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**Identification of montmorillonite particle edge orientations by atomic-force  
microscopy**

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24 **ABSTRACT**

25           Statistical information on the edge surface area and edge crystallographic orientation of clay  
26 nanoparticle surfaces is essential for proper accounting of the protonation-deprotonation reactions  
27 as a part of mechanistic surface complexation models. A combination of atomic-force microscopy  
28 (AFM) measurements and molecular dynamics computer simulations made it possible to quantify  
29 the relative contributions of the most frequently occurring montmorillonite edge surfaces to the  
30 total edge surface area. Edge surfaces normal to the [110] and [010] crystallographic directions are  
31 found to be the most abundant (~60% and ~20%, respectively), in agreement with previous  
32 estimations.

33

34 **Keywords:** clay nanoparticles, montmorillonite, edges ratio, AFM, MD simulations

35

## 36 INTRODUCTION

37           The adsorption and resulting retardation of many contaminants by clay minerals make them  
38 ideal for use in natural or engineered barrier systems (ANDRA, 2005; Gates et al. 2009; Marty et  
39 al., 2010). The determination of a macroscopic retardation coefficient is a first step towards the  
40 quantification of sorption and thus retardation of ions by mineral surfaces, but a sound mechanistic  
41 understanding of the molecular-scale interaction between ions and surfaces is mandatory to the  
42 building of reliable geochemical models (Tournassat et al., 2013; Borisover and Davis, 2015).  
43 However, accurate mechanistic modeling of ion adsorption on clay mineral surfaces remains  
44 challenging because of the diversity of adsorption sites on the basal and edge surfaces of clay  
45 mineral particles (Churakov, 2006). The view that the acid-base properties of amphoteric groups at  
46 the edge surfaces as well as the free energy of specific adsorption of cations ( $\text{Ni}^{2+}$ ,  $\text{UO}_2^{2+}$ , *etc.*) are  
47 dependent on the crystallographic orientation of the surface (Everett, 1998) is supported by *ab initio*  
48 molecular dynamics (MD) computer simulations (Churakov, 2006; Liu et al., 2008, 2012, 2013,  
49 2014, 2015a,b; Zhang et al., 2017), and the construction of mechanistic surface complexation  
50 models (SCM) for clay minerals thus necessitates to have a statistical information on the edge  
51 surface area and edge crystallographic orientation of clay mineral layer surfaces (Bourg et al.,  
52 2007, Tournassat et al., 2016, Zhang et al., 2018). In the present study, we focused our efforts on  
53 montmorillonite, *i.e.* the dioctahedral smectite of which the adsorption properties have been the  
54 most studied in the literature.

55           Previous classical and *ab initio* molecular dynamics (MD) simulations of hydrated  
56 montmorillonite edges suggested that the nanoparticle surfaces normal to the [110] crystallographic  
57 direction may be significantly more stable than the surfaces normal to the [010] direction (Bickmore  
58 et al, 2003; Churakov, 2006; Newton et al, 2015, 2016; Kwon and Newton, 2016). Cleavage  
59 energies ( $\Delta E$ ) and corresponding Gibbs free energies ( $\Delta G$ ) for edge surfaces predicted by density  
60 functional theory (DFT) are also in agreement with these findings. For example, Lavikainen et al.  
61 (2015) calculated that the ratio of (110), (010) and (100) edge surfaces of pyrophyllite, an uncharged

62 clay mineral with a layer structure similar to montmorillonite, is 69%, 29%, and 2%, respectively,  
63 while the (130) edge surface represents less than 1% of the total surface area. However,  
64 montmorillonite layers exhibit significant differences with the pyrophyllite layers. First of all,  
65 montmorillonite layers are negatively charged due to the presence of isomorphous substitutions in  
66 their octahedral and tetrahedral sheets. Secondly, pyrophyllite has a trans-vacant layer structure,  
67 while most montmorillonite samples have a cis-vacant layer structure (Tsipursky and Drits, 1984).  
68 Hence, the relative proportions of different edge faces contributing to the total surface area of the  
69 charged montmorillonite nanoparticles is still largely unknown.

70 Numerous recent atomic force microscopy (AFM) studies of different clays prove the  
71 possibility to achieve a real atomic scale resolution of clay structures. For instance, Ferrage et al.  
72 (2006) used X-ray and electron diffraction for the interpretation of their AFM atomic scale images.  
73 Siretanu et al. (2016), studied surface defects of different clay materials, including montmorillonite,  
74 and demonstrated that AFM can provide insights on the morphology and atomic scale structure of  
75 clay layers.

76 At the same time, atomistic computer simulations have been already demonstrated to be  
77 very insightful in interpreting the AFM images of hydrated mineral surfaces enabling one to clarify  
78 the underlying imaging mechanism in the AFM experiments (Kobayashi et al., 2016; Umeda et al.,  
79 2017; Reischl et al., 2019).

80 In the present work, we used AFM experiments for visualization and quantitative  
81 characterization of the geometry and size distribution of montmorillonite particles, as well as for  
82 reliable determination of the crystallographic orientation of their edges. Fourier peaks of the AFM-  
83 images were then decoded using the insight from the atomistic computer simulations of the same  
84 systems.

85

## 86 MATERIALS AND METHODS

## 87 **Clay mineral**

88           The Kunipia-P sample used in this study is a purified Na-montmorillonite produced by  
89 Kunimine industries Co. Ltd., and which contains nearly 100% montmorillonite (Tachi and Yotsuji,  
90 2014; Orucoglu et al. 2018). Kunipia-P montmorillonite was dispersed in deionized water at a solid  
91 concentration of 0.01 g L<sup>-1</sup> and ultrasonicated for 10 min. A droplet of the dispersion was then  
92 deposited on a freshly cleaved mica surface (purity grade V1, Ted Pella, Inc.) and dried overnight  
93 in a desiccator.

## 94 **AFM samples preparation**

95           AFM measurements were carried out with samples mounted in dry- and fluid-cells using a  
96 Dimension Icon AFM (Bruker) microscope in contact and peak force modes. The AFM images  
97 were obtained in air with lateral force microscopy - friction data channel (Erlandsson et al., 1988;  
98 Marti et al., 1990), using SNL-10 silicon nitride cantilevers (Bruker Inc.). The scan parameters  
99 were: rate 5 Hz, angle 0, gains 0.3. Particles perimeter and surface area were estimated by  
100 processing the AFM image using the FemtoScan (Filonov et al., 2001) and ImageJ  
101 (<https://imagej.nih.gov>) softwares.

