Acidity of edge surface sites of montmorillonite and kaolinite

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ABSTRACT Acid-base chemistry of clay minerals is central to their interfacial properties, but up to now a quantitative understanding on the surface acidity is still lacking. In this study, with first principles molecular dynamics (FPMD) based vertical energy gap technique, we calculate the acidity constants of surface groups on (010)-type edges of montmorillonite and kaolinite, which are representatives of 2:1 and 1:1-type clay minerals, respectively. It shows that ≡Si-OH and ≡Al-OH$_2$OH groups of kaolinite have pKas of 6.9 and 5.7 and those of montmorillonite have pKas of 7.0 and 8.3, respectively. For each mineral, the calculated pKas are consistent with the experimental ranges derived from fittings of titration curves, indicating that ≡Si-OH and ≡Al-OH$_2$OH groups are the major acidic sites responsible to pH-dependent experimental observations. The effect of Mg substitution in montmorillonite is investigated and it is found that Mg substitution increases the pKas of the neighboring ≡Si-OH and ≡Si-OH$_2$ groups by 2~3 pKa units. Furthermore, our calculation shows that the pKa of edge ≡Mg-(OH)$_2$ is as high as 13.2, indicating the protonated state dominates under common pH. Together with previous adsorption experiments, our derived acidity constants suggest that ≡Si-O- and ≡Al-(OH)$_2$ groups are the most probable edge sites for complexing heavy metal cations.
1. Introduction

Clay minerals, the ubiquitous components in soils and sediments, play important roles in numerous natural interfacial processes (Bergaya et al., 2006). Acid-base chemistry of clay minerals is essential to their interfacial properties, e.g. surface reactivity and colloidal property (Adams and McCabe, 2006; Lagaly, 2006; Lagaly et al., 2006). Clay minerals are widely applied in many industrial and engineering fields and the acid-base chemistry is also important for the practical applications, such as in catalysis industry and in environment engineering (Adams and McCabe, 2006; Lagaly, 2006; Lagaly et al., 2006). However, a quantitative understanding on their surface acidity is still lacking. For example, classical molecular simulations that are often used to study mineral water interfaces still require detailed protonation/deprotonation states of surface sites as an input because classical simulations cannot produce such information (Croteau et al., 2009; Rotenberg et al., 2007).

The crystal structures of layered silicates are formed by stacking structural layers along the c-axis. Generally, there are two major types of structural layers: 1:1-type and 2:1-type (Bergaya and Lagaly, 2006). In the former, the structural layer consists of stacked tetrahedral sheet (Si-O tetrahedrons) and octahedral sheet (mainly Al-O octahedrons) while in the latter, the structural layer is composed of octahedral sheet sandwiched by two tetrahedral sheets. Kaolinite and montmorillonite are the most two representative members of 1:1 and 2:1-type clay minerals, respectively. Due to the layered structures of clay minerals, there are two typical surface structures, namely, basal surfaces (i.e. interlayer surfaces) and edge surfaces (i.e. broken surfaces) (Schoonheydt and Johnston, 2006).

Montmorillonite has one type of basal surface (i.e. siloxane surface) and kaolinite has two: siloxane surface and hydroxyl surface. As extensive studies have been performed, the properties of the basal surfaces have been well documented (Schoonheydt and Johnston, 2006). Siloxane surfaces normally behave as adsorbing region for foreign molecules such as waters and cations, e.g. (Anderson et al., 2010; Liu and Lu, 2006; Vasconcelos et al., 2007). The OHs of hydroxyl basal surfaces of kaolinite can interact with foreign molecules via H-bonding (Tunega et al., 2002a) but they have minimal chemical reactivity and almost have no contribution to the acid-base chemistry of kaolinite (Brady et al., 1996; Schoonheydt and Johnston, 2006; Sposito, 1984). Therefore, the properties of clay basal surfaces are
considered to be pH-independent e.g. (Schoonheydt and Johnston, 2006; Vasconcelos et al., 2007). In contrast, edge surfaces have more complicated structures and more subtle chemical properties, which are generally pH-dependent. At these surfaces, many dangling bonds are present (e.g. \( \equiv \text{Al–O} \), \( \equiv \text{Si–O} \) and \( \equiv \text{Mg–O} \)) and under ambient conditions, they are usually saturated by chemically adsorbed water (Lagaly, 2006). The edge surface sites are normally amphoteric: as environmental pH increases, the ligand gradually changes from \( \text{–OH}_2 \) to \( \text{–O} \) via \( \text{–OH} \). This behavior leads to the pH-dependent interfacial properties, such as complexing of heavy metal cations and organics (Lagaly, 2006).

