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Complete List of Authors:	Kéri, Annamária; Paul Scherrer Institute, Laboratory for Waste Management; University of Bern, Institute of Geological Sciences; Hungarian Academy of Sciences Centre for Energy Research, Environmental Physics Department Daehn, Rainer; Paul Scherrer Institut, Laboratory for Waste Management Marques Fernandes, Maria; Paul Scherrer Institut, Laboratory for Waste Management Scheinost, Andreas; The Rossendorf Beamline (BM20), European Synchrotron Radiation Lab Krack, Matthias; Paul Scherrer Institute, Laboratory for Scientific Computing and Modelling Churakov, Sergey; Paul Scherrer Institute, Laboratory for Waste Management; University of Bern, Institute of Geological Sciences

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# Iron adsorption on clays inferred from atomistic simulations and XAS spectroscopy

Annamária Kéri<sup>1,2,3,\*</sup>, Rainer Dähn<sup>1</sup>, Maria Marques Fernandez<sup>1</sup>, Andreas Scheinost<sup>4</sup>,  
Matthias Krack<sup>5</sup>, Sergey V. Churakov<sup>1,2,\*</sup>

<sup>1</sup>Laboratory for Waste Management, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

<sup>2</sup>Institute for Geological Sciences, University of Bern, CH-3012 Bern, Switzerland

<sup>3</sup>Centre for Energy Research, H-1121 Budapest, Hungary

<sup>4</sup>The Rossendorf Beamline at the European Synchrotron Radiation Facility (ESRF), Avenue des Martyrs 71, 38043 Grenoble, France

<sup>5</sup>Laboratory for Scientific Computing and Modelling, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

\*Corresponding authors' e-mail: [keri.annamaria@energia.mta.hu](mailto:keri.annamaria@energia.mta.hu); [sergey.churakov@psi.ch](mailto:sergey.churakov@psi.ch)

Tel: +41 56 310 4113

Fax: +41 56 310 2199

## Abstract

The atomistic-level understanding of iron speciation and the probable oxidative behavior of iron ( $\text{Fe}_{\text{aq}}^{2+} \rightarrow \text{Fe}_{\text{surf}}^{3+}$ ) in clay minerals is fundamental for environmental geochemistry of redox reactions. Thermodynamics analysis of wet chemistry data suggests that iron adsorbs on the edge surfaces of clay minerals at distinct structural sites commonly referred as *strong-* and *weak-*sites (with high and low affinity, respectively). In this study, we applied *ab initio* molecular dynamics simulation to investigate the structure and stability of edge surfaces of *trans-* and *cis-*vacant montmorillonites. These structures were further used to evaluate the surface complexation energy and to calculate reference *ab initio* X-ray absorption spectra (XAS) for distinct inner-sphere complexes of Fe. The combination of *ab initio* simulations and XAS allowed us to reveal the Fe-complexation mechanism and to quantify the Fe partitioning between the high and low affinity sites as function of the oxidation state and loadings. Although, iron is mostly present in  $\text{Fe}^{3+}$  form,  $\text{Fe}^{2+}$  increasingly co-adsorb with increasing loadings. *Ab initio* structure relaxations of several different clay structures with substituted  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the bulk or at the surface site showed that the oxidative sorption of ferrous iron is an energetically favored process at several edge surfaces of Fe-bearing montmorillonite.

## 32 Introduction

33 Clay minerals are important redox agent in the global iron cycle and redox geochemistry as  
34 they contain structural and surface adsorbed iron in both ferrous and ferric forms ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ )<sup>1,2</sup>.  
35 Due to the high surface area and exceptional sorption capacity, clay minerals are widely used  
36 as hydraulic barriers for geological disposal of radioactive waste (e.g. bentonite, argillaceous  
37 rock formation)<sup>3,4</sup>. Structural iron in Fe-bearing clay minerals influences the surface uptake of  
38 ferrous iron<sup>5,6</sup>, other transition<sup>7-9</sup> (e.g.  $\text{UO}_2^{2+}$ ,  $\text{Tc}^{7+}$ ) and divalent<sup>10</sup> (e.g.  $\text{Zn}^{2+}$ ) ions. Wet  
39 chemistry and spectroscopic experiments show that ferrous iron competes with  $\text{Zn}^{2+}$  for the  
40 limited amount of binding sites of clay minerals<sup>10</sup>. At the same time, strong uptake of iron  
41 traces in excess of other divalent transition metals can be explained by the possible surface-  
42 induced oxidation of the  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  on clay mineral surfaces<sup>5,6,10</sup>. The extent of the oxidative  
43 sorption processes greatly depends on the pH, the concentration of the dissolved ferrous iron  
44 in the electrolyte as well as the oxidation state and the distribution of structural iron in the  
45 clay<sup>5,6,10</sup>. Despite the importance of the iron redox cycle and contaminant immobilization, the  
46 exact sorption mechanism of iron on clay minerals remain unclear<sup>11</sup>.

47 The structure of smectites can be described as layers of pseudo-hexagonally ordered sheets of  
48 alumina octahedral (O) sandwiched between two siloxane tetrahedral (T) sheets (the so-called  
49 TOT-layer)<sup>12</sup>. Most of the Fe-bearing clay minerals belong to the 2:1 type of dioctahedral  
50 smectites in which only two thirds of the possible octahedral positions are occupied<sup>12</sup>. One  
51 third of the octahedral sites are *trans*-symmetric and two thirds of the octahedral sites are *cis*-  
52 symmetric with respect to the orientation of the hydroxyl ( $\text{OH}^-$ ) groups<sup>12,13</sup>. Montmorillonite  
53 typically occurs in *cv*-vacant form having equal amount of *cis*- and *trans*-occupied sites<sup>14</sup>. The  
54 most stable surfaces of montmorillonite are the basal plane (001) and the (010) and (110)  
55 edges<sup>1,15</sup>. The sorption properties of the basal surface have comprehensively been studied by  
56 atomistic simulations<sup>16</sup>. The reactivity of the edge surfaces is less known because edges are  
57 difficult to isolate experimentally and the theoretical studies should rely on computationally  
58 expensive quantum mechanical simulations<sup>16,17</sup>. For instance, edge surfaces of montmorillonite  
59 shows high variation in reactivity because of the anisotropy of its structure<sup>18</sup>.