## 102 **Montmorillonite and muscovite structural models for MD simulations**

103           Classical MD simulations were performed with the LAMMPS software (Plimpton, 1995)  
104 for a montmorillonite model that was built from an orthogonal pyrophyllite structure (Drits *et al.*,  
105 2012), by randomly distributing Al/Si and Mg/Al isomorphic substitutions (Ngouana and  
106 Kalinichev, 2014) in the tetrahedral and octahedral sheets of the layers, respectively. The simulation  
107 supercell had dimensions of 4.1×3.6×10.5 nm<sup>3</sup> and contained a montmorillonite clay particle  
108 consisting of three T-O-T layers, each having 32 unit cells with the chemical composition  
109 [Si<sub>7.75</sub>Al<sub>0.25</sub>][Al<sub>3.5</sub>Mg<sub>0.5</sub>]O<sub>20</sub>(OH)<sub>4</sub>Na<sub>0.75</sub>(H<sub>2</sub>O)<sub>10</sub>, in which the layer charge of -0.75|e| per unit cell  
110 was neutralized by Na<sup>+</sup> ions. The layer-to-layer distance was selected and fixed to represent a  
111 bilayer hydrate of Na-montmorillonite, with 10 H<sub>2</sub>O/Na<sup>+</sup> in each of the interlayers (Ngouana and

112 Kalinichev, 2014). The remaining volume of the simulation box was filled with 3280 H<sub>2</sub>O  
113 molecules to represent the interfacial liquid water at a density of 1 g/cm<sup>3</sup>, corresponding to ambient  
114 conditions (Fig.1).

115 The muscovite model for classical MD simulations was built similarly from the same  
116 orthogonal pyrophyllite structure (Drits *et al.*, 2012) by randomly distributing Al/Si isomorphic  
117 substitutions in the tetrahedral sheets of the clay layers to achieve the chemical composition of  
118 [Si<sub>6</sub>Al<sub>2</sub>][Al<sub>4</sub>]O<sub>20</sub>(OH)<sub>4</sub>K<sub>2</sub>] (see, e.g., Loganathan and Kalinichev, 2017). The simulation supercell  
119 was a little shorter and had the dimensions of 4.1×3.6×8.5 nm<sup>3</sup>. The layer charge of -2.0|e| per unit  
120 cell was neutralized by the corresponding number of interlayer and interfacial K<sup>+</sup> ions and the rest  
121 of the simulation cell was filled with 2960 H<sub>2</sub>O molecules to achieve the liquid water density of  
122 1 g/cm<sup>3</sup>, corresponding to ambient conditions (Fig.1).

## 123 **MD simulations parameters and procedure**

124 For both montmorillonite and muscovite models, the MD simulation protocol was the same.  
125 The ClayFF force field (Cygan *et al.*, 2004) was used to calculate all the interatomic interactions  
126 for each model. Periodic boundary conditions were applied and Ewald summation was used to  
127 account for the long range electrostatic interactions in the system. The equations of atomic motion  
128 were numerically integrated using a time step of 1 fs and each model was initially equilibrated  
129 under ambient conditions ( $T = 300$  K,  $P = 1$  bar) during a 1 ns MD run in the *NPT* statistical  
130 ensemble, followed by an additional 0.5 ns equilibration run in the *NVT* ensemble, before a 1 ns  
131 *NVT* production MD run was started. The results of that equilibrium *NVT* MD run were then  
132 statistically analyzed to extract various properties of the simulated systems.

133

## 134 **RESULTS AND DISCUSSION**

### 135 **Montmorillonite particle size and shape measurements**

136 A few individual particles of montmorillonite had a lath-like shape, which is typical for  
137 mica crystals (Bauer et al., 2000; Güven, 2001) (Fig. 2). Some other montmorillonite particles had  
138 fairly well defined straight boundaries, which suggests that they belonged to certain  
139 crystallographic directions (Fig. 2 and 3).

140 To facilitate the calculation of the total edge surface area from the AFM images, the  
141 concentration of montmorillonite was selected during sample preparation so that its particles  
142 occupied the maximum area on the surface of the substrate but did not overlap each other (Fig. 3a).  
143 Because most of the particles imaged by AFM were montmorillonite single layer particles (Fig. 3),  
144 the edge specific surface area ( $SSA_{Edge}$ ) was estimated from the computation of the perimeter to  
145 area ratio (Tournassat et al., 2003, Yokohama et al., 2005, Le Forestier et al., 2010, Marty et al.,  
146 2011, Reinholdt et al., 2013):

$$147 \quad SSA_{Edge} = \frac{Ph}{m} = \frac{Ph}{S_b h \rho} = \frac{P}{S_b} \times \frac{1}{\rho}$$

148 (2)

149 where  $P$  is the perimeter (m),  $h$  the height (m),  $S_b$  the basal surface area (m<sup>2</sup>) and  $\rho$  the density  
150 (kg/m<sup>3</sup>) of the particle.

151 Montmorillonite particles do have a size distribution associated with the nature of  
152 montmorillonite and the distribution of surface charge (Assemi et al., 2015). The range of values  
153 of the  $P/S_b$  parameter calculated from more than 500 observed montmorillonite particles is shown  
154 on Figure 3b. The strongest variations were observed for smaller particles with a basal area of less  
155 than 0.1  $\mu\text{m}^2$  (about 20% of total) and the sub-range from particle to particle varied between 13-59  
156  $\mu\text{m}^{-1}$ . Approximately 60% of the particles had basal surface area in the range of 0.1-0.4  $\mu\text{m}^2$ , their  
157  $P/S_b$  parameter varied in the range of 8-13  $\mu\text{m}^{-1}$ . The remaining 20% of the particles had a basal  
158 area of more than 0.4  $\mu\text{m}^2$ , their  $P/S_b$  varies from 4-8  $\mu\text{m}^{-1}$ .



