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Atomic-scale structures of interfaces between phyllosilicate edges and water

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Abstract

We report first-principles molecular dynamics (FPMD) studies on the structures of interfaces between phyllosilicate edges and water. Using FPMD, the substrates and solvents are simulated at the same first-principles level, and the thermal motions are sampled via molecular dynamics. Both the neutral and charged silicate frameworks are considered, and for charged cases, the octahedral (Mg for Al) and tetrahedral (Al for Si) substitutions are taken into account. For all frameworks, we focus on the commonly occurring (010)- and (110)-type edge surfaces.

With constrained FPMD, we calculated the free energy of the leaving processes of coordinated water of octahedral cations; therefore, the coordination states of those edge cations are determined. For (010)-type edges, both the 5- and 6-fold coordination states of Al are stable and occur with a similar probability, whereas only the 5-fold coordination is stable for Mg cations. For (110)-type edges, only the 6-fold states of Al cations are stable. However, for Mg cations, both coordination states are stable. In the 5-fold case, the solvent water molecules form H-bonds with the bridging oxygen atoms (i.e., $\equiv\text{Mg}-\text{O}-\text{Si}\equiv$). The free energy results indicate that there should be a considerable number of 5-fold coordinated octahedral sites (i.e., $\equiv\text{Mg}-\text{OH}/\equiv\text{Al}-\text{OH}$) at the interfaces. The interfacial structures and acid/base groups were determined by detailed H-bonding analyses. (1) *Bridging oxygen sites*. For (010) edges, the bridging oxygen atoms are not effective proton-accepting sites because they are inaccessible from the solvent. For (110) edges, the oxygen atoms of neutral and octahedrally substituted frameworks (i.e., $\equiv\text{M}-\text{O}-\text{Si}\equiv$ for $\text{M}=\text{Al}/\text{Mg}$) are proton-accepting sites. For T-sheet substituted cases, the bridging oxygen site becomes a proton-donating group (i.e., $\equiv\text{Al}-\text{OH}-\text{Si}\equiv$) through the capture of a proton. (2) *T-sheet groups*. All T-sheet edge groups are $\equiv\text{M}-\text{OH}$ ($\text{M}=\text{Si}/\text{Al}$) and act as both proton donors and acceptors. (3) *O-sheet groups*. For (010) edges with 6-fold Al, the active surface groups include $\equiv\text{Al}-(\text{OH})(\text{H}_2\text{O})$ and $\equiv\text{Al}-(\text{OH})_2$, whereas for Mg cations, the edge group is $\equiv\text{Mg}-(\text{OH})_2$. For 5-fold coordination, the active groups are $\equiv\text{Al}-\text{OH}$. At (110) edges, proton-donating sites include $\equiv\text{Al}-\text{OH}$, $\equiv\text{Al}-\text{OH}_2$ and $\equiv\text{Mg}-\text{OH}_2$ groups. Overall, our results reveal the significant effects of isomorphic substitutions on the interfacial structures, and the models provide a molecular-level basis for understanding relevant interfacial processes.

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1. INTRODUCTION

Phyllosilicates of the 2:1 type are ubiquitously distributed in soils and sediments and play important roles in many geological and (bio)geochemical processes. Understanding phyllosilicate–water interfaces is critical to understanding

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many processes in nature, such as adsorption, crystallization, and the transport and fixation of elements (Bergaya et al., 2006). This information also provides important guidelines for the syntheses of advanced hybrid materials and for environmental and industrial applications of phyllosilicates (Adams and McCabe, 2006; Lagaly et al., 2006).