60 Furthermore, Fe may form inner-sphere or outer-sphere complexes, which strongly depends on  
61 the ionic strength of iron in the electrolyte<sup>19</sup>. In the former case, the cation directly binds to the  
62 clay surface on one side and to a number of water molecules on the other side, whereas in outer-  
63 sphere hydration complexes, the interlayer cation is completely surrounded by water  
64 molecules<sup>20</sup>. Outer-sphere complexes are preferentially present at the basal site, while inner-

65 sphere complexes are formed at the edge surfaces<sup>20</sup>. Because of the distinct structural  
66 environment, inner- and outer-sphere complexation can be identified by spectroscopic  
67 techniques (e.g. EXAFS-, Mössbauer-spectroscopy)<sup>19</sup>. In the range of high to neutral pH, the  
68 sorption of Fe is strongly dominated by inner-sphere surface complexation at the edge  
69 sites<sup>10,21,22</sup>. The sorption measurements and spectroscopic studies indicated two distinct edge  
70 surface complexes, the so-called *strong-* ( $\equiv\text{S}^{\text{S}}\text{OH}$ ) and *weak-site* ( $\equiv\text{S}^{\text{W}}\text{OH}$ )<sup>22,23</sup>. Recent *ab*  
71 *initio* simulations demonstrate that *weak-sites* represent bidentate surface complexes attached  
72 to the octahedral sheet, whereas *strong-sites* correspond to the incorporation of ions into the  
73 edge surface terminating octahedral<sup>24</sup>. Although, *strong/weak-site* complexation has different  
74 structural characteristics, the exact coordination environment of the two inner-sphere  
75 complexation models is still lacking<sup>23</sup>. In addition, previous studies showed that the sorption  
76 of ferrous iron on clay minerals cannot satisfactorily be modeled without considering the redox  
77 properties of both the structural iron and the surface complexes<sup>5,10</sup>.

78 In our recent works, the structural distribution of substituting cations (e.g. amount of Fe–Fe  
79 and Mg–Fe clusters) and the preferred oxidation state of iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$  proportion) in different  
80 montmorillonites could be identified<sup>25,26</sup>. Furthermore, a quantitative characterization of Zn  
81 uptake processes at the water-clay interface at the atomistic level was achieved<sup>24</sup>. In this work,  
82 extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure  
83 (XANES) spectra were interpreted using *ab initio* molecular dynamics (MD) simulations based  
84 on density functional theory (DFT+U). The linear combination fit of the calculated spectra to  
85 the experimental ones allowed us to quantify the proportion of the different sorption process at  
86 different environmental conditions.

## 87 2. Materials and methods

### 88 2.1. Modelling setup

89 In this study, the two most common edge surfaces of montmorillonite, namely the {110} and  
90 the {010} were investigated<sup>27</sup>.  $\text{OH}^-$  groups were manually added to the surface to build edge  
91 surface with zero net surface charge<sup>17,28</sup>. The crystallographic (lattice) parameters were fixed  
92 during the simulations, while the atomic positions were relaxed. The edge surfaces of (110)  
93 and ( $\bar{1}\bar{1}0$ ) (Figure 1a) as well as (010) and ( $0\bar{1}0$ ) (Figure 1b) are not equivalent for the *cis*-  
94 vacant polymorphs of montmorillonite in contrast to *trans*-vacant phyllosilicates. To determine  
95 the energetically favored position for ferrous and ferric iron, the relaxed structures of single  
96  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions incorporated into the octahedral sheet at different (bulk and surface)

97 positions were calculated for the (110), ( $\bar{1}\bar{1}0$ ) (010) and (0 $\bar{1}0$ ) edge surface models  
98 (Figure 1a,b).  $2 \cdot 2 \cdot 2 \cdot 7 = 56$  distinct model structures (considering the oxidation state of iron,  
99 the orientation of the edge surfaces and *cis/trans*-occupational sites) were investigated. The  
100 composition of the clay platelet in these simulations was  $\text{Al}_{56}\text{Si}_{112}\text{O}_{264}(\text{OH})_{88}$ . The dimensions  
101 of the orthorhombic supercell were  $a = 50.0 \text{ \AA}$ ,  $b = 20.8 \text{ \AA}$ ,  $c = 15.0 \text{ \AA}$ . Similar to previous  
102 works, the cell parameter in the  $a$ - and  $c$ -direction had larger values to reduce the interaction  
103 between the periodic images<sup>24,25,28</sup>.

104 Edges of clay particles are strongly hydrophilic and covered with phys- and chem-adsorbed  
105 water molecules<sup>19,28,29</sup>. To have the best representation of natural conditions, the planar pores  
106 between edges were filled with water molecules to maintain the average equilibrium density of  
107 1.0 g/ml in the middle of inter-particle space. The interlayer was free of water for the sake of  
108 computational efficiency as we primarily focused on Fe complexation at the edge sites of  
109 montmorillonite. Molecular dynamics (MD) simulations were performed for systems  
110 containing bidentate inner-sphere  $\text{Fe}^{2+}/\text{Fe}^{3+}$  complexes to the octahedral sheet at the clay edge  
111 surface including isomorphic substitution of Fe for Al in the near surface octahedral sites  
112 (Figure 2).

113 Two iron atoms with the same oxidation state forming *strong-like* or *weak-like* inner-sphere  
114 complexes at the either sides of the (010) and (110) edges were simulated simultaneously  
115 (Figure 2, Table 1). The total composition of the system in these simulations was  
116  $[\text{Fe}_x^{2+}\text{Fe}_y^{3+}\text{Al}_{38}\text{Si}_{80}\text{O}_{184}(\text{OH})_{72} \cdot 144\text{H}_2\text{O}]^{x-}$  for iron at the *strong-site* and  
117  $[\text{Al}_{40}\text{Si}_{80}\text{O}_{186}(\text{OH})_{70}]^{2-} \cdot 2[\text{Fe}_x^{2+}\text{Fe}_y^{3+}(\text{OH})_2(\text{H}_2\text{O})_2 \cdot 136\text{H}_2\text{O}]^{y+}$  at the *weak-site* with the  
118 stoichiometry  $x = 0$  and  $y = 2$  or  $x = 2$  and  $y = 0$ , respectively. The cell parameters were fixed  
119 at  $a = 41.4 \text{ \AA}$ ,  $b = 20.8 \text{ \AA}$ ,  $c = 10.2 \text{ \AA}$  values.  $c$ -lattice parameter corresponds to a typical  
120 interlayer distance in dehydrated smectites<sup>30</sup>, while parameter  $a$  was chosen to be large enough  
121 to minimize the interaction between periodic images across the slit pore.