Acid-base chemistry of edge surfaces is very difficult to study by using current experimental techniques. While in situ techniques (e.g. spectroscopic methods) are still unable to provide quantitative estimates, many macroscopic measurements such as titration have been carried out for phyllosilicates including kaolinite and montmorillonite, e.g. see the recent studies of (Gu and Evans, 2008; Gu et al., 2010) and references therein. In those studies, titration curves are fitted based on empirical adsorption models and hence the proton binding constants can be derived. Although a large body of data have been reported, the assignment of individual pKas to different surface groups is impossible. Therefore, the accurate molecular level picture of acid chemistry of clay minerals is still unclear up to now, e.g. the identities of active edge groups and their pristine pKas.

The study of interfacial structures and acidity was a challenge for first principles methods. By combining static quantum mechanical calculations and bond valence theory, some researchers (Bickmore et al., 2003; Bickmore et al., 2006; Churakov, 2006) derived acidity constants of edge groups of pyrophillite (a neutral end member of 2:1 type phyllosilicates). The major shortcoming of such approach is the oversimplification of solvent effects, which introduces errors to the interfacial properties.

First principles molecular dynamics (FPMD) or density functional theory based molecular dynamics (DFTMD) has been playing more and more important roles in research on mineral interface systems (Boulet et al., 2006; Cygan et al., 2009; Marx and Hutter, 2009; Skelton et al., 2011; Suter et al., 2009; Tunega et al., 2011). By combining electronic structure calculation and molecular dynamics, FPMD treats the solute and solvent at the same theoretical level. FPMD has been used to investigate clay
In previous studies, FPMD simulations were employed to investigate the structures of edge-water interfaces for kaolinite and montmorillonite (Churakov, 2007; Liu et al., 2012a; Liu et al., 2012b). According to these studies, the microscopic interfacial structures are revealed and it is found that around point of zero charge, stable edge sites include $≡$Si-OH, $≡$AlOH$_2$OH and $≡$Mg-(OH)$_2$. FPMD based vertical energy gap method makes it feasible to calculate pKas of interfacial groups (Costanzo et al., 2011; Sulpizi and Sprik, 2008). This method has been successfully tested on many compounds including both molecules (Cheng et al., 2009; Costanzo et al., 2011; Mangold et al., 2011; Sulpizi and Sprik, 2008) and surface groups of minerals including rutile (Cheng and Sprik, 2010), quartz (Sulpizi et al., 2012) and pyrophillite (Tazi et al., 2012). Comparisons on acids and bases spanning 20 pKa units show that an accuracy of 2 pKa units can be achieved (Cheng et al., 2009; Costanzo et al., 2011; Sulpizi and Sprik, 2008; Sulpizi and Sprik, 2010).

In this study, we employ the vertical energy gap technique to calculate the acidity constants of (010)-type edge sites of montmorillonite and kaolinite. We collect experimentally derived acidity data in literature as extensively as we can. The comparison shows that the calculated pKas of $≡$Si-OH and $≡$Al-OH$_2$OH groups are overall in consistence with the experimental ranges of deprotonation constants and therefore, they are assigned to the major edge acidic sites. The effects of Mg substitution in montmorillonite are also studied. By integrating previous adsorption experiments, our derived acidity constants imply that the major edge sites for complexing heavy metal cations are $≡$Si-O and $≡$Al-(OH)$_2$.

2. Methodology

2.1. Models

The (010)-type interface models of kaolinite and montmorillonite (Fig. 1) are taken from our previous studies (Liu et al., 2012a; Liu et al., 2012b). Their chemical formulae are Al$_4$Si$_4$O$_{10}$(OH)$_8$ and Li$_{0.5}$[Si$_8$[Al$_3$Mg$_0.5$]O$_{20}$(OH)$_4$ respectively, which are derived from the reports of Bish (Bish, 1993) and Viani et al. (Viani et al., 2002). The edge surface model is cut from the unit cell and repeated along the a axis (x direction in Fig. 1) and each simulated model contains two unit cells. For the initial edge surface
models, the dangling $≡\text{Si-O}$ and $≡\text{Al-O}$ bonds are all saturated by protons. These edge models are placed in 3D periodically repeated orthorhombic cells with the sizes of 10.34Å$\times$30.0Å$\times$7.39Å and 10.36Å$\times$31Å$\times$8.98Å for kaolinite and montmorillonite, respectively. These boxes have a solution space of about 20 Å in the direction vertical to the edge surfaces (y direction in Fig. 1). The solution regions of kaolinite and montmorillonite models contain 45 and 50 water molecules respectively. That corresponds to a density of 0.98 g/ml, close to the density of bulk water at ambient conditions. Kaolinite and montmorillonite systems contain totally 215 and 244 atoms, respectively.