The interface chemistry of layered silicates is very complex, mainly due to their surface structures. The crystal structure of 2:1-type phyllosilicates is formed by stacking “T–O–T” layers along the *c*-axis; these layers are composed of an octahedral sheet (O-sheet) between two tetrahedral sheets (T-sheet) (Brindley and Brown, 1980; Bleam, 1993). Because of their layered structures, the surfaces of phyllosilicates are commonly classified as basal surfaces (i.e., (001)) and edge surfaces or broken surfaces (such as (010), (110)) (White and Zelazny, 1988; Bleam, 1993). Extensive studies have detailed the structures and properties of basal surfaces. The surfaces have been shown to be terminated with siloxanes, the Si–O rings of which are important adsorbing sites for many cations (Cygan et al., 2004, 2009; Bergaya et al., 2006; Liu and Lu, 2006; Liu et al., 2007, 2008a,b; Anderson et al., 2010). In contrast, the edge surfaces have more complex structures and thus more subtle properties. At these surfaces, many broken bonds exist, and under ambient conditions, they are usually saturated by chemically adsorbed water molecules (Lagaly, 2006). These edge groups are usually amphoteric, which is responsible for the pH-dependent behavior of many interfacial processes, such as cation complexation. Ubiquitous isomorphic substitutions further enhance the complexity of phyllosilicates’ interfacial chemistry (Lagaly, 2006).

Currently, the most accurate molecular-level pictures of edge–water interfaces remain incomplete, which significantly limits the understanding of relevant interfacial processes. Moreover, it is still unfeasible to investigate these interfaces, even with the advanced EXAFS (Extended X-ray Absorption Fine Structure) technique (Denecke, 2006). This is because of the irregularity of broken surfaces and the very similar bond lengths of surface groups, such as $\equiv\text{Al}-\text{O}$, $\equiv\text{Si}-\text{O}$ and $\equiv\text{Mg}-\text{O}$. Furthermore, the protonation states of edge groups are very difficult to determine.

Using PBC (periodic bond chain) theory (Hartman and Perdock, 1955a,b,c), White and Zelazny (1988) proposed that (010), (110) and (1 $\bar{1}$ 1) are the major edge surface types, the latter two of which have approximately equivalent surface atomic configurations. In their models, the edge cations are 4- and 6-fold coordinated in T-sheets and in O-sheets, respectively, and as the environmental pH increases, their ligand gradually changes from $-\text{OH}_2$ to $-\text{O}$ via $-\text{OH}$. Similar configurations have been derived for the cases of Mg substitution in O-sheets and Al substitution in T-sheets. Because these models are derived from crystallography, many details remain inaccessible, such as the microscopic hydration characteristics of edge sites. Given the presence of isomorphic replacements, the local electronic structures are transformed; therefore, one can expect that the edge structures are different from their non-substituted counterparts. Such factors have been significantly oversimplified in PBC approaches.

The application of quantum–mechanical simulations has significantly promoted interface geochemistry research in areas that are difficult to explore with experimental approaches (e.g., Cygan, 2001; Sherman, 2001; Bickmore et al., 2003, 2006; Greenwell et al., 2003, 2006; Boulet et al., 2006; Churakov, 2006, 2007; Kubicki et al., 2007, 2008; Rotenberg et al., 2007, 2010; Tunega et al., 2007; Cygan et al., 2009; Churakov and Kosakowski, 2010). Using static quantum calculations, Bickmore et al. (2003) optimized (010) and (110) surfaces of neutral 2:1 phyllosilicates (octahedral cations are Al(III) and Fe(III), respectively) and calculated the acidity constants of edge hydroxyls. Using a similar technique, Churakov (2006) investigated (010), (110), (100) and (130)-type surfaces of pyrophyllite. The major shortcoming of static calculations is the oversimplification of solvent effects, which leads to an inaccurate treatment of entropy contributions. Churakov (2007) employed FPMD simulations to study the interfaces between pyrophyllite edges and confined water films. According to these simulation studies, it is revealed that under pH conditions close to the PZC (point of zero charge), the stable surface group in T-sheets is $\equiv\text{Si}-\text{OH}$, and $\equiv\text{Al}-(\text{OH})(\text{OH}_2)$ and $\equiv\text{Fe}-(\text{OH})(\text{OH}_2)$ are stable in O-sheets. However, such simulation studies are rare, and many relevant issues remain unresolved. In the above-mentioned studies, the O-sheet cations are all assumed as be 6-fold coordinated, i.e., 4 oxygen atoms inside the substrate + 1 hydroxyl + 1 H_2O ligand; this is based on the 6-fold scenario for Al^{3+} and Mg^{2+} in liquid water. It is necessary to ask if the 5-fold coordinations are stable on edge surfaces (i.e., without the H_2O ligand) because it has been proved that the 5-fold form $\text{Al}(\text{H}_2\text{O})(\text{OH})^{2+}$ is predominant in water with a pH range of 3–7 (Swaddle et al., 2005). This is important because it is related to the estimation of the density of edge acid/base sites (Bourg et al., 2007). Furthermore, the effects of isomorphic substitutions have not been addressed.