## 122 2.2. *Ab initio* calculations

123 The structure relaxations and the molecular dynamics simulations were performed based on  
124 the density functional theory (DFT) using the Gaussian plane wave (GPW) method as it is  
125 implemented in the QUICKSTEP module of the CP2K code<sup>31-33</sup>. The scalar-relativistic norm-  
126 conserving pseudopotentials of Goedecker, Teter and Hutter (GTH)<sup>34,35</sup> were applied to avoid  
127 the explicit consideration of the core electrons. The medium-core pseudopotential of iron was  
128 composed of a [Ne] core with  $3s^2 3p^6 4s^2 3d^6$  valance orbitals. The wave functions of the

129 valence electrons were described by a linear combination of contracted Gaussian-type orbitals  
130 using MOLOPT basis sets optimized for the corresponding GTH pseudopotentials<sup>31</sup>. All  
131 calculations were performed with a spin polarized implementation of the Perdew, Burke and  
132 Ernzerhof (PBE) exchange and correlation functional<sup>36</sup>. An auxiliary basis set of plane waves  
133 up to cutoff energy of 400 Ry was employed to expand the electronic density. An empirical  
134 van der Waals (vdW) correction PBE+D2 has been applied to improve the description of  
135 hydrogen bonding interaction<sup>37</sup>. A sufficiently strict convergence criterion ( $\epsilon_{\text{SCF}} = 3 \cdot 10^{-7}$  a. u.)  
136 for the wave function gradients during the self-consistent field (SCF) cycle was enforced  
137 ensuring a convergence of the total energy to a similar accuracy. Simulations with single iron  
138 in the (tetrahedral or octahedral) sheet were performed with a multiplicity  $(2S+1)_{\text{Fe}^{2+}} = 5$  for  
139 systems with a single ferrous iron and  $(2S+1)_{\text{Fe}^{3+}} = 6$  for systems with a single ferric iron,  
140 respectively. For models with two iron ions (with the same oxidation state), the multiplicity  
141 was set to  $(2S+1)_{\text{Fe}^{2+}-\text{Fe}^{2+}} = (2S+1)_{\text{Fe}^{3+}-\text{Fe}^{3+}} = 1$ .

142 Conventional DFT is known to underestimate the Coulomb repulsion between the 3d-electrons  
143 of iron which results in delocalized 3d-electrons<sup>38</sup>. The so-called DFT+U method was applied  
144 to improve the description of these states within the DFT formalism<sup>39,40</sup>. In this method, the  
145 conventional DFT equations are augmented with the so-called Hubbard term ( $U_{\text{eff}}$ ), which  
146 applies an additional potential enforcing selective localization of the Fe 3d-states. The value of  
147  $U_{\text{eff}}$  depends on the implementation and has to be calibrated<sup>25</sup>. The calibration for Fe-bearing  
148 montmorillonites was performed in our previous papers<sup>25</sup>, and was fixed for the sake of  
149 consistency at  $U_{\text{eff}} = 1.9$  eV.

150 Eight system setups — representing distinct bidentate Fe complexes (*strong/weak-site*) with  
151 different oxidation state ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) at the two most relevant edge surface ((010) or (110))  
152 sites — were pre-equilibrated with empirical force field ClayFF<sup>41</sup>. The equilibration was  
153 performed by classical MD simulations in the canonical ensemble (NVT) using LAMMPS  
154 package<sup>42</sup>. Each system was kept at 300 K with Nose-Hoover thermostat for 9 ns. Afterwards,  
155 Born-Oppenheimer *ab initio* molecular dynamics (MD) simulations were performed within the  
156 canonical (NVT) ensemble controlled by a stochastic thermostat through velocity rescaling  
157 (CSVR)<sup>43</sup>. The integration of the Brillouin zone was performed with  $\Gamma$ -point only. *Ab initio*  
158 MD simulations were performed with time step of 0.5 fs. The systems were equilibrated for  
159 4 ps at the target temperature of 300 K followed by *ab initio* MD production runs of 16 ps  
160 duration.

### 161 2.3. Calculations of EXAFS spectra

162 To obtain theoretical XAS spectra, 320 molecular configurations separated by 50 fs time  
163 intervals were retrieved from molecular dynamics trajectories for each complex type. For each  
164 molecular configuration EXAFS spectra were calculated based on real space multiple  
165 scattering theory implemented in the FEFF 8.40 code<sup>44</sup>. Multi-scattering paths up to eight legs  
166 with path lengths up to 7.0 Å were taken into account. The scattering potential of the atoms  
167 were calculated self-consistently,<sup>44,45</sup> for cluster radius 5.0 Å. The amplitude reduction factor  
168 ( $S_0^2$ ) was set to 1.0. The default values were retained for the remaining parameters<sup>46</sup>. All  
169 calculated and measured spectra were normalized to the value of the first oscillation.  
170 Reference spectra for each complex type were obtained averaging 320 individual spectra of  
171 uncorrelated molecular configurations to account for statistical and thermal disorder,  
172 accordingly. The calculated XAS spectra served as the basis for the qualitative and quantitative  
173 interpretation of the experimental data after max-min normalization. The linear combination  
174 fit of the calculated EXAFS spectra served as a basis for the quantitative interpretation of  
175 experimental ones. Quantitative comparison were performed based on the quality of the fit as  
176 it is defined in Equation 1, respectively<sup>24,25</sup>.

$$177 \quad Q_{\text{EXAFS}} = \left( k^3 \sum_i \left( a_i^2 \chi_i(k) \right) - \chi^{\text{exp}}(k) \right)^2 + \sum_i a_i^2 \rightarrow \min \quad (1)$$

178 where  $\chi_i(k)$  are the calculated reference spectra and  $\chi^{\text{exp}}(k)$  is the experimental EXAFS  
179 spectra,  $a_i^2$  are the optimized fitting parameters. The term  $\sum_i a_i^2$  was included following  
180 Tikhonov<sup>47</sup> regularization approach to avoid overfitting. The fittings were limited to the  
181 interval of EXAFS spectroscopy to  $k[\text{Å}^{-1}] \in [3.0, 9.0]$ . The fit was accepted as “best fit” (Fit1)  
182 if the indicator of quality number ( $Q_{\text{EXAFS}}$ ) was the lowest.