159 A small but significant difference between the *dry*- and *fluid-cell* samples,  $4.7\pm 0.3 \text{ m}^2 \text{ g}^{-1}$   
160 and  $4.1\pm 0.2 \text{ m}^2 \text{ g}^{-1}$ , respectively, was observed. Very small particles may have been less strongly  
161 attached to the mica substrate surface in the presence of liquid than larger particles. Consequently,  
162 small particles with the highest perimeter to area ratio may have been lost. Assuming that the  
163 density of montmorillonite is about  $2.7\text{-}2.8 \text{ g cm}^{-3}$  (Tournassat and Appelo, 2011),  $SSA_{Edge}$  of  
164 Kunipia-P particles was estimated to be  $\sim 4.3\pm 0.2 \text{ m}^2 \text{ g}^{-1}$ , in good agreement with a previously  
165 reported value for a similar material,  $5.3 \text{ m}^2 \text{ g}^{-1}$  (Yokoyama et al., 2005).

### 166 **Crystallographic orientation of montmorillonite particle edge surfaces**

167 AFM images taken at high resolution evidenced structures with a period of  $\sim 0.45 \text{ nm}$  when  
168 scanning from top to bottom and  $\sim 0.51 \text{ nm}$  when scanning from bottom to top. The interpretation  
169 of such atomic-resolution AFM images should be done however with extreme care due to the  
170 possibility of instrumental artefacts such as vibration noise or piezo ceramic hysteresis (e.g.,  
171 Rodriguez-Fortun et al., 2011). To confirm that the periodic signal being analyzed actually  
172 corresponds to the crystallographic structure of the particle and does not represent a periodic noise,  
173 a series of control experiments with rotation of scanning direction were performed. Rotation of the  
174 scanning angle led to the rotation of the observed periodic structure (Fig S1, more details on these  
175 control experiments are provided in the supplementary materials to this paper). Thus, it was  
176 concluded that the observed structure was due to the nature of the sample, and was not an artifact  
177 of the piezoscanner.

178 In previous studies of muscovite (Kuwahara, 1999; Liu and Brown 1997, Leiro 2014), the  
179 authors correlated the periodic structure images obtained by AFM with the structure of the surface  
180 of the silica tetrahedral sheet. Ferrage et al. (2006) investigated the surface of talc crystals and also  
181 brought it in correspondence with the periodic structure of the silica tetrahedral sheet. Teschke et  
182 al. (2010) proposed that when performing the AFM scanning of clay mineral, the surface layer of  
183  $\text{H}_2\text{O}$  molecules should be taken into account in the interpretation of the signal. They indeed  
184 observed, on a mica surface, a periodic structure of  $0.45 \text{ nm}$  that corresponded to the ice-Ih

185 (hexagonal) type, predicted by atomistic simulations (Odelius, 1997; Wang et al., 2005a, 2005b).  
186 More detailed studies of the first several layers of water on the mica surface were performed using  
187 oscillatory AFM techniques, which allow to construct force curves (Fukuma et al., 2005, 2010;  
188 Kimura et al., 2010; Kobayashi, et al., 2013). Using MD simulations, Kobayashi et al. (2016)  
189 investigated the interaction between a carbon nanotube (as an AFM probe) and a mica surface and  
190 evaluated the contribution of various forces to such interaction, thus allowing them to construct a  
191 density map of water molecules in the first and second hydration layers of the surface.

192 Hydration layers could be not taken in account if one identify reflections in the FFTs of high-  
193 resolution electron microscopy study of montmorillonite (Drummy et al., 2005). Present AFM  
194 experiments were performed under ambient relative humidity conditions of 20% and above. Under  
195 these conditions, it is expected that approximately one to two monolayers of water are present at  
196 clay surface (Cases et al., 1992).

197 In the present study, we performed MD simulations of hydrated mica and montmorillonite  
198 surfaces for better understanding and interpretation of the nature of these periodic structures. The  
199 ClayFF force field used in the simulations is primarily based on electrostatic interactions between  
200 partial charges assigned to individual atoms and Lennard-Jones (12-6) function (Cygan et al.,  
201 2004). Assuming that the main contribution to the interaction of the silicon nitride cantilever and  
202 the surface of montmorillonite or mica is due to the electrostatic interactions (e.g., Gan, 2009), we  
203 calculated the electrostatic potential induced by the distribution of atomic charges at every point in  
204 space and compared the two-dimensional maps of the electrostatic potential along the clay surface  
205 with the AFM images.

206 To calculate the surface electrostatic potential from MD simulations, the model supercell was  
207 divided into a three-dimensional mesh with a resolution of  $0.03 \times 0.03 \times 0.03 \text{ nm}^3$ . For each element  
208 of the mesh the electrostatic potential was computed according to:

$$U = \frac{1}{4\pi\epsilon} \sum_{k=1}^n \frac{q_k}{r_k} \quad (1)$$

where  $q_k$  – are the partial atomic charges of the ClayFF model (Cygan et al., 2004) and  $r_k$  – are the instantaneous distances between this particular element of the mesh and the charged atom. The calculation was performed every 10 ps along the equilibrium MD trajectory and the results were then time-averaged over the entire trajectory.

The averaging of the electrostatic potential calculated along the (001) plane at different distances from the solid/liquid interface over the entire MD-generated trajectory showed that, for mica, the  $K^+$  on the surface are well localized and could contribute significantly to the AFM signal. This result is in agreement with previous findings using MD simulations (Kobayashi et al. 2016). On the contrary, on the surface of Na-montmorillonite, the averaged contribution of the  $Na^+$  to the surface electrostatic potential is significantly blurred over the 1 ns time scale of the simulation (Fig. 4), and it is thus unlikely that  $Na^+$  on the montmorillonite surface contribute significantly to the periodic patterns observed on AFM images.

Fast Fourier transform (FFT) of the periodic structures observed in high resolution the AFM images were further compared with the FFT of the calculated electrostatic potential maps of the first hydration layer obtained from MD simulations (Fig. 5). The FFT maps from the AFM images and the calculated electrostatic maps are qualitatively similar. Their main difference is in the absence of secondary peaks on the FFT maps from the AFM image due to experimental noise and/or structural disorder such as bending, slight variation in atomic positions, anisotropic displacement factors, vacancies and isomorphic substitutions. The most intense contributions to the FFT maps (dominant frequencies of the periodic signal) was assigned to the direction perpendicular to the [010] crystallographic direction with a periodicity of ~0.45 nm, ~0.23 nm (1/2 and 1/4 of the  $b$  crystallographic unit cell dimension, Fig. 5) and to the direction perpendicular to the [100] direction

233 with the periodicity of  $\sim 0.26$  nm ( $1/2$  of the  $a$  crystallographic unit cell dimension, Fig. 5).  
 234 Consequently, we assumed that the bright reflex on the FFT of the AFM images with the periodicity  
 235 of  $\sim 0.45$  nm corresponded to the  $b$  direction of the particles.