In this study, to shed light on the microscopic structures of the interfaces between phyllosilicate edges and water, we perform systematic FPMD simulation studies. Both neutral and charged frameworks are investigated, and the commonly occurring isomorphic substitutions are taken into account. To explore the coordination environments of O-sheet cations, constrained molecular dynamics is applied to investigate the free-energy changes for the leaving processes of the coordinated water ligands. According to the simulations, the interfacial topologies are constituted, and the acid–base active sites have been illustrated.

2. METHODOLOGY

2.1. Systems

The phyllosilicate models are derived from Viani et al. (2002). The unit cell formula is $\text{X}_{(12-a-b)}^+[\text{Si}_a\text{Al}_{8-a}][\text{Al}_b\text{Mg}_{4-b}]\text{O}_{20}(\text{OH})_4$, where X, Al_{8-a} and Mg_{4-b} stand for the monovalent counterion, T-sheet substitution and O-sheet substitution, respectively. The crystallographic parameters are $a = 5.18 \text{ \AA}$, $b = 8.98 \text{ \AA}$, $c = 10 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The (010) and (110) edges types are explored because they are the main ones predicted by PBC theory (White and Zelazny,

Fig. 1. The models of (010) and (110) types used for the neutral frameworks. O = red, H = white, Si = gray and Al = cyan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1988; Bickmore et al., 2003). The edge surface structures are cut from the unit cell and repeated along the a axis; therefore, the simulated models contain two unit cells (Fig. 1). For the initial surface models, the dangling $\equiv\text{Si}-\text{O}$ and $\equiv\text{Al}-\text{O}$ bonds are all saturated by protons; similar edge surface models have been applied in previous simulation studies (Churakov, 2006, 2007; Liu et al., 2008b). For the charged frameworks, the most common isomorphic substitutions were explored: one Al for one Si in T-sheets and one Mg for one Al in O-sheets, respectively. Therefore, the non-substituted framework is used to model the neutral end-member pyrophyllite (Churakov, 2006, 2007), and the substituted frameworks are invoked for the charged layered silicates, e.g., smectites and muscovite. In the charged models, the substituting cations replace the outermost Si/Al atoms (i.e., those closest to water) and both edge types – (010) and (110) – are built. The substitution leads to a negatively charged framework, which is compensated by inserting one Li^+ cation in the interlayer.

These initial surface models are placed in 3D periodically repeated boxes, which feature a solution space of approximately 20 Å along the direction vertical to the surface, as illustrated in Fig. 1. Fifty water molecules are inserted into the solution space, which reproduces the approximate bulk water density under ambient conditions.

2.2. Car–Parrinello MD

The electronic structures are calculated within the framework of density functional theory with the BLYP functional (Becke, 1988; Lee et al., 1988). The BLYP functional has been found to accurately describe the properties of water and protons, and its performance is better than that of PBE and BP functionals (e.g., Laasonen et al., 1993; Marx

et al., 1999; Sprik, 2000). The norm-conserving Martins–Troullier pseudopotentials (Troullier and Martins, 1991) and the Kleinman–Bylander scheme (Kleinman and Bylander, 1982) are used to describe the interactions of the valence and the core states. The orbitals are expanded in plane-wave basis sets with a kinetic energy cutoff of up to 70 Ry.