Our previous study shows that for Mg cations at edge surface, only the 6-fold coordination is stable i.e. the edge site is $≡\text{Mg-(OH}_2\text{)}_2$ (Liu et al., 2012a). For Al at the edges of the two clay minerals, both the 6-fold and 5-fold coordinations are possible with the former being more stable, and therefore, only the 6-fold cases are investigated in this study. The investigated proton donating groups include $≡\text{Si-OH}$, $\text{OH}_2$ ligand of $≡\text{Al-OHOH}_2$ and $≡\text{Mg-(OH}_2\text{)}_2$ (for montmorillonite), and proton accepting sites are oxygen of $≡\text{Si-OH}$ and OH of $≡\text{Al-OHOH}_2$ (Liu et al., 2012a; Liu et al., 2012b). For proton accepting sites, we calculate the pKas of their respective conjugate acids, that is, $≡\text{Si-OH}_2$ and $\text{OH}_2$ of $≡\text{Al-OH}_2\text{OH}_2$. To reveal the effects of Mg substitution, two Si sites denoted as Si1 and Si2 are calculated: Si2 connects with both Mg and Al while Si1 connects with Al only (Fig. 1).
Figure 1. The used edge surface models of kaolinite and montmorillonite. The solution regions are on $y$ direction. O = red, H = white, Si = grey, Mg = green, and Al = pink. In the montmorillonite model, Si2 connects with Mg via a bridge oxygen atom while Si1 connects with Al.

Our calculations indicate that $\equiv\text{Si-OH}$ and $\equiv\text{Al-(OH)}_2$ groups have similar pKas and they are potential heavy metal cation complexing sites (see section 3.4). By taking $\text{Fe}^{2+}$ as an example, we perform simulations of $\text{Fe}^{2+}$ adsorbed on montmorillonite. For these simulations, the deprotonated group, i.e. $\equiv\text{Si-O}$- or $\equiv\text{Al-(OH)}_2$ serves as the complexation site. The protons are removed from the initial surface groups (i.e. $\equiv\text{Si-OH}$ or $\equiv\text{Al-(OH)}_2$), and then $\text{Fe}^{2+}$ cation is placed about 2.5 Å away from the O sites (this distance is taken from the $\text{Fe}^{2+}-\text{O}_{\text{water}}$ RDF in aqueous solutions) (Herdman and Neilson, 1992).

2.2. First principles MD

The simulations are performed using CP2K/QUICKSTEP package (VandeVondele et al., 2005a). The electronic structures are calculated with density functional theory, which is implemented based on a
hybrid Gaussian plane wave (GPW) approach (Lippert et al., 1997). BLYP functional is used for the exchange-correlation (Becke, 1988; Lee et al., 1988). Goedecker-Teter-Hutter pseudopotentials (Goedecker et al., 1996) are employed to avoid calculations of core configurations. The plane wave kinetic energy cut off is set to be 280 Ry. For the simulations of Fe$^{2+}$-adsorbed systems, spin polarization calculation is performed with the high-spin state of Fe$^{3+}$.

Born-Oppenheimer molecular dynamics (BOMD) simulations are carried out with a wave function optimization tolerance of 1.0E−6 that allows a time step of 0.5 fs with reasonable energy conservation. The temperature is controlled at 330 K with the Nosé-Hoover chain thermostat. This temperature was used to avoid the glassy behaviour of BLYP liquid water as found at lower temperatures (VandeVondele et al., 2005b). For each system, an equilibration simulation is firstly performed for at least 2.0 ps and after that, the production run is carried out for 8.0 ps ~ 20.0 ps.