236 To evaluate the relative abundances of different crystallographic edge surface orientations of  
 237 montmorillonite nanoparticles, the AFM images were rotated in such a way that the edge  
 238 perpendicular to the  $b$  direction was horizontal and became the reference vector for the angles  
 239 characterizing the remaining edges (Fig. 6). Note that this method does not allow us to distinguish  
 240 the edges perpendicular to the direction  $[110]$  from the edges perpendicular to the opposite direction  
 241  $[\bar{1}\bar{1}0]$  and the like.

242 In the case of a single monocrystalline particle, the crystallographic directions defining the  
 243 orientations of its edge surfaces can be determined from AFM images on a nanometer scale (Fig. 6;  
 244 supplementary materials).

245

246 **Table 1.** Calculated relative ratios of the edge lengths for a typical montmorillonite particle shown  
 247 in Fig. 7, compared with the pyrophyllite particle edge ratios predicted by DFT  
 248 calculations using two different methods marked  $\Delta E$  (minimization of the cleavage  
 249 energies) and  $\Delta G$  (minimization of Gibbs free energies) (Lavikainen et al. 2015).

Edge surface normal to	Angle ( $^{\circ}$ )	Edge surface area ratios based on		
		AFM (this work)	DFT calculations from (Lavikainen et al. 2015)	
			$\Delta E$	$\Delta G$
[010]	0	0.20	0.33	0.29
[130]	30	0.09	0.00	0.00
[110]	60	0.56	0.61	0.69

[100]	90	0.03	0.06	0.02
unidentified	-	0.12	-	-

250

251 To determine the ratio of the edge lengths corresponding to each specific orientation, the  
 252 results were averaged over a large number of measurements. Figure 7 shows the total histogram of  
 253 the resulting distribution measured for individual 26 particles. The surfaces normal to the [110]  
 254 direction was significantly more prevalent than the surfaces normal to the [010] direction (Fig. 7  
 255 and Table 1), in good agreement with the predictions from recent atomistic simulations (Lavikainen  
 256 at al. 2015, Newton et al., 2016).

257

## 258 CONCLUSIONS

259 The combination of atomic-force microscopy (AFM) measurements and molecular  
 260 dynamics (MD) computer simulations enabled to identify and quantify the relative abundances of  
 261 the most frequently occurring edge surfaces of montmorillonite. The total edge specific surface area  
 262 was evaluated to be  $SSA_{Edge} \sim 4.3 \pm 0.2 \text{ m}^2\text{g}^{-1}$ . MD simulations were used to construct a 3D map of  
 263 the electrostatic potential around montmorillonite particles placed on the surface of muscovite  
 264 (mimicking the conditions of experimental observations). Fourier transformation of the calculated  
 265 3D electrostatic potential maps made it possible to identify characteristic reflexes at  $\sim 0.45 \text{ nm}$  and  
 266  $\sim 0.23 \text{ nm}$  on the Fourier-transformed experimental AFM images. The reflex at  $\sim 0.45 \text{ nm}$   
 267 corresponds to the periodicity along the crystallographic  $b$  direction, while the reflex at  $\sim 0.26 \text{ nm}$   
 268 corresponds to the periodicity along the crystallographic  $a$  direction. The knowledge of the particle  
 269 orientations made it possible to quantify the relative abundance of crystallographic directions of  
 270 the montmorillonite edge surfaces. The edge surface normal to the [110] and [010] crystallographic  
 271 directions were found to be the most abundant ( $\sim 60\%$ ,  $\sim 20\%$  respectively), in agreement with  
 272 previously published estimations based on DFT simulations. According to our measurements, the

273 contribution of the edge surface normal to the [130] to the total  $SSA_{Edge}$  is equal to 10%, a value  
274 which exceeds the prediction made using DFT simulations.