FPMD simulations are performed with the CPMD package (Car and Parrinello, 1985). All hydrogen atoms are assigned the mass of deuterium. The fictitious electronic mass is set to 800 a.u., and the equation of motion is integrated with a time step of 0.144 fs. With these settings, the adiabatic conditions of CPMD, which are reflected by the fictitious electronic kinetic energies, are reasonably maintained. The temperature is controlled at 300 K using the Nosé–Hoover chain thermostat (Marx and Hutter, 2009). In the simulations of Al-substituted (110) edges (Section 3.2.1) and Mg-substituted surfaces (Section 3.3), reactive events occur very quickly. The systems are equilibrated while constraining the coordination numbers of central atoms to prevent the reactions from occurring. In the production stages, the constraints are removed. For each unconstrained MD run, the equilibration stage lasts at least 12 ps, and the production stage lasts for more than 50 ps. Each constrained MD simulation includes a prior equilibration run of at least 3 ps and a production step of over 12 ps. The statistics are collected every five steps for all simulations.

2.3. Free energy calculation

To investigate the coordination states of O-sheet cations, a series of constrained FPMD simulations are applied to induce the breaking of $\text{M}-\text{OH}_2$, and the free-energy changes (ΔF) are calculated by integrating the mean force

(f) along the reaction coordinates according to the thermodynamic integration relation (Carter et al., 1989; Sprik, 1998, 2000; Sprik and Ciccotti, 1998),

$$\Delta F(Q) = - \int_{Q_0}^Q dQ' f(Q') \quad (1)$$

In this study, the coordination number (CN) of surface cations is selected as the reaction coordinate (Q) to represent the reaction progress.

In the simulations, the CN runs over all H₂O molecules in the system,

$$n_o = \sum_{i=1}^{N_o} S(|r_{o_i} - r_M|) \quad (2)$$

The function $S(r)$ weights the contributions of all H₂O oxygens with a distance-dependent function. In this study, the Fermi function is employed (Sprik, 1998, 2000),

$$S(r) = \frac{1}{\exp[\kappa(r - r_c)] + 1} \quad (3)$$

where κ and r_c denote the inversion of the width and the cutoff. In our calculations, the values 0.2 and 2.8 Å are used for κ and r_c , respectively.

3. RESULTS AND DISCUSSION

3.1. Neutral frameworks

For both interface systems (i.e., (010) and (110)), no reactive event occurs within the simulation periods. With PBE-functional-based CPMD, Churakov (2007) observed a spontaneous proton-transfer reaction from $\equiv\text{Si}-\text{OH}$ to $\equiv\text{Al}-(\text{OH})$ for the (010) interface. Because that study mainly explored the water confined between two edge surfaces, a very thin water film was modeled: only 18 free water molecules in a solution region of approximately 6 Å. For such a small system, the edge groups must be influenced by the opposite surface, despite the fact that the water and the associated nano-confinement can enhance the chemical reactivity. Therefore, it is reasonable to observe the dissociation of surface hydroxyls. As revealed by the trajectories, the acid sites at (010) include $\equiv\text{Al}-(\text{OH})(\text{H}_2\text{O})$ and $\equiv\text{Si}-\text{OH}$ groups, and at (110) $\equiv\text{Al}-(\text{H}_2\text{O})$ and $\equiv\text{Si}-\text{OH}$ are proton-donating groups. The hydroxyl oxygen atoms of these $\equiv\text{Si}-\text{OH}$ groups and $\equiv\text{Al}-(\text{OH})(\text{H}_2\text{O})$ at (010) can also accept H-bonds from solvent water and thus serve as base sites.

Fig. 2. Free-energy profiles calculated for the leaving processes of H₂O ligands of Al at (010) and (110) interfaces of non-substituted models. The curves are used to ease visualization.

Fig. 3. RDFs (radial distribution functions) and running CNs (coordination numbers) for (A) water O around H of $\equiv\text{Al}-\text{OH}$ and (B) water H around O of $\equiv\text{Al}-\text{OH}$ at the (010) interface of the neutral framework.