### 183 2.4. XAS experiments

184 The experimental XAS spectra used in this study were obtained to investigate Fe uptake  
185 mechanism on clay minerals as function of loading<sup>48</sup>. The EXAFS samples consisted of a  
186 synthetic iron free montmorillonite (IFM)<sup>49,50</sup> equilibrated for 1 week with different  $\text{Fe}^{2+}$   
187 concentrations at pH 7 in 0.1 M NaCl. The resulting Fe loadings were 6 mmol/kg; 9 mmol/kg;  
188 18 mmol/kg; 37 mmol/kg, respectively. Sample preparation, phase separation as well as the  
189 transfer of the wet clay pastes into the sample holders took place inside an anoxic glovebox  
190 under controlled  $\text{N}_2$  atmosphere ( $\text{O}_2 < 0.1$  ppm). Further preparation procedures were similar  
191 as described by Soltermann et al.<sup>50</sup>. Once removed from the glovebox, the samples were  
192 immediately flash-frozen in  $\text{LN}_2$  and stored in an  $\text{LN}_2$  dewar to prevent sample oxidation. After



193 transport to the Rossendorf Beamline at ESRF (Grenoble, France), the samples were  
194 individually removed from the LN<sub>2</sub> dewar and transferred to a closed-cycle He cryostat  
195 operating at 10 K for the XAS measurements. Measurements at <15 K protect samples from  
196 oxidation and improve signal quality by reducing thermal broadening. The XAS spectra were  
197 collected in fluorescence mode at the Fe K-edge (7112.0 eV) using a 13-element high-purity  
198 Ge solid state detector (Canberra) with digital signal analysis (XIA XMap). The polychromatic  
199 synchrotron beam was monochromatized using a pair of water-cooled Si(111) crystals, and  
200 higher-order harmonics were rejected by a Si mirror. Individual XAS scans were energy-  
201 calibrated against a simultaneously measured Fe foil, corrected for fluorescence dead time and  
202 averaged using SIXpack<sup>51</sup>, while subsequent data reduction steps and shell fits were conducted  
203 using WinXAS<sup>52</sup>.

### 204 3. Results and Discussion

#### 205 3.1. Preferred position of Fe<sup>2+</sup> and Fe<sup>3+</sup> in montmorillonite

206 The preferred positions of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the octahedral sheet of a clay layer were determined  
207 by comparing the total energies of the different edge surface models. First, the preferred  
208 protonation schemes for the two idealized edge surfaces were determined  
209 (Supporting Information 1). It is clearly visible that the two most relevant edge surfaces of *cis*-  
210 vacant montmorillonite (110)/( $\bar{1}\bar{1}0$ ) and (010)/(0 $\bar{1}0$ ) edge surfaces are not related by  
211 symmetry. Ferrous and ferric iron might preferentially be incorporated into the bulk (“P2”-  
212 “P6” positions in Figure 1) or remain at the surface (“P1” and “P7” positions in Figure 1). The  
213 energies of (010) and (110) surface models with Fe<sup>2+</sup> and Fe<sup>3+</sup> located in “P1”-“P7” positions  
214 were calculated and plotted as function of distance to the edge surface (Figure S2 in  
215 Supporting Information 1). These raw data were crucial to correct the polarity of the surfaces  
216 as electrostatic potential difference could be imposed across the simulated clay platelet due to  
217 the asymmetric protonation. The correction procedure and the origin of the surface potential  
218 are discussed in details in Supporting Information 1. The energies of Fe<sup>2+</sup> and Fe<sup>3+</sup> in *cis*- and  
219 *trans*- position at different distance to the edge corrected for surface potential difference are  
220 shown in Figure 3. The energy of the *bulk-like* iron in the position “P4” is taken as the  
221 reference.

222 The calculated energies of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the octahedral sheet of a montmorillonite layer and  
223 on the edge surface indicate that the oxidation of ferric iron at the surface coupled with  
224 reduction of ferrous iron in the bulk is energetically highly favored for the (110) edge surface

225 (Figure 3), while such a trend can not be confirmed for the (010) edge site. The energy  
226 difference between “P1” and “P7” terminated by the (110) surface suggest preferential leaching  
227 of Fe<sup>3+</sup> at “P7” terminated edge and its precipitation at the “P1” terminated edge. No such  
228 energy difference is predicted for (010) edge surface as Fe incorporation energies are  
229 comparable for “P1” and “P7” positions terminated (010) surface and the bulk.  
230 The performed *ab initio* calculations did not address the thermodynamics and kinetic of the  
231 redox reaction explicitly which depends on many environmental factors (e.g. Fe loading, pH  
232 condition and the protonation of the surface). In addition, redox-active iron may be present as  
233 *weak-site* inner-sphere complexes (Figure 2c,d) at the edge surfaces of the clay layer.

### 234 3.2. Sorption mechanism of Fe on montmorillonite edge sites

235 The interpretation of experimental XAS spectra based on *ab initio* modelling is a promising  
236 approach to quantify the uptake processes in minerals, which can be used to directly investigate  
237 the interplay between the metal loading and the sorption mechanism<sup>24,25,53–55</sup>.

238 The *ab initio* Fe K-edge EXAFS spectra for Fe<sup>2+</sup> or Fe<sup>3+</sup> bidentate inner-sphere complexes at  
239 the *cis*- and *trans*-like site of the (010) and (110) edge surface representing *strong*- and *weak*-  
240 *site* are shown in Figure 4. The spectra for ferrous and ferric iron are clearly different. The most  
241 prominent difference is the shift in the first oscillation at  $k \sim (4.10-4.25)/(4.35-4.55) \text{ \AA}^{-1}$ , and  
242 at the second oscillation at  $k \sim (5.70-6.3) \text{ \AA}^{-1}$  for ferrous iron and  $k \sim (6.0-7.0) \text{ \AA}^{-1}$  for ferric  
243 iron, respectively.

244 The measured EXAFS spectra of the four montmorillonite samples with increasing iron  
245 loadings from 6 mmol/kg to 37 mmol/kg looks rather similar. Detailed analysis allows,  
246 however, to reveal several sample specific features (Figure 5). The second oscillation shifts to  
247 lower  $k$  values (from  $k \sim 6.6 \text{ \AA}^{-1}$  to  $k \sim 6.2 \text{ \AA}^{-1}$ ) with increasing Fe loadings. In addition, there  
248 is a significant shape difference in the third oscillation of EXAFS spectra (double-bounced or  
249 single oscillation with right shoulder) below and above  $\sim 30$  mmol/kg of iron loading. To  
250 quantify the effect of the iron loading on the uptake mechanism and to identify the preferred  
251 oxidation state of the adsorbed complexes, the measured EXAFS spectra were interpreted as a  
252 linear combination of reference spectra obtained from MD simulation of model surface  
253 complexes (Figure 5 and 6, Table S1 in Supporting Information 2).