275

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283

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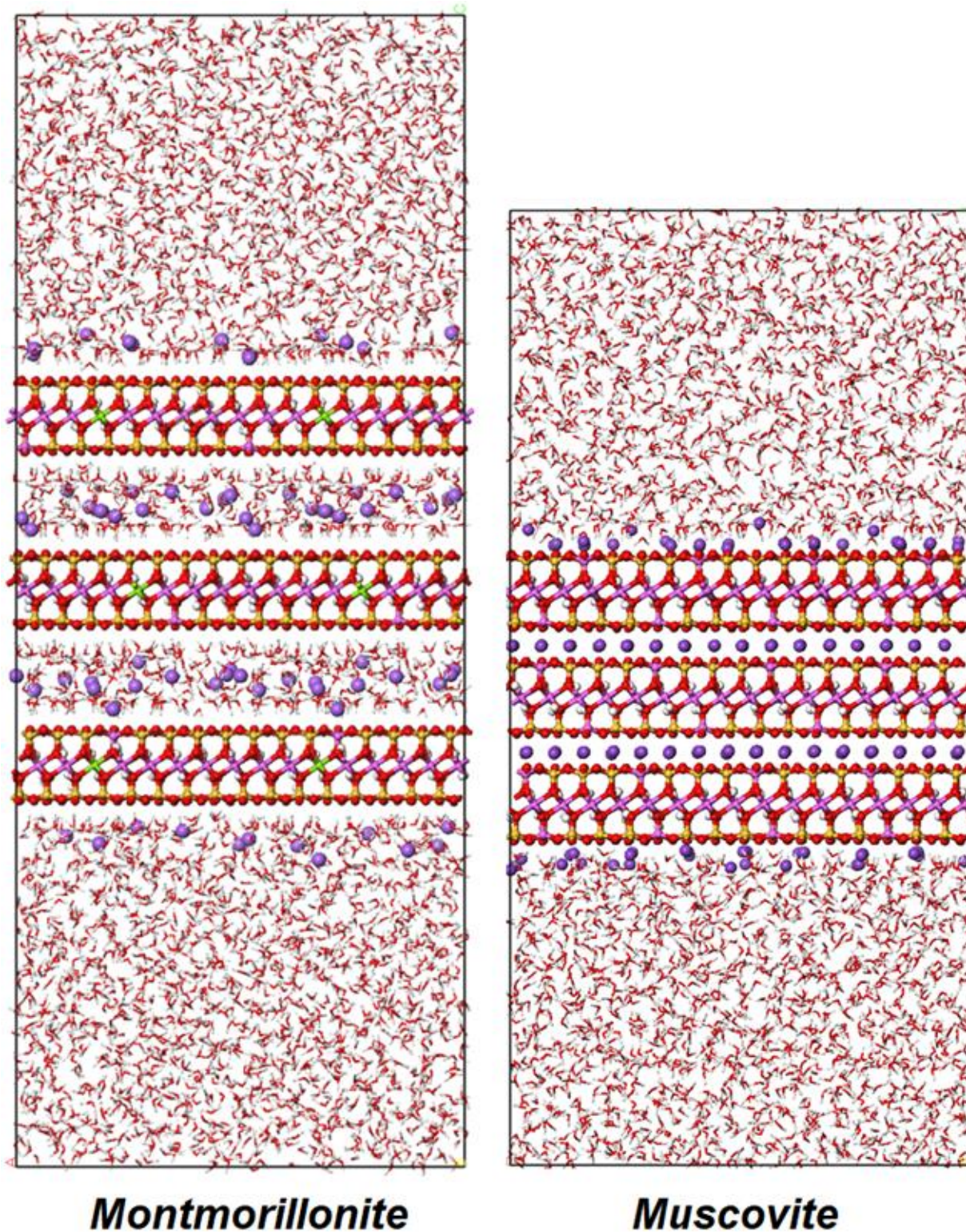
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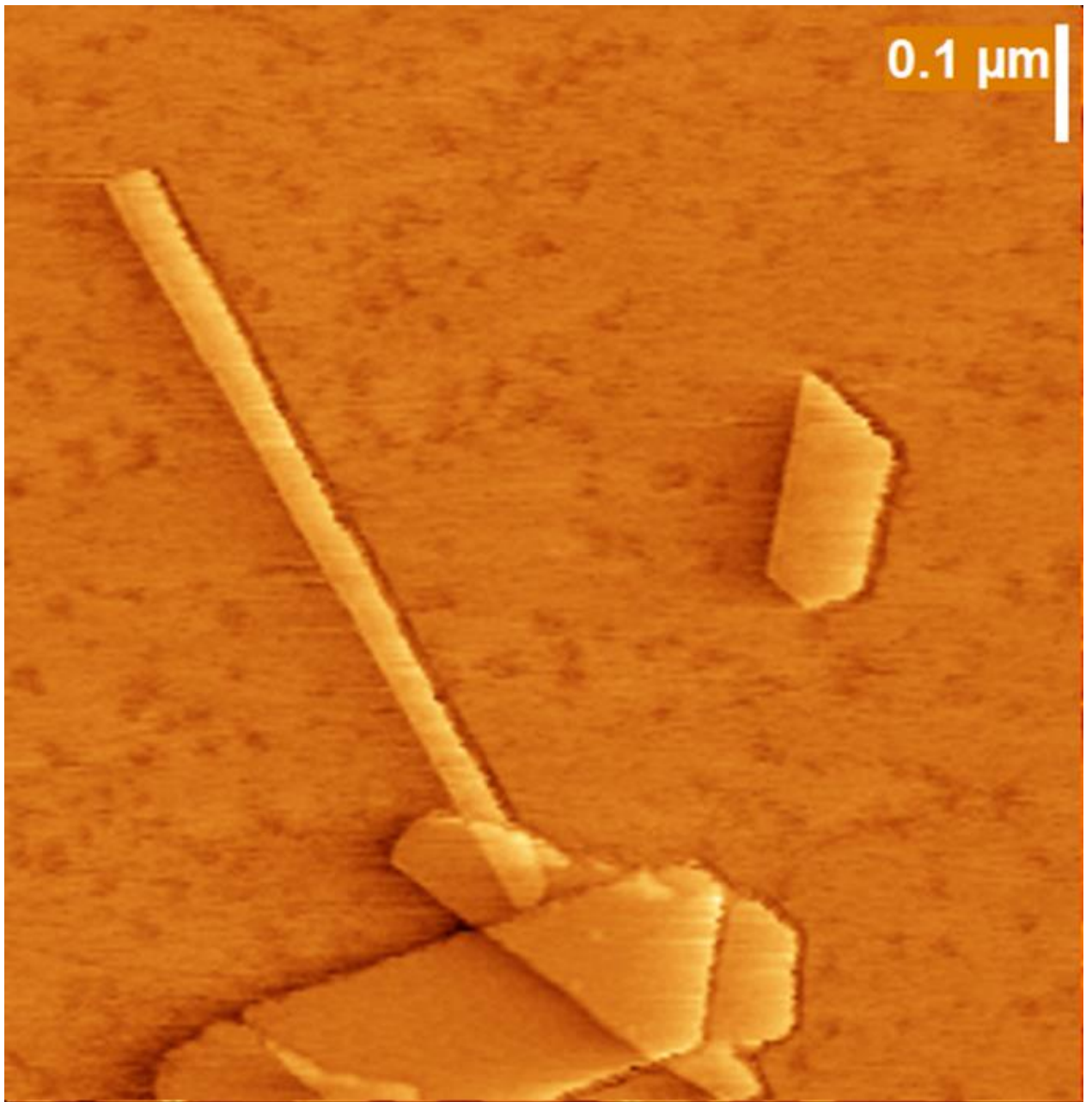
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446 Figure 1. General initial views of the simulation supercells of montmorillonite (left) and muscovite