Fig. 4. Snapshot of (010) system with 5-fold coordinated Al. For clarity, the other water molecules and some framework atoms have been removed. O = red, H = white, Si = gray and Al = cyan. The green numbers denote the H-bond lengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 2, the two systems present different free-energy-curve patterns for the leaving processes of H_2O ligands of Al. It is clear that for the (010) system both the 5- and 6-fold coordinations occur as stable states, whereas for (110) system, only the 6-fold state is stable. For (010), the 5-fold state has a free energy approximately 3 kcal/mol higher than the free energy of the 6-fold state. This indicates that at (010) interfaces, both structures are

Fig. 6. RDFs and running CNs between $\equiv\text{Al}-\text{OH}-\text{Al}\equiv$ and water O at the Al-substituted (110) interface.

possible and the 6-fold is slightly more thermodynamically favorable, whereas at the (110) interface the only possible structure is the 6-fold state (i.e., with one H_2O ligand).

During the dissociation process of the (010) system, as the H_2O ligand goes into the solvent the OH ligand of Al is gradually lifted upward and eventually becomes nearly parallel to the basal surface (Fig. 4). This structural rearrangement makes the Al cation inaccessible from the solution, which stabilizes the system. The predicted reverse barrier is approximately 2 kcal/mol (Fig. 2A), but in simu-

B

Fig. 5. (A) Trajectories of O1–H1 and O2–H2 distances. These notations refer to the snapshots in (B). (B) The initial (left panel) and the final (right panel) snapshots of Al-substituted (110) interface. For clarity, the other water molecules and some framework atoms have been removed. O = red, H = white, Si = gray and Al = cyan. The green numbers denote the lengths of the H-bonds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lations (i.e., tens of picoseconds), the adsorption event is not observed.

At this interface, $\equiv\text{Al}-\text{OH}$ groups behave as both proton donors and acceptors. On the radial distribution functions (RDF) and the running coordination numbers (CN) curves (Fig. 3), it can be seen that $\equiv\text{Al}-\text{OH}$ donates an H-bond to the solvating water and the hydroxyl oxygen accepts an H-bond from another water molecule. Fig. 4 shows a representative snapshot of the system.

3.2. Al substitution in T-sheet

3.2.1. (110) interface

The simulation proves that Al substitution leads to significant transformations of the initial structures. Fig. 5 shows that at approximately 0.5 ps (Fig. 5A), one proton (H_1 in Fig. 5B) of the $\equiv\text{Al}-\text{OH}_2$ group simultaneously dissociates and combines with a water molecule and, at the same time, that water donates a proton (H_2 in Fig. 5B) to

Fig. 7. (A) Distribution of H-bond distances between H of $\equiv\text{Al}-\text{OH}$ and O of $\equiv\text{Si}-\text{OH}$ in Al-substituted (110) system. (B) RDFs and running CNs for water H around O of $\equiv\text{Al}-\text{OH}$ in Al-substituted (110) system.

Fig. 8. RDFs and running CNs for water molecules around (A, B) T-sheet $\equiv\text{Al}-\text{OH}$ group and (C, D) $\equiv\text{Si}-\text{OH}$ group in Al-substituted (110) system.

Fig. 9. Snapshot of Al-substituted (010) system. For clarity, the other water molecules and some framework atoms have been removed. O = red, H = white, Si = gray and Al = cyan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the O atom of $\equiv\text{Al}-\text{O}-\text{Al}\equiv$ site (O_2 in Fig. 5B). These proton transfer events happen very quickly. Therefore, in the equilibration stage, geometric constraints have been imposed to prevent these reactive events from occurring. After these events, the water containing H1 gradually enters the solution (Fig. 5A) and the initial $\equiv\text{Al}-\text{O}-\text{Al}\equiv$ site is protonated (see right panel in Fig. 5B). This structure remains throughout the simulation.

The newly formed $\equiv\text{Al}-\text{OH}-\text{Al}\equiv$ is a proton-donating site. As seen from the RDF and running CN curves (Fig. 6), the first RDF peak (centered approximately 1.90 Å) denotes the H-bond between the proton, and a water molecule (marked in the right panel of Fig. 5B) and the second peak (centered approximately 2.35 Å) is indicative of the relationship with the O atom of the $\equiv\text{Al}-\text{OH}$ group (O_1 in Fig. 5B).