### 2.3. pKa calculations

The half-reaction scheme of the vertical energy gap method is employed to calculate pKas (Cheng et al., 2009; Costanzo et al., 2011). With this scheme, the proton of the acid (denoted as AH) is gradually transformed into a dummy (i.e. a classical particle with no charge). The free energy of the transformation for the acid is calculated with a thermodynamic integration technique:

\[
\Delta \eta E_{AH} = \int_0^1 d\eta \left\langle \Delta_{\eta} E_{AH} \right\rangle_{\eta}
\]

(1)

Here \( \Delta_{\eta} E \) is the vertical energy gap, defined as the difference of potential energies of the reactant state and the product state, which is calculated from the MD trajectories.

The averages of vertical energy gaps (\( \Delta_{\eta} E \)) are calculated over the restrained mapping Hamiltonian:

\[
H_\eta = (1-\eta)H_k + \eta H_\rho
\]

(2)

Where \( \eta \) is the coupling parameter which is increased from 0 (reactant) to 1 (product).

In practice, the Simpson rule is applied to evaluate the integral in Eq. 1, which requires the simulations at \( \eta = 0, 0.5 \) and 1, respectively:
A restrained harmonic potential \( V_r \) is applied to keep the dummy atom in a location which resembles that of the acid proton of the reactant state:

\[
V_r = \frac{1}{2} \sum_{\text{bonds}} k_d (d - d_0)^2 + \frac{1}{2} \sum_{\text{angles}} k_\alpha (\alpha - \alpha_0)^2 + \frac{1}{2} \sum_{\text{dihedrals}} k_\chi (\chi - \chi_0)^2
\]

This potential consists of the bonding, angle bending and torsions terms whose equilibrium values are \( d_0 \), \( \alpha_0 \) and \( \chi_0 \), respectively. The equilibrium values used for each surface group are obtained from the prior simulations without restraints and the restraining parameters have been selected according to the prescriptions of our previous studies (Cheng et al., 2009; Sulpizi and Sprik, 2008). Details of \( V_r \) are collected in Table 1.

The same procedure is applied to transform a proton of a hydronium located in the solution region into a dummy and the free energy of this transformation is denoted as

\[
\int_0^1 d\eta \left\langle E_{\text{H}_3\text{O}^+} \right\rangle_m.
\]

The overall formula for pKa calculation reads:

\[
2.30 k_B T \ln k_a = \int_0^1 d\eta \left\langle E_{\text{H}_3\text{O}^+} \right\rangle_m - \int_0^1 d\eta \left\langle E_{\text{H}_2\text{O}} \right\rangle_m + k_B T \ln [c^0 \Lambda_H^3].
\]

\( c^0 = 1 \text{mol/L} \) is the unit molar concentration and \( \Lambda_H \) is the thermal wavelength of proton (Costanzo et al., 2011). The third term \( k_B T \ln [c^0 \Lambda_H^3] \) accounts for the translational entropy generated by the acid dissociation and it is approximated by the chemical potential of a free proton at standard concentration. This term is equal to \(-0.19 \text{ eV}\) or equivalently \(-3.2 \text{ pK} \) units.

Table 1. The parameters used in the harmonic potentials (Eq. 4) restraining the dummy protons for kaolinite and montmorillonite. \( \text{H}_d \) means the dummy proton. \( n_d \), \( n_\alpha \) and \( n_\chi \) stand for the numbers of the restrained bonds, angles and torsions, respectively. Equilibrium bond lengths \( (d_0) \) are in Bohr and equilibrium angles \( (\alpha_0) \) and torsions \( (\chi_0) \) are in radians. All the coupling constants are in a.u.
<table>
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<tr>
<th>Acids</th>
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<th>k_α</th>
<th>n_γ</th>
<th>α_0</th>
<th>k_γ</th>
<th>n_δ</th>
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<td></td>
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<tr>
<td>≡Si-OHH_d</td>
<td>2</td>
<td>1.92</td>
<td>1.0</td>
<td>2</td>
<td>1.87(H-O-H_d)</td>
<td>0.1</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>≡Si-OH_d</td>
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<td>1</td>
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<td>1</td>
<td>0.52</td>
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<td>2</td>
<td>1.85(H-O-H_d)</td>
<td>0.1</td>
<td>0</td>
<td>-</td>
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</tr>
<tr>
<td>≡Al-OH_d</td>
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<td>1.85(H-O-H_d)</td>
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<td>H_2H_dO'</td>
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<tr>
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<td>0.1</td>
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<tr>
<td>H_2H_dO'</td>
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<td>2</td>
<td>1.94(H-O-H_d)</td>
<td>0.1</td>
<td>0</td>
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</tbody>
</table>