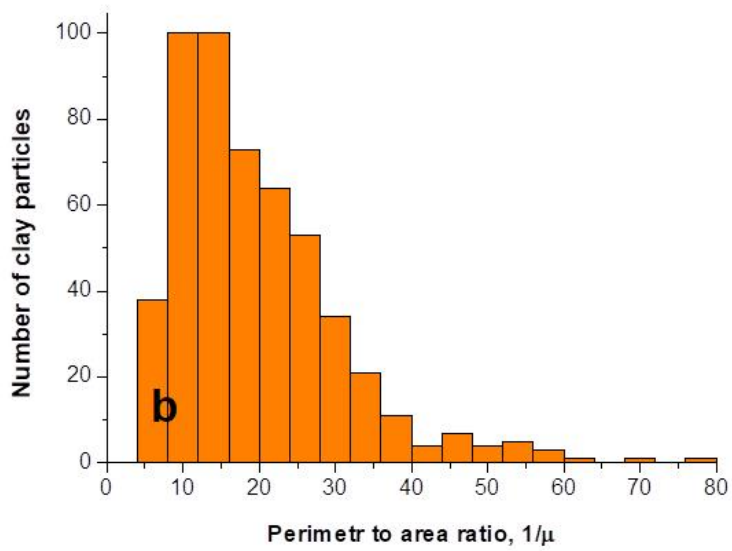
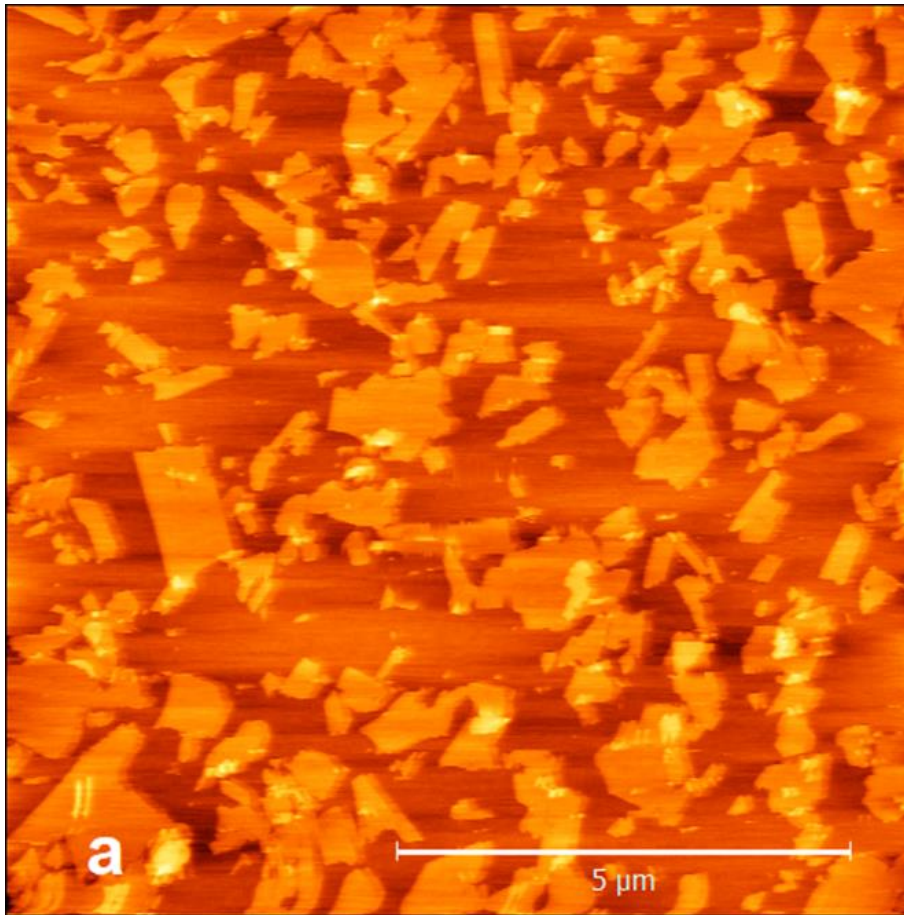
447 (right) used in the MD simulations.



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449 Figure 2. Contact mode deflection AFM image of a clay particle with lath shape, and other particles

450 with well-defined straight boundaries.