254 The qualitative analysis on the linear combination fits of the experimental data to the reference  
255 *ab initio* spectra reveal clear change in the preferred oxidation state and in the uptake  
256 mechanism as function of Fe loading (Figure 5). The data analysis shows that at low loading

257 iron is mostly present in  $\text{Fe}^{3+}$  form at the *strong-sites*. With increasing Fe loadings, the ratio  
258  $\text{Fe}_{\text{Ws}}^{3+}/\text{Fe}_{\text{Ss}}^{3+}$  increases indicating raising co-adsorption of  $\text{Fe}^{3+}$  on *weak-sites*. In addition, the  
259 contribution of  $\text{Fe}_{\text{Ws}}^{2+}$  shows an increasing trend with the loading suggesting an increasing  
260 competition between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Finally, at the loading above 30 mmol/kg the contribution  
261 of  $\text{Fe}_{\text{Ss}}^{2+}$  becomes significant. The overall results indicate increasing  $\text{Fe}^{2+}$  co-adsorption at higher  
262 Fe loadings.

263 The observed trend in the changes of the oxidation state of the adsorbed Fe and the uptake  
264 mechanism are generally consistent with the prediction of a thermodynamic sorption model.  
265 The few differences in the theoretical fit and the experimental spectra, especially for the second  
266 and third oscillation (Figure 5c), however, are worth a discussion. These discrepancies can be  
267 explained by the relatively high background noise. The shape difference in the third oscillation  
268 of EXAFS spectra (double-bounced or single oscillation with right shoulder) below and above  
269  $\sim 30$  mmol/kg of iron loading (Figure 5c,d) could not accurately be modelled. It might indicate  
270 an increased impact of outer-sphere complexation, which was not considered in the model.

271 According to the thermodynamic sorption model, the total amount of Fe adsorbed on the  
272 surface should be increased by a factor of six when loading increases from 6 mmol/kg to  
273 37 mmol/kg. Furthermore, the thermodynamic model suggests that almost all *strong-sites* are  
274 occupied by Fe at  $\sim 6$  mmol/kg (Figure 6 and Table S1 in Supporting Information 2). Thus,  
275 further uptake of Fe should take place on the *weak-sites*, whereas the absolute amount of total  
276 Fe adsorbed on *strong-sites* should remain constant. It would mean a relative increase of the  
277 EXAFS signal from *weak-sites* with respect to the signal due to *strong-sites*. Contrary, the  
278 modelling results suggest that the proportion of the *weak-* and *strong-site* sorption sites remains  
279 constant ( $\sim 30\%:70\%$ ). These discrepancies could be explained by the moderate quality of the  
280 linear combination fit.

281 The results of the theoretical XANES spectroscopy and their comparison with the experimental  
282 spectra are present in Supporting Information 2. The XANES spectra of ferrous and ferric iron  
283 surface complexes are rather similar for both *strong-* and *weak-sites* making the XANES linear  
284 combination fit unreasonable.

#### 285 **4. Discussion and conclusions**

286 *Ab initio* molecular dynamics simulations were successfully applied to reveal the structure and  
287 the stability of edge surfaces of *trans-* and *cis-* vacant montmorillonites. For the first time, the  
288 surface structure and surface energies of *cis-*vacant montmorillonite were analyzed in details.  
289 The molecular configurations from MD simulations used to obtain reference XAS spectra for

290 distinct Fe inner-sphere complexes on the edge of montmorillonite. The combination of *ab*  
291 *initio* simulations and XAS allowed us to reveal the iron complexation mechanism and its  
292 partitioning between high and low affinity sorption sites depending on the oxidation state and  
293 loading. The quantitative interpretation of the atomistic modelling based XAS spectra  
294 measured on samples with different Fe loadings indicated a particularly complex behavior of  
295 iron. Iron is mostly present in Fe<sup>3+</sup> form, although, its extent decreases at increasing Fe  
296 loadings.

297 Calculated energy of Fe<sup>2+</sup>/Fe<sup>3+</sup> incorporation into different octahedral sites confirm that the  
298 oxidative sorption of Fe<sup>2+</sup> at the most relevant edge surface of montmorillonite is an  
299 energetically favored process. Rosso et al. demonstrated similar oxidative sorption processes  
300 takes place at the edge surface of iron-oxides (e.g. hematite<sup>56</sup>), clay minerals (e.g. nontronite<sup>57</sup>)  
301 and micas<sup>58</sup> with high Fe-content. Furthermore, they calculated the kinetics of the of charge  
302 transport in the different minerals<sup>57,59,60</sup>. The interplay of the different electron transfer  
303 processes as Fe<sup>2+</sup>/Fe<sup>3+</sup> valence interchange between nearest-neighbor iron atoms via a small  
304 polaron hopping mechanism was determined and simulated. In addition, the impact of several  
305 structural defect on the electron transfer was described.

306 The combination of atomistic simulations and XAS spectroscopy on samples with different Fe  
307 loading showed that the sorbed amount of iron has an impact on the efficiency on the oxidative  
308 iron uptake. At higher Fe loading, larger quantities of ferrous iron remain in this oxidation  
309 state, since all possible electron donors are consumed. It explains that although *strong-site* Fe<sup>3+</sup>  
310 complexes are present in the highest amount at the edge surface site, its extent is decreasing.  
311 In this study, iron free montmorillonite (IFM) without structural Fe<sup>3+</sup> was investigated, which  
312 give rise to speculation about the possible electron donor. As no Fe<sup>3+</sup> is present in the clay  
313 lattice of IFM, other reactive surface sites on IFM might induce the electron transfer between  
314 sorbed Fe<sup>2+</sup> species and the clay particles<sup>50,61</sup>. The process may play a crucial role in the long-  
315 term mineralogical alteration of smectites into non-swelling phyllosilicates that are challenging  
316 to study experimentally. Future studies should aim a more complete description including the  
317 Fe<sup>2+</sup>/clay redox cycle and the oxidative uptake mechanisms of Fe<sup>2+</sup> on montmorillonite.