The $\equiv\text{Al}-\text{OH}$ group formed from the dissociation of $\equiv\text{Al}-\text{OH}_2$ donates an H-bond to the O atom of the adjacent $\equiv\text{Si}-\text{OH}$ group (marked in Fig. 5B). The trajectory indicates that this bond holds during the simulation period and that the hydroxyl of $\equiv\text{Al}-\text{OH}$ never changes the orientation. This can also be inferred from the distribution of H-bond lengths (centered at approximately 1.9 Å), as shown in Fig. 7A. Fig. 7B shows the RDFs for water H around the O of $\equiv\text{Al}-\text{OH}$, where the first RDF peak approximately 1.0 Å denotes the covalent OH bond and the second peak approximately 1.75 Å denotes the H-bond accepted from the solvent water (marked on the right panel of Fig. 5B). These observations show that this $\equiv\text{Al}-\text{OH}$ group does not donate H-bonds to solvents and therefore only acts as a proton-accepting site.

As shown in the RDFs (Fig. 8A and B), the T-sheet $\equiv\text{Al}-\text{OH}$ group donates an H-bond to the waters and its hydroxyl O accepts an H-bond from the waters. Therefore, this group behaves as both a proton acceptor and donor, whereas the O-sheet $\equiv\text{Al}-\text{OH}$ group is only a proton-accepting site, as discussed above. The curves for the counterpart $\equiv\text{Si}-\text{OH}$ group are shown in Fig. 8C and D. For $\equiv\text{Al}-\text{OH}$, the first two RDF peaks (i.e., $\text{H}_{\text{Al}-\text{OH}}-\text{O}_{\text{water}}$

Fig. 10. Free-energy profile calculated for the leaving process of H_2O ligand of Al (O-sheet) at Al-substituted (010) interface. The curve is used to ease visualization.

and $\text{O}_{\text{Al}-\text{OH}}-\text{H}_{\text{water}}$) are centered on 1.96 Å and 1.71 Å, respectively, and for $\equiv\text{Si}-\text{OH}$ the peak positions are 1.75 Å and 1.95 Å, respectively. These data indicate that $\equiv\text{Si}-\text{OH}$ has a potentially higher acidity and lower basicity than the T-sheet $\equiv\text{Al}-\text{OH}$ group.

3.2.2. (010) interface

Unlike the (110) edge, the Al-substituted (010) interface is found to be stable (the structure is shown in Fig. 9). At this interface, the active groups include $\equiv\text{Al}-\text{OH}$ and $\equiv\text{Si}-\text{OH}$ in T-sheets and $\equiv\text{Al}-(\text{OH})(\text{OH}_2)$ in O-sheets. The T-sheet Al substitution makes the linking bridge O (i.e., O of $\equiv\text{Al}-\text{O}-\text{Al}\equiv$ site) more negative. However, that O atom is hidden from the solvents, as shown in Fig. 9. Therefore, it is not a potential proton-accepting site, and the proton-transfer reaction that occurs in the (110) case never takes place.

Fig. 10 shows the calculated free-energy curve for the release of an H_2O ligand of $\equiv\text{Al}-(\text{H}_2\text{O})(\text{OH})$. It is clear that the profile is quite similar to that for the neutral (010) case (Fig. 2B). Therefore, both the 5- and 6-fold coordinated states are stable, and the 6-fold state is more favorable, with a free energy of approximately 2.8 kcal/mol. The interface structure of the 5-fold state is very similar to that of the neutral case (Fig. 3), where the O-sheet $\equiv\text{Al}-\text{OH}$ is nearly parallel to the basal surface and behaves as both a proton donor and acceptor.

Fig. 11 shows that T-sheet $\equiv\text{Al}-\text{OH}$ and $\equiv\text{Si}-\text{OH}$ act as both proton donors and acceptors. By comparing the first RDF peaks (Fig. 11), one can observe an important similarity that is shared with the Al-substituted (110) case: $\equiv\text{Si}-\text{OH}$ is more acidic and less basic than T-sheet $\equiv\text{Al}-\text{OH}$.