3. Results and discussion
184 3.1. Kaolinite

185

186 Figure 2. Accumulating averages of vertical energy gaps for groups on kaolinite (010) surface.

187 Table 2 Free energies (in eV) and pKas of edge surface groups of kaolinite.

<table>
<thead>
<tr>
<th>Groups</th>
<th>$\equiv$Si-OH</th>
<th>$\equiv$Al-OH$_2$OH</th>
<th>$\equiv$Al-OH$_2$OH$_2$</th>
<th>H$_2$O$^+$</th>
</tr>
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<tbody>
<tr>
<td>$\Delta A$</td>
<td>17.23±0.03</td>
<td>17.16±0.01</td>
<td>16.83±0.02</td>
<td>16.63±0.03</td>
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<tr>
<td>pKa</td>
<td>6.9±1.0</td>
<td>5.7±0.7</td>
<td>5.28 (≡AlOH)</td>
<td>8.23 (≡SiOH)</td>
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188 The error in pKa is calculated as the sum of the error in the deprotonation free energy of each surface group and of the error in the deprotonation free energy of the hydronium. Statistical errors in deprotonation free energies are calculated as the semi-difference between the values using the first half or the second half of the trajectory only.

189

190 Table 3 Acidity constants of kaolinite derived from experiments. SOH denotes proton active sites.

<table>
<thead>
<tr>
<th>Surface groups</th>
<th>$\equiv$SOH$_2^+$ $\rightarrow$ $\equiv$SOH$+$ $\rightarrow$ $\equiv$SO$+$ $\rightarrow$ $\equiv$SO$+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Schindler et al., 1987)</td>
<td>-4.37</td>
</tr>
<tr>
<td>(Brady et al., 1996)</td>
<td>2.33 (≡AlOH$_2^+$)</td>
</tr>
<tr>
<td>(Angove et al., 1998)</td>
<td>-3.24</td>
</tr>
</tbody>
</table>
Figure 2 illustrates the accumulating averages of vertical energy gaps for sites on kaolinite (010) surface and Table 2 lists the derived free energy values and pKas. The statistical error (Table 2) in each pKa is obtained as the sum of the error in deprotonation free energy of each surface site and of the error in deprotonation calculation of the hydronium. The error in each deprotonation free energy is calculated as the semi-difference between the values using the first half or the second half of the trajectory. It can be seen that these errors are in 0.7~1.0 pKa units and such errors are of the same order as in our previous study of the acidity of quartz (Sulpizi et al., 2012).

Table 3 collects the experimentally fitted acidity constants in literature, where one can see that most studies employed 1-site model except the study of Brady et al (Brady et al., 1996). The calculated pKas of ≡Si-OH and OH₂ of ≡Al-OH₂OH are very close: 6.9 vs 5.7. These values coincide with the experimentally fitted acidity range based on 1-site model: 5.28~9.18 (see Table 3). This agreement indicates that ≡Si-OH and the OH₂ of ≡Al-OH₂OH correspond to the proton-donating sites detected in titration measurements.

≡Si-OH₂ has a pKa of -6.7, about 2 pKa units smaller than the lower limit of the experimental range of -4.63~3.24 (Table 3). The pKa of ≡Al-(OH₂) is predicted to be 0.2, which does not have a correspondence in the experimental results. Similar discrepancy has been found in the case of montmorillonite (see section 3.2) and these are discussed for the two minerals in section 3.3.

### 3.2. Montmorillonite
Figure 3. Accumulating averages of vertical energy gaps for groups of montmorillonite (010) surface.

Table 4 Free energies (in eV) and pKas of edge surface groups of montmorillonite.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Si1-OH / Si1-OH₂</th>
<th>Si2-OH / Si2-OH₂</th>
<th>Al-OH₂OH / Al-OH₂OH₂</th>
<th>Mg-OH₂OH₂</th>
<th>H₃O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔA</td>
<td>16.77±0.02</td>
<td>16.98±0.01</td>
<td>16.83±0.04</td>
<td>17.12±0.01</td>
<td>16.15±0.02</td>
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<tr>
<td>pKa</td>
<td>7.0±0.7</td>
<td>10.8±0.5</td>
<td>8.3±1.0</td>
<td>13.2±0.5</td>
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</table>

The error in pKa is calculated as the sum of the error in the deprotonation free energy of each surface group and of the error in the deprotonation free energy of the hydronium. Statistical errors in deprotonation free energies are calculated as the semi-difference between the values using the first half or the second half of the trajectory only.