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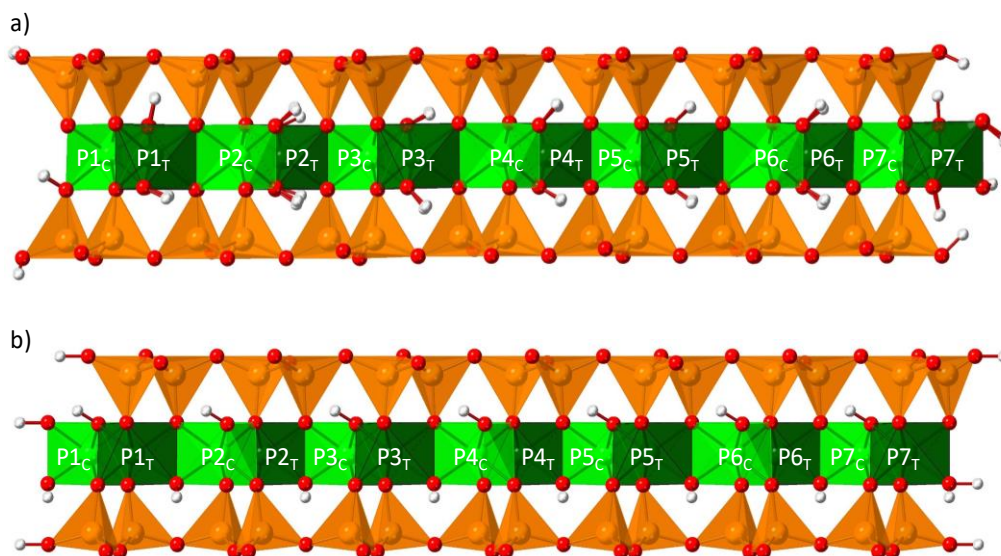


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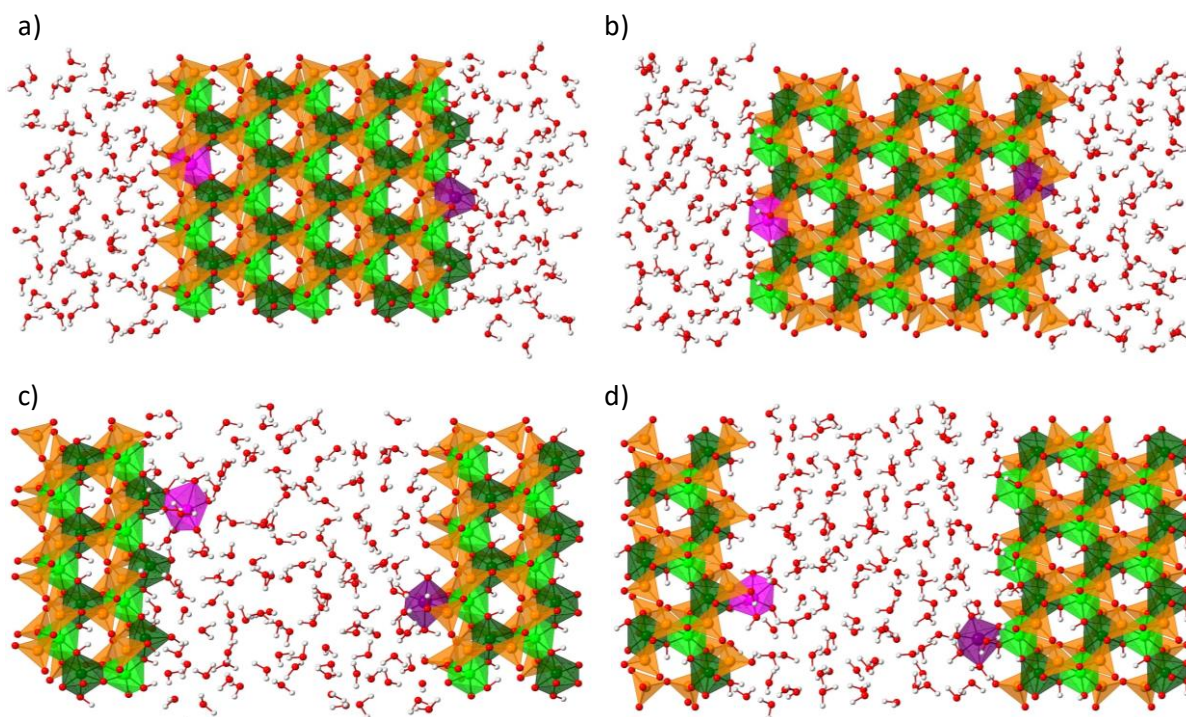
497 **Table 1.** Bidentate inner-sphere Fe complexation models, associated short names and panels  
 498 of Figure 2 in which the corresponding model structures are.

Edge surface	Inner-sphere complexation model	Oxidation state of iron	Surface site	Short name of the model	Panel in Figure 2
(010)	<i>strong-site</i>	Fe <sup>2+</sup>	<i>cis-like</i>	010cSsFe2	a)
			<i>trans-like</i>	010tSsFe2	
		Fe <sup>3+</sup>	<i>cis-like</i>	010cSsFe3	
			<i>trans-like</i>	010tSsFe3	
(110)	<i>weak-site</i>	Fe <sup>2+</sup>	<i>cis-like</i>	010cWsFe2	b)
			<i>trans-like</i>	010tWsFe2	
		Fe <sup>3+</sup>	<i>cis-like</i>	010cWsFe3	
			<i>trans-like</i>	010tWsFe3	
(110)	<i>strong-site</i>	Fe <sup>2+</sup>	<i>cis-like</i>	110cSsFe2	c)
			<i>trans-like</i>	110tSsFe2	
		Fe <sup>3+</sup>	<i>cis-like</i>	110cSsFe3	
			<i>trans-like</i>	110tSsFe3	
(110)	<i>weak-site</i>	Fe <sup>2+</sup>	<i>cis-like</i>	110cWsFe2	d)
			<i>trans-like</i>	110tWsFe2	
		Fe <sup>3+</sup>	<i>cis-like</i>	110cWsFe3	
			<i>trans-like</i>	110tWsFe3	