3.3. Mg substitution in O-sheet

3.3.1. (110) interface

For the Mg-substituted (110) system, the free-energy profile (Fig. 12) shows that both the 6- and 5-fold coordinated states of Mg are stable. One can see that the barriers for desorption and adsorption are only approximately 2.6 kcal/mol and 0.5 kcal/mol, respectively. Indeed, we observe the spontaneous water exchange events for Mg in the

Fig. 11. RDFs and running CNs for water molecules around (A, B) T-sheet $\equiv\text{Al}-\text{OH}$ group and (C, D) $\equiv\text{Si}-\text{OH}$ group in Al-substituted (010) system.

Fig. 12. Free-energy profile calculated for the leaving process of H_2O ligand of Mg at (110) interface. The curve is used to ease visualization.

unconstrained simulation. From the trajectories in Fig. 13, one can see that the initially bonded water escapes at approximately 11 ps. It returns several times but eventually enters the solvent after approximately 22 ps. During the following 25 ps, Mg remains 5-fold coordinated, as illustrated in Fig. 14. At approximately 47 ps, a water molecule becomes coordinated by Mg but only for 4 ps. The RDF and running CN for water around Mg (Fig. 15A) shows that during this period, the average number of Mg-coordinated water molecules is only 0.02 at a distance of 2.7 Å.

Fig. 13. Trajectories for $\text{Mg}-\text{O}_{\text{water}}$ distances at (110) interface.

Fig. 15B shows that the O of $\equiv\text{Mg}-\text{O}-\text{Si}\equiv$ site accepts 2 H-bonds from the water, as shown in Fig. 14. Due to Mg substitution, O should be more negative than its counterpart in the non-substituted $\equiv\text{Al}-\text{O}-\text{Si}\equiv$ site.

3.3.2. (010) interface

For the Mg-substituted (010) system, the initial structure (Fig. 16, left panel) is unstable and evolves via a series of proton-transfer reactions. As shown in Fig. 16, within the first 0.5 ps, the proton of an $\equiv\text{Si}-\text{OH}$ group transfers to the OH group of $\equiv\text{Mg}(\text{OH}_2)(\text{OH})$. This process produces a dangling $\equiv\text{Si}-\text{O}$ and $\equiv\text{Mg}(\text{OH}_2)_2$ (Fig. 16, middle panel). This process is similar to the proton-transfer

Fig. 14. Snapshot of the (110) interface with 5-fold coordinated Mg. For clarity, the other water molecules and some framework atoms have been removed. O = red, H = white, Si = gray, Mg = green and Al = cyan. The green numbers denote the H-bond lengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reaction observed by Churakov (2007): a proton transfers from $\equiv\text{Si}-\text{OH}$ to OH of $\equiv\text{Al}-(\text{OH})(\text{H}_2\text{O})$. After approximately 10 ps, one proton of $\equiv\text{Al}(\text{OH}_2)$ (OH) is transferred to $\equiv\text{Si}-\text{O}$ through several proton-transfer events, which eventually generate $\equiv\text{Al}(\text{OH})_2$ and $\equiv\text{Si}-\text{OH}$ groups (Fig. 16, right panel). The final structure holds stably in a simulation lasting 45 ps.

The RDFs and running CNs in Fig. 17A show that the H-bonding between the protons of $\equiv\text{Mg}-(\text{OH}_2)_2$ and water O shows a RDF peak approximately 1.9 Å, which amounts to only 0.2 on the CN curve. This suggests that

the H_2O ligands of $\equiv\text{Mg}-(\text{OH}_2)_2$ behave as very weak proton donors. This is consistent with the weak promoter role played by Mg^{2+} in water dissociation: the pK_a of Mg^{2+} -aqua is 11.4 (Westermann et al., 1986), which is far higher than that of Al^{3+} -aqua, 5.5 (Martin, 1988). Fig. 17B shows that the hydroxyl of $\equiv\text{Al}-(\text{OH})_2$ accepts one H-bond from solvating waters, as shown in Fig. 18. Due to its orientation, $\equiv\text{Al}-(\text{OH})_2$ does not typically donate H-bonds to water (Fig. 18).

Fig. 19 illustrates