Table 5. Acidity constants of montmorillonite derived from experiments. SOH stands for proton active surface sites.

<table>
<thead>
<tr>
<th>Clay source</th>
<th>=SOH₂⁺→=SOH+H⁺</th>
<th>=SOH→=SO+H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Schindler et al., 1987) Wyoming</td>
<td>-8.16 (=SiOH₂)</td>
<td>8.71 (=SiOH) 5.77 (=SiOH)</td>
</tr>
<tr>
<td>(Charlet et al., 1993) SWy-1</td>
<td>-4.80</td>
<td>6.96</td>
</tr>
<tr>
<td>(Wanner et al., 1994) -</td>
<td>-5.4</td>
<td>6.7</td>
</tr>
<tr>
<td>(Zachara and Smith, 1994) Wyoming</td>
<td>0.95 (=SiOH₂)</td>
<td>6.65 (=SiOH)</td>
</tr>
</tbody>
</table>
Figure 3 shows the accumulating averages of vertical energy gaps for montmorillonite-(010) sites. Table 4 lists the calculated free energies and pKas, where one can see that similar to the results of kaolinite (Table 2), the statistical errors are within 1.0 pKa unit. Due to the much more complex compositions, montmorillonite has more complicated acid chemistry than kaolinite. As shown in Table 5, previous experimental works on montmorillonite present obviously bigger variations than that of kaolinite: from 4.8 to 11.5 for $\equiv$SOH sites and from -10.5 to 0.95 for $\equiv$SOH$_2$ sites. Even with the similar samples, different acidity constants are obtained by different groups, e.g. for SWy-2 clay, Barbier et al (2000) derived 5.26 for $\equiv$SOH while Tombacz et al. (2004) reported 7.9.
Just as the case of kaolinite, there are more 1-site based fitting studies than multi-site works for montmorillonite. For the 1-site based studies, the pKa range for the deprotonation constants of $≡$S-OH site is 5.26–8.5. For the multi-site based works, the pKa range is very similar: 4.8–8.71 given that the two high values, 10.5 (Bradbury and Baeyens, 1997) and 11.5 (Zachara and Smith, 1994), are not included.

From the derived data set in Table 4, one can see that the pKas of $≡$Si1-OH and $≡$Al-OH$_2$ of $≡$Al-OH$_2$OH, i.e. 7.0 and 8.3, are in good consistence with the experimental range. These two values also agree with the pKas of their counterpart edge sites (6.8 and 7.6 for $≡$Si-OH and $≡$Al-OH$_2$OH respectively) reported in a recent study (Tazi et al., 2012), where the neutral clay framework (i.e. without substitution) is investigated. In contrast, $≡$Si2-OH site where Si atom connects with Mg atom via one bridge oxygen (Fig. 1) has a significantly higher pKa, 10.8. This indicates that the effect of isomorphic substitution on the acidity of edge site is relatively short ranged.

$≡$Mg-(OH)$_2$$_2$ has a pKa of 13.2, only 2 pKa units lower than pKw, which agrees with the fact that Mg$^{2+}$ is a poor hydrolyzing cation (pKa=11.4) (Westermann et al., 1986). This pKa indicates that under common pH range, all of $≡$Mg-(OH)$_2$$_2$ groups are protonated and do not take part in common acid titration processes. Table 4 shows that Mg substitution increases the pKas of adjacent $≡$Si-OH and $≡$Si-OH$_2$ groups: $≡$Si2-OH and $≡$Si2-OH$_2$ have pKa values of 10.8 and -10.9, which are over 3 pKa units higher than those of Si1 site. The pKa of $≡$Si2-OH is close to the values of the weak sites of pKas, 10.5 and 11.5 as mentioned above (Zachara and Smith, 1994; Bradbury and Baeyens, 1997). This implies that the high pKa values may originate from Mg substitutions, which are ubiquitous in montmorillonite.

The pKa of $≡$Al-(OH)$_2$$_2$ site is predicted to be 3.1 (Table 4), which may correspond to the low pKa constants in Table 5, i.e. 4.8 (Tournassat et al., 2004), 5.26 (Barbier et al., 2000) and 5.5 (Kraepiel et al., 1999).