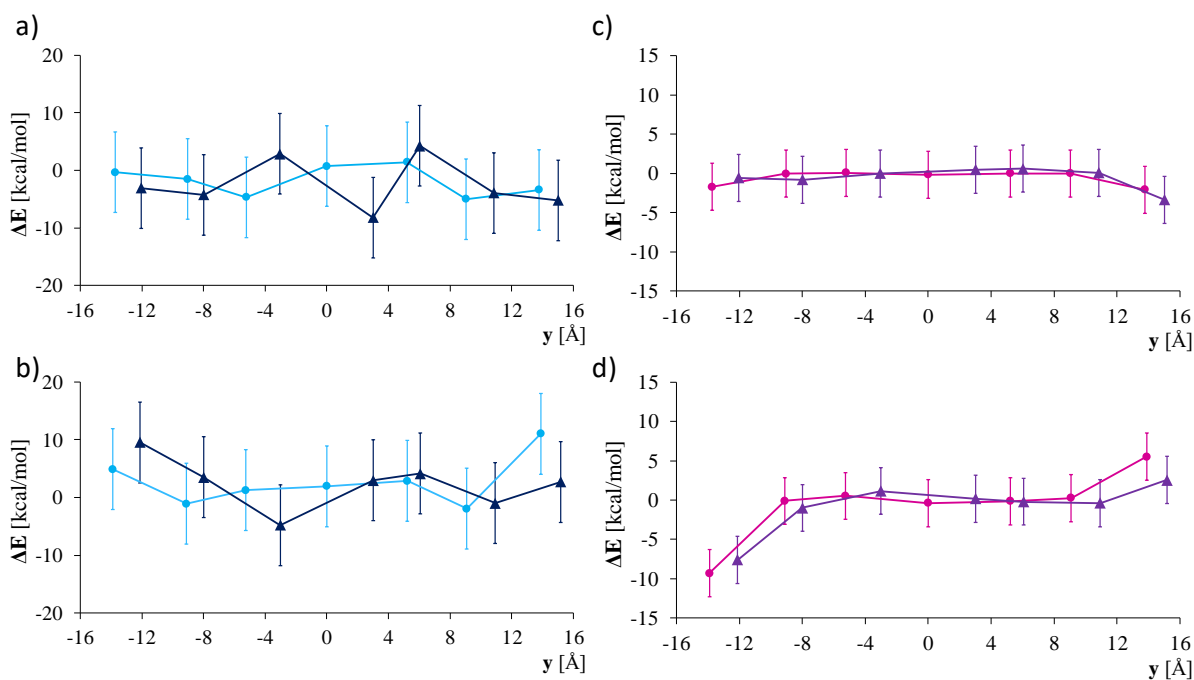
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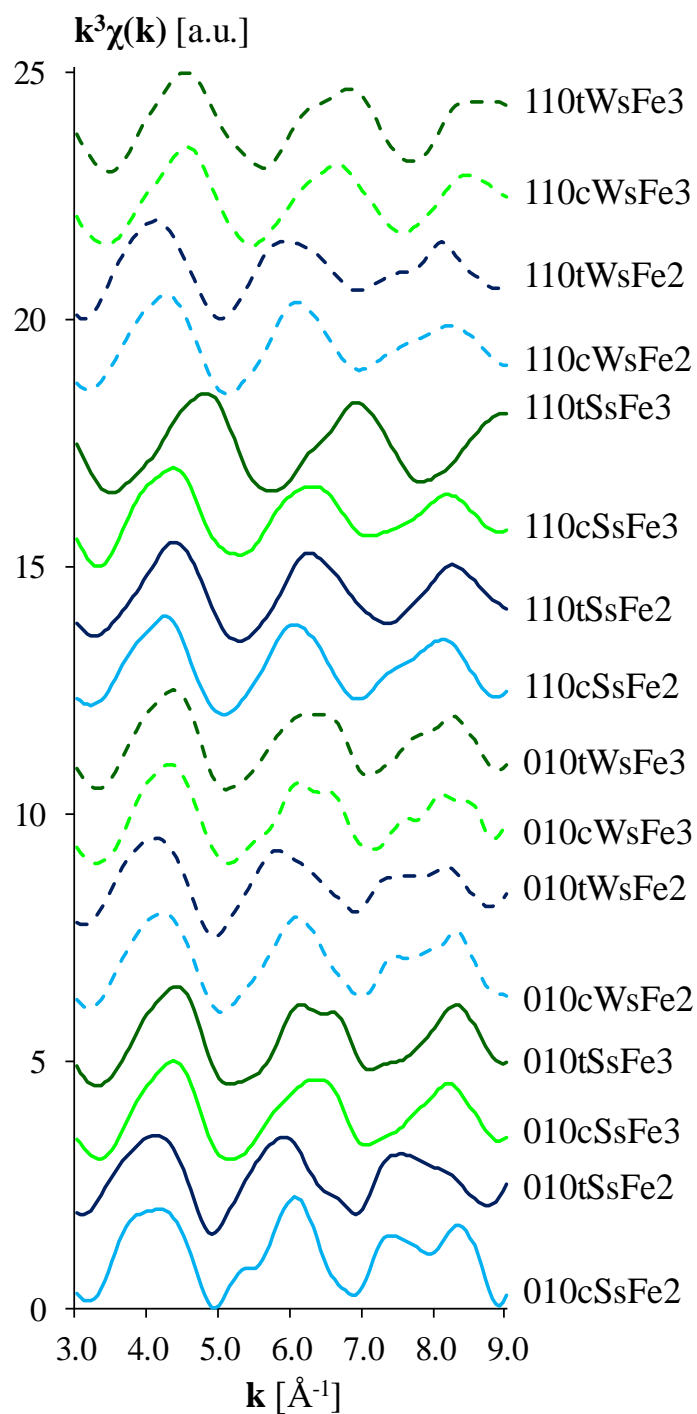
**Figure 1.** Views of iron substitution models. A single clay particle with (010) and (110) edge surface are shown in panels a and b, respectively. Position of iron substitution are labeled on the octahedral sheet. Alumina octahedra are shown in green, silica tetrahedra are orange, while red and grey colors correspond to oxygen and hydrogen atoms, respectively. *Cis*-octahedra are marked with light green, while dark green color corresponds to *trans*-octahedra. *Cis*- and *trans*-octahedral sites can be distinguished by the different relative position of hydroxyl ( $\text{OH}^-$ ) groups. “P1” positions correspond to *cis*-like, while “P7” to *trans*-like sites.