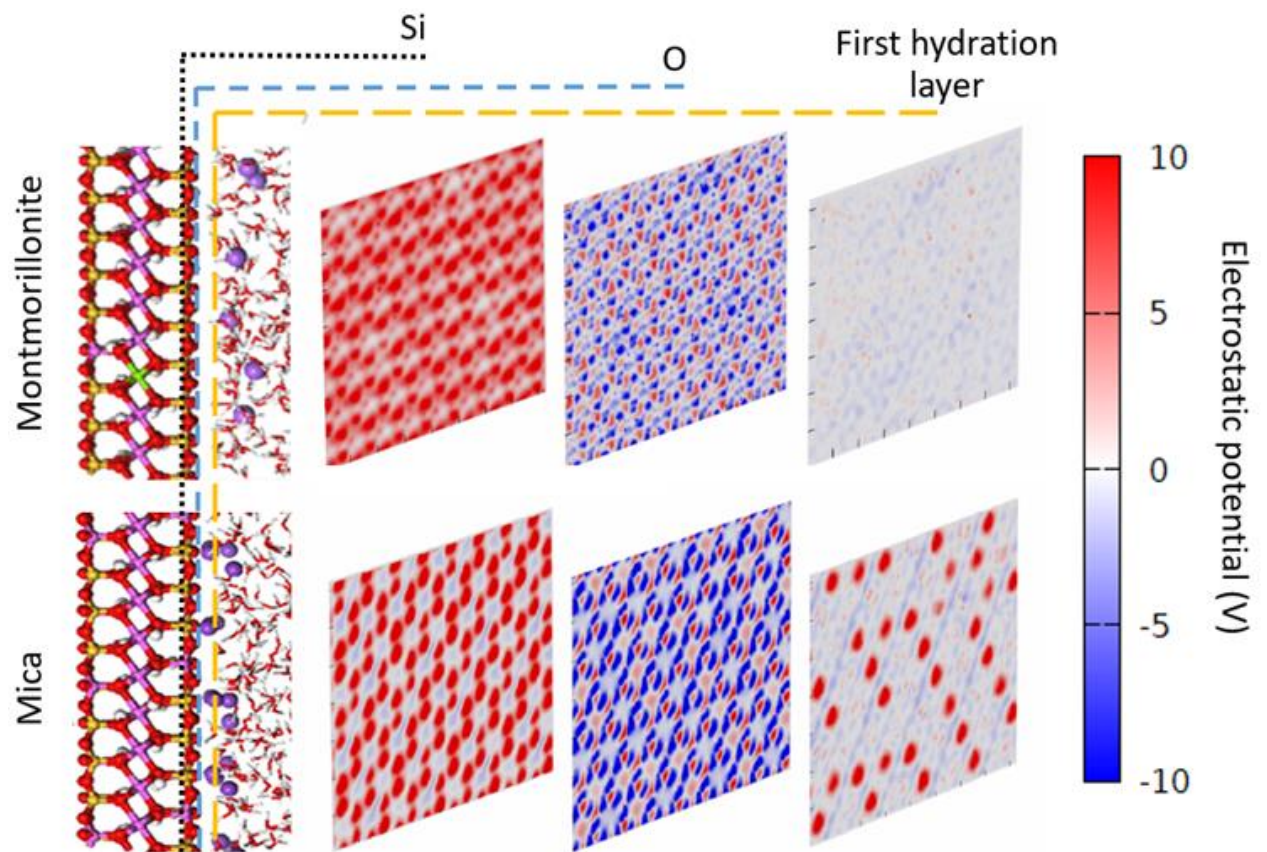


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452 Figure 3. (a) Contact mode height AFM image of montmorillonite particles on the surface of  
453 muscovite. (b) Histogram of perimeter-to-area ratio distribution of the measured montmorillonite  
454 particles.

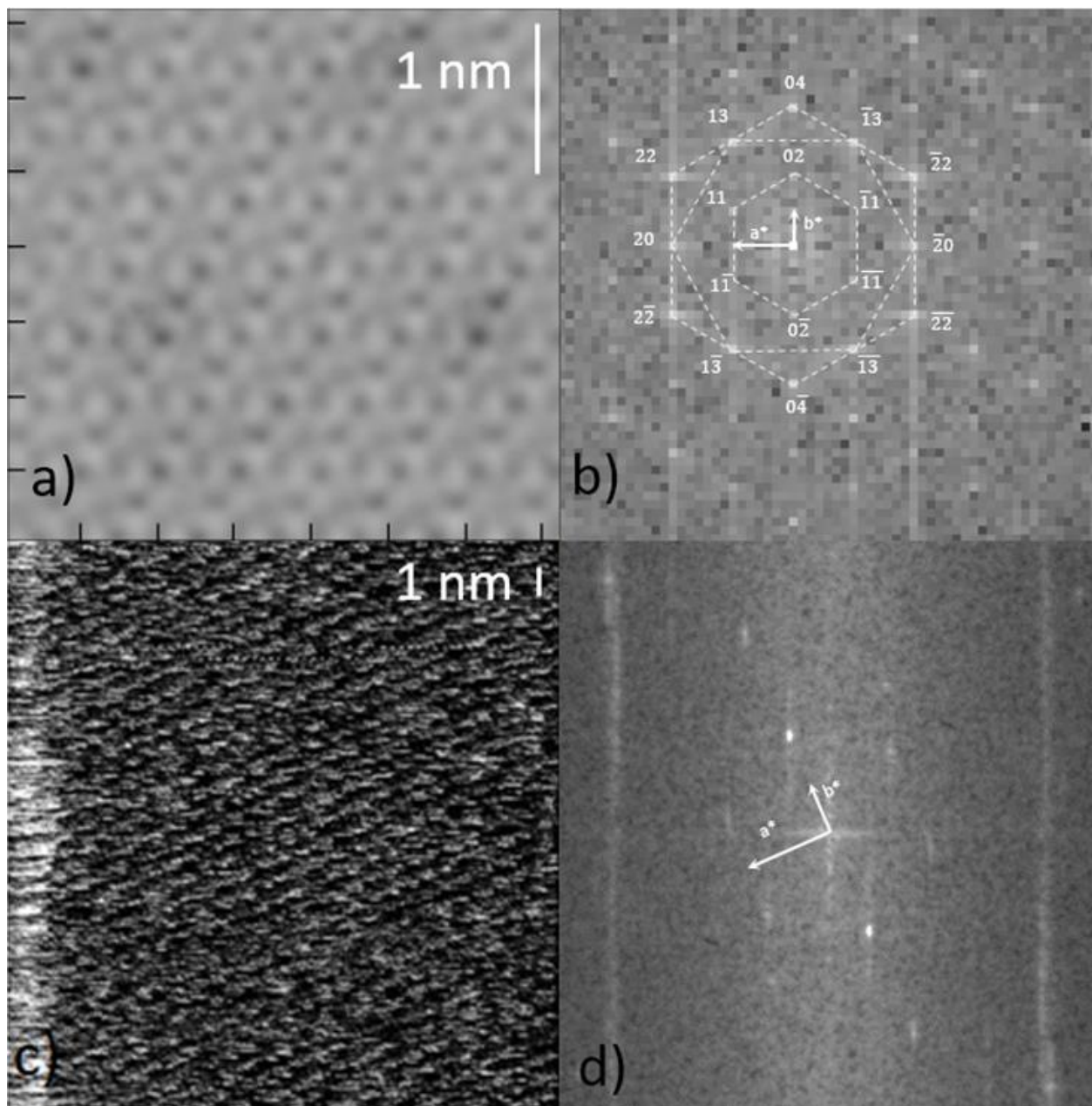
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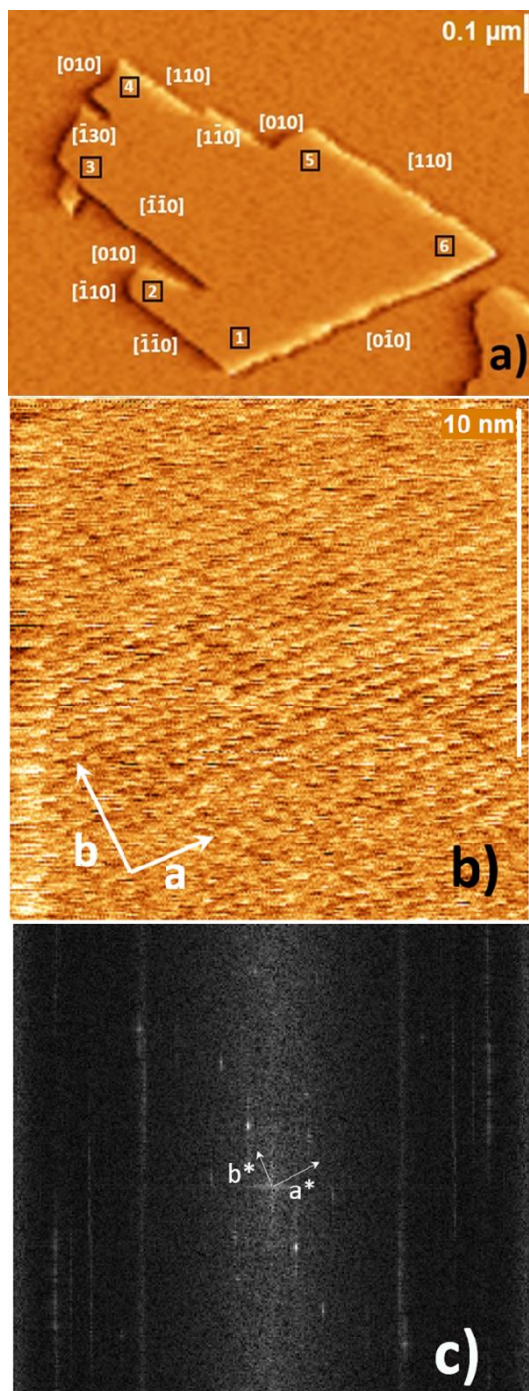
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457 Figure 4. Maps of the time-averaged electrostatic potential (V) parallel to the (001) surface at  
 458 different cross sections calculated from MD simulations. Maps drawn through the planes of time-  
 459 averaged positions of the Si and O atoms of the clay show a honeycomb-like structure. The maps  
 460 of electrostatic forces in the first hydrated surface, defined here as the plane 0.3 nm away from the  
 461 plane of the surface O atoms, are much less ordered. In the case of montmorillonite, the honeycomb-  
 462 like pattern is just barely distinguishable at the same color scale. In the case of the first hydration  
 463 layer on the surface of the mica, the main contribution to the electrostatic forces is due to the  
 464 absorbed  $K^+$  counterions.



