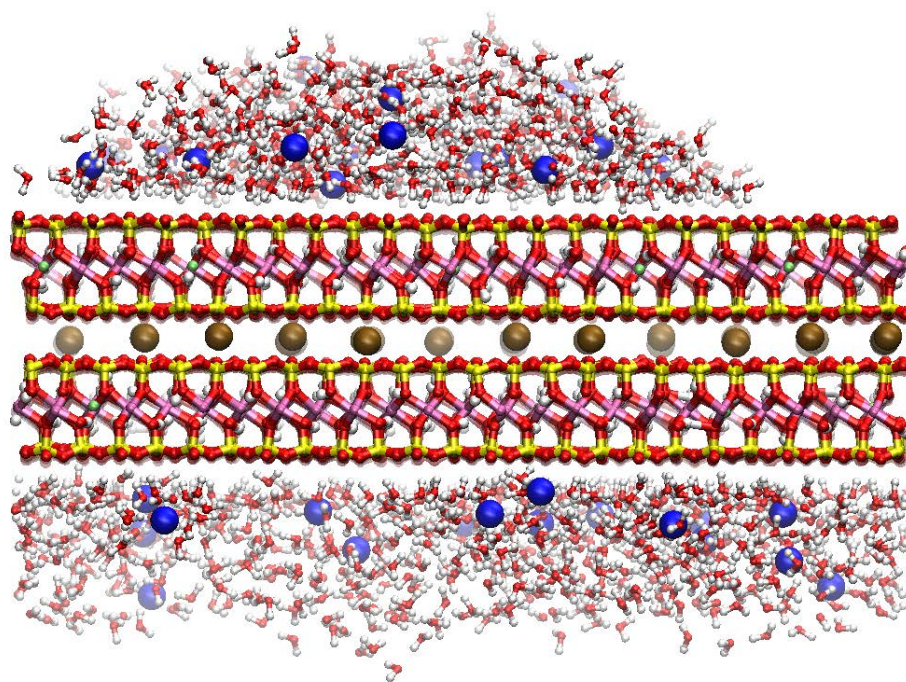


Figure S2. Final snapshot of simulation for **Mtm02**.

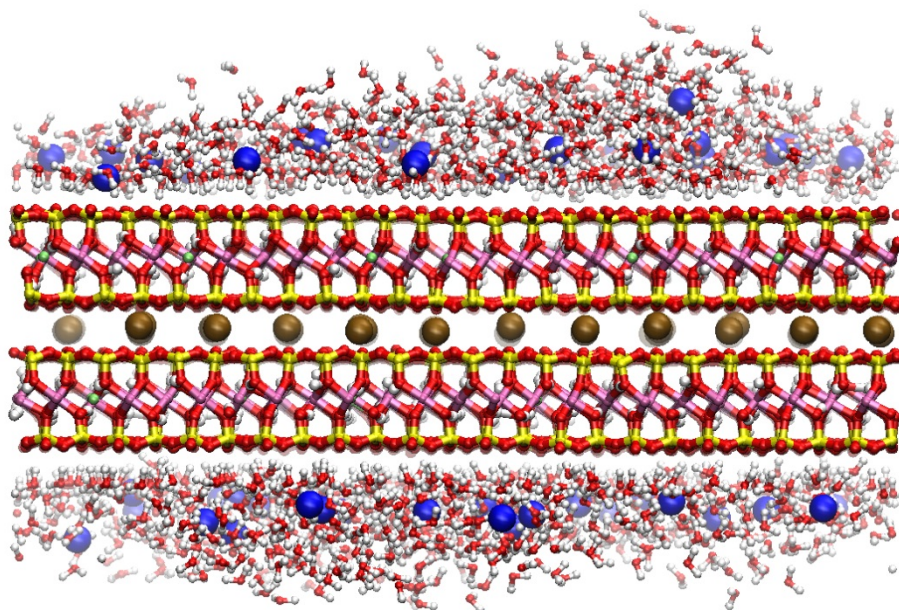


Figure S3. Final snapshot of simulation for **Mtm03**.

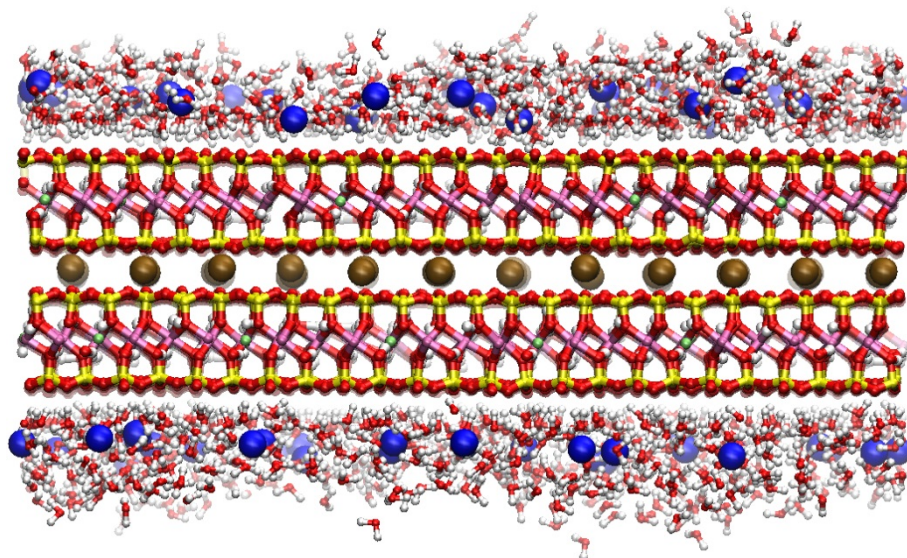


Figure S4. Final snapshot of simulation for **Mtm04**.

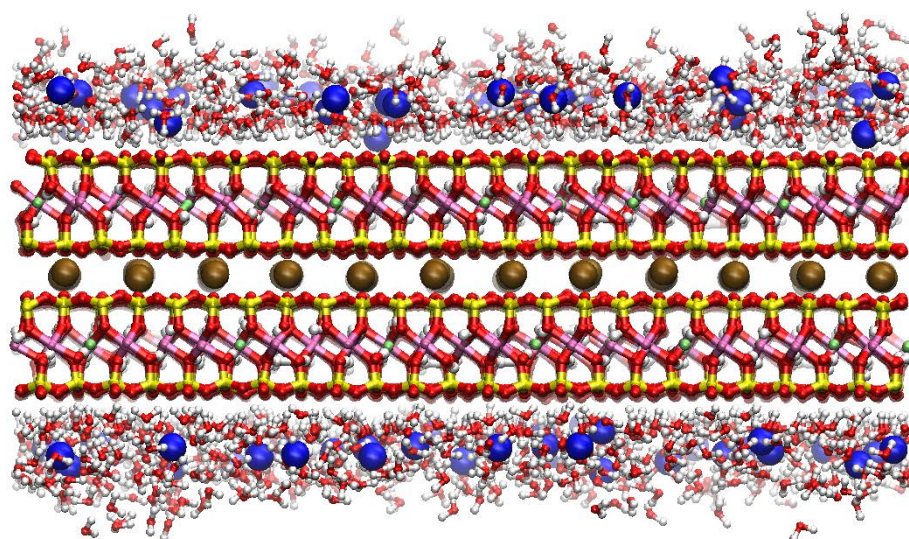


Figure S5. Final snapshot of simulation for **Mtm05_order**.