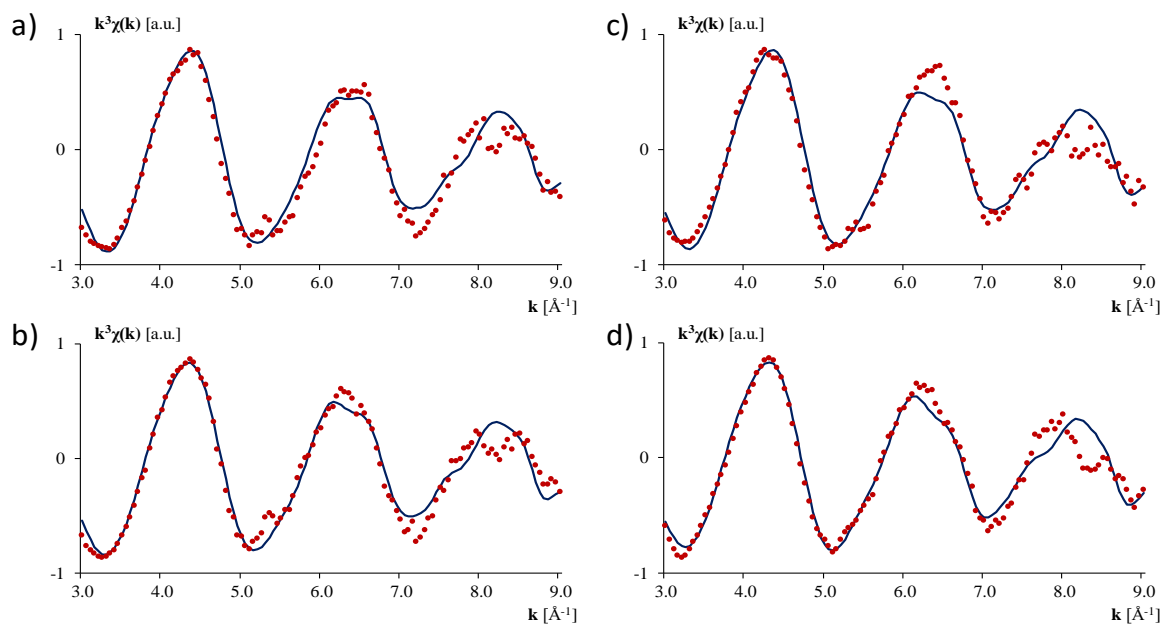
**Figure 2.** Views of bidentate inner-sphere sorption complexation models. The complexes referred as *strong-site* are shown in panel (a) and (b), while structures shown in panel c and d are referred as *weak-site*. In panel a and c, complexes at the (010) edge sites are shown, while view of surface complexes at the (110) edge can be seen in panel (b) and (d). Alumina octahedra are shown in green, silica tetrahedra are orange, iron is marked with pink color, while red and grey colors correspond to oxygen and hydrogen atoms, respectively. The different octahedral occupational sites can be distinguished by the different relative position of hydroxyl ( $\text{OH}^-$ ) groups (*cis-site* is marked with lighter, while *trans-site* is shown with darker colors). A more detailed explanation can be found in Table 1.



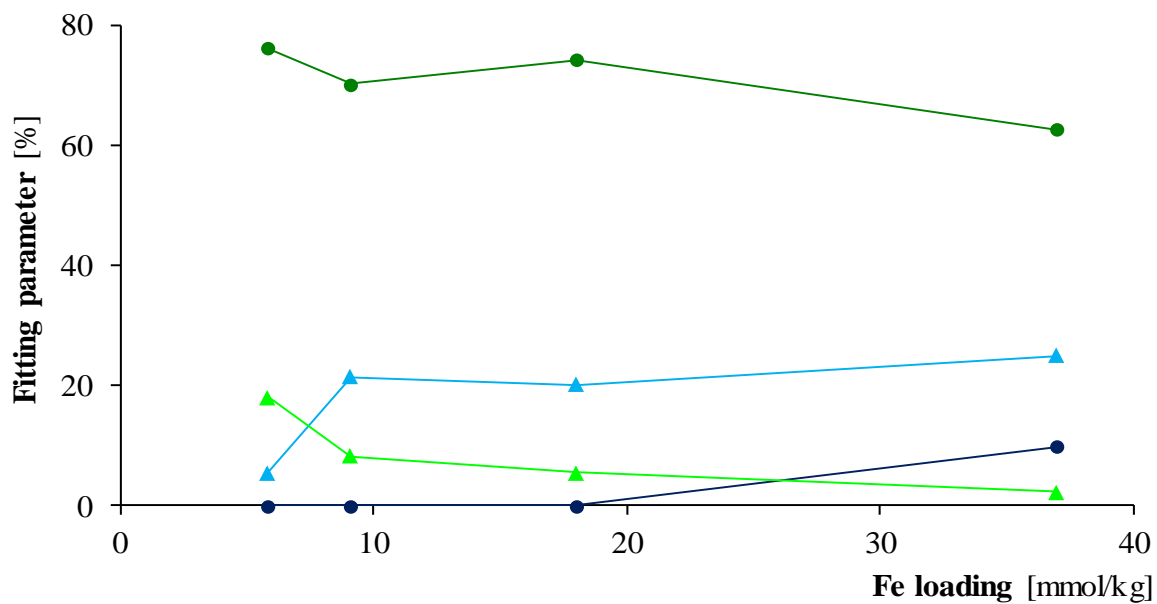
**Figure 3.** Relative energy for different structural position of Fe in montmorillonite structures with ferrous (panel a and b) and ferric (panel c and d) iron corrected for finite size effects, surface dipole and periodic boundary conditions (Supporting Information 1). Diagrams in panel a and c show relative energies of (010) edge sites, while diagrams in panel b and d correspond to (110) edge surface.  $\text{Fe}_{cis}$  is marked with lighter colors, while darker colors correspond to iron at the *trans*-site.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  positions (e.g. “P1”, “P2”) are marked in Figure 1. Original energy values are plotted in Figure S2 in Supporting Information 1. The lines are drawn just to guide the eyes.



**Figure 4.** Theoretical EXAFS spectra of montmorillonite edge surface models representing different Fe uptake mechanisms. Blue color corresponds to  $\text{Fe}^{2+}$ , while green color indicates  $\text{Fe}^{3+}$  surface complexes. EXAFS spectra with solid lines show *strong-site*, while dashed lines represent *weak-site* complexation models. Based on the legend, a more detailed explanation can be found in Table 1.



**Figure 5.** Experimental EXAFS spectra (red dots) and the best linear combination fits (solid lines). Contributions of individual compounds are summarized in Table S1 in Supporting Information 2. In the panels, the measured EXAFS spectra were collected from montmorillonite samples at different Fe loadings (panel a: 6 mmol/kg; panel b: 9 mmol/kg; panel c: 17 mmol/kg; panel d: 37 mmol/kg).



**Figure 6.** Contribution of the reference Fe complexes to the measured EXAFS as the function of adsorbed Fe loadings. Green colors represent Fe<sup>3+</sup>, blue colors show Fe<sup>2+</sup>. Darker colors and circles correspond to iron sorption on the *strong-site*, while lighter colors and triangles show sorption on *weak-site*.