OH$_2$ ligands of $≡$Al-OHOH$_2$ and $≡$Al-(OH)$_2$$_2$ have pKa values of 8 and 3.1, respectively (Table 4) and these values are 2–3 pKa units higher than those of $≡$Al-(OH)$_2$$_2$ site in kaolinite. For this group, the difference between the two minerals is that in kaolinite, the edge Al atom connects with two OHs on the basal surface whereas in montmorillonite, the Al atom connects with two bridge oxygen bonding with Si
in tetrahedral layers (see Fig. 4). In a view of electronegativity, bridge oxygen is more negative than the oxygen of the surface OHs in kaolinite: Mulliken population analyses show that the bridge O has an average partial charge of -1.15e while the OH oxygen atom has -1.05e (Cygan et al., 2004). This eventually leads to that the OH$_2$ ligand in montmorillonite is less acidic than that OH$_2$ in kaolinite.

![Figure 4. Models of (010)-type edge surfaces highlighting the Al-O octahedrons. O = red, H = white, Si= grey and Al = cyan.](image)

### 3.3. Implication for titration experiments

It was thought that the comparison between ab initio predicted and titration derived acidity constants is not possible and therefore previous studies made comparisons with results from bond valence theory rather than experiments (Bickmore et al., 2003; Tazi et al., 2012). However, as discussed above, one finds good agreement between the pK$_a$s of ≡Si-OH and ≡Al-OHOH$_2$ sites and experimental values. For each clay mineral, the two acidic sites (i.e. ≡Si-OH and ≡Al-OHOH$_2$) have very close pK$_a$ values: 6.9 vs 5.7 for kaolinite and 7.0 vs 8.3 for montmorillonite, that is, the difference is within only 1.3 pK$_a$ units. Although montmorillonites have considerable Mg substitutions, the calculated pK$_a$ for ≡Mg-(OH)$_2$, 13.2, is significantly beyond the common experimental pH range (3~9) and therefore these groups do not contribute to proton dissociation. These data explain why the 1-site based approach generally works well in numerical fitting of titration curves for both minerals. On the other hand, one can easily understand that due to the similar deprotonation constants, they cannot be distinguished through the titration curve fitting approach.

In contrast, for their conjugate acids (i.e. ≡Si-OH$_2$ and ≡Al-(OH)$_2$)$_2$, it is not easy to make direct comparison with experiments. For montmorillonite, the calculated values of ≡Si1-OH$_2$/≡Si2-OH$_2$ and
\( \text{Al(OH}_2\text{)}_2 \) are -14.3/-10.9 and 3.1, respectively and for kaolinite, the results are -6.7 and 0.2 respectively. These \( \equiv \text{Si-OH}_2 \) pK\( \text{as} \) are in line with the strong acid characteristics of \( \equiv \text{Si-OH}_2 \) site (Sulpizi et al., 2012). One can see that the p\( \text{Kas} \) of these conjugate acids envelope the fitted acidity ranges of strong acid sites (i.e. \( \equiv \text{Si-OH}_2 \) sites: -4.63~2.33 for kaolinite in Table 3 and -10.5~0.95 for montmorillonite in Table 5). One important reason is that they have relatively bigger differences in p\( \text{Kas} \) and therefore, when one tries to fit the titration data with 1-site model, error is inevitable to be included.

Another origin for this discrepancy is the lack of titration data at the low pH end. Almost all titration measurements are performed over the common pH, i.e. 3~9 and the limited pH range makes it hard to investigate the sites of low p\( \text{Kas} \), because those sites only show significant proton binding in very low pH range. Unfortunately, one serious problem with low pH is the acid induced mineral dissolution, which is very hard to circumvent in practice and therefore, the experimental data in low pH range are in bad need.

### 3.4. Implication for heavy metal cations complexing

Adsorption of heavy metal cations on clay minerals is an important chemical process controlling their migration and bioavailability in soils and aquifers. On the other hand, clays are applied as environmental materials to fix toxic heavy metals. Therefore, this topic has attracted significant attentions (Churchman et al., 2006). Numerous experiments have shown that adsorption of heavy metal cations on clay minerals consists of two stages as pH increases: cation exchange and edge complexing steps, e.g. ((Gu and Evans, 2008; Gu et al., 2010) and references therein). The first step happens between foreign cations and interlayer exchangeable cations, which is pH independent. The second step happens on edge surfaces and it is obviously pH dependent. It is generally accepted that the pH for the start of edge complexing step is approximately 5~7. For example, for Zn\( ^{2+} \) adsorption on montmorillonite and kaolinite, Ikhsan obtained 7.0 for the starting pH for edge complexing stage (Ikhsan et al., 2005); Schultz and Grundl show that the starting pH for Fe\( ^{2+} \) complexation on montmorillonite is 6.75 (Schultz and Grundl, 2004); Gu et al obtained about 6.0 for Ni\( ^{2+} \), Cd\( ^{2+} \), Cu\( ^{2+} \),
Zn\(^{2+}\) on montmorillonite (Gu et al., 2010) and around 5.0 for kaolinite (Gu and Evans, 2008). Although many experimental works have been carried out, the accurate adsorption mechanism is still unclear.