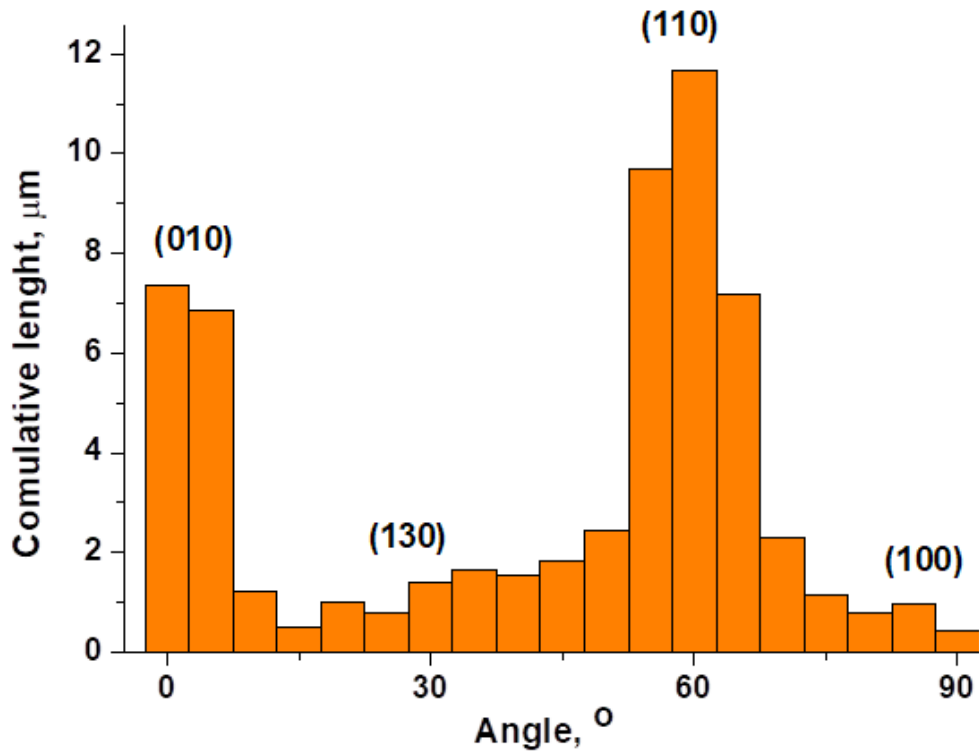
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466 Figure 5. Electrostatic potential distribution into first hydration layer along the basal (001) surface  
 467 of montmorillonite calculated from MD simulations (a) and its fast Fourier transform (b), compared  
 468 with an friction mode AFM-image of the montmorillonite  $15 \times 15 \text{ nm}^2$  surface (c) and its fast Fourier  
 469 transform (d). In both FFT images one pair of reflections corresponding to a spatial periodicity of  
 470  $0.45 \text{ nm}$  is brighter than the other two pairs. We are using this brightest pair to define the  
 471 crystallographic direction  $b$ .



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473 Figure 6. (a) AFM image of the montmorillonite particle; (b) atomic resolution AFM image  
 474 captured on the square spot #1; (c) FFT of (b). The direction of vector  $b$  is chosen according to the  
 475 brightest reflex with the  $0.46 \text{ nm}$  period, the sign of the vector is determined arbitrarily. To prove  
 476 that the particle is, indeed, monocrystalline, several other atomic resolution images corresponding  
 477 to spots #2-6 were obtained and provided as supplementary materials. The crystallographic indexes  
 478 of the edge surfaces were defined by measuring the angle between the direction of the edge and the  
 479 vector  $b$ .



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481 Figure 7. Distribution histogram of montmorillonite particle edge surface orientations, with  
 482 cumulative total lengths of the correspondingly oriented edges.

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	Angle (°)	Edge surface area ratios based on
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Edge surface normal to		AFM (this work)	DFT calculations from (Lavikainen et al. 2015)	
			$\Delta E$	$\Delta G$
[010]	0	0.20	0.33	0.29
[130]	30	0.09	0.00	0.00
[110]	60	0.56	0.61	0.69
[100]	90	0.03	0.06	0.02
unidentified	-	0.12	-	-

491

492 Table 1. Calculated relative ratios of the edge lengths for a typical montmorillonite particle shown  
 493 in Fig. 7, compared with the pyrophyllite particle edge ratios predicted by DFT calculations using  
 494 two different methods marked  $\Delta E$  (minimization of the cleavage energies) and  $\Delta G$  (minimization  
 495 of Gibbs free energies) (Lavikainen et al., 2015).

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