Our calculated acidity constants (Table 2 and Table 4) show that as pH increases to be above 5.0, the deprotonated forms of \(\equiv\text{Si-OH}\) and \(\equiv\text{Al-OHOH}_2\) gradually become predominant. Therefore, the edge sites (i.e. \(\equiv\text{Si-O}\) and \(\equiv\text{Al-(OH)}_2\)) become potential sites for heavy metal cations to form inner-sphere complexes. By taking Fe\(^{2+}\) as an example, the simulations show that monodentate and bidentate Fe\(^{2+}\)-complexes form on \(\equiv\text{Si-O}\) and \(\equiv\text{Al-(OH)}_2\) sites respectively, i.e. Si-O-Fe(H\(_2\)O)\(_5\) and Al-(OH)\(_2\)-Fe(H\(_2\)O)\(_4\) (Fig. 5). In the simulation periods of over 20 ps, these complexes hold stable. For Si-O-Fe(H\(_2\)O)\(_5\), the average Fe\(^{2+}\)-O bond length is about 2.02 Å, which is consistent with our previous study of \(\equiv\text{Si-O-Fe}^{2+}\) complex at the edge of neutral clay frameworks (Liu et al., 2012c). For Al-(OH)\(_2\)-Fe(H\(_2\)O)\(_4\) complex, the two Fe\(^{2+}\)-O lengths are around 2.08 Å but the two Al-O bonds should strengthen the complexing.

There are still many open questions that need to be addressed to understand acid-base chemistry of clay minerals at a molecular level, and such a fundamental understanding is most likely to be achieved through the synergy between experiments, modeling and atomistic simulations. By combining FPMD derived pKas and the modeling approach (Bourg et al., 2007), the titration curve could be reproduced for clay minerals and can be compared with the experimental data. On the other hand, FPMD simulations are able to provide precise structural data which can be used for fitting EXAFS (Extended X-ray absorption fine structure) measurements and furthermore, FPMD based free-energy calculation methods (e.g. metadynamics (Laio and Parrinello, 2002), constrained MD (Sprik, 2000; Sprik and Ciccotti, 1998)) can give reasonable estimates of the free-energy surfaces of complexes (Churakov and Daehn, 2012), e.g. adsorption free energies of complexes on silanol and aluminol sites and thus their relative populations. This will be addressed in our future research.
4. Summary

By using the recently developed FPMD based vertical energy gap method, we derive the acidity constants of (010)-type edge surfaces of montmorillonite and kaolinite. It shows that \( \equiv \text{Si-OH} \) and \( \equiv \text{Al-OH}_2\text{OH} \) groups of kaolinite have pKas of 6.9 and 5.7 and those sites of montmorillonite have pKas of 7.0 and 8.3, respectively. For each mineral, the calculated acidity constants coincide with the acidity ranges derived from titration curve fitting. Therefore, the edge acidic sites responsible to pH dependent phenomena are assigned to these two surface groups. Because for both minerals, \( \equiv \text{Si-OH} \) and \( \equiv \text{Al-OH}_2\text{OH} \) sites have very close pKas, they are almost indistinguishable in titration experiments. For the ubiquitous Mg substitution in montmorillonite, it is found that \( \equiv \text{Mg-(OH)}_2 \) is the usual form under common pH ranges due to its high pKa of 13.2 and Mg substitution increases the pKas of the neighboring \( \equiv \text{Si-OH}/\equiv \text{Si-OH}_2 \) groups by 2–3 pKa units. Together with previous adsorption experiments, our derived acidity constants imply that the deprotonated forms of \( \equiv \text{Si-OH} \) and \( \equiv \text{Al-OH}_2\text{OH} \) (i.e. \( \equiv \text{Si-O} \) and \( \equiv \text{Al-(OH)}_2 \) groups) are the most probable sites for complexing heavy metal cations.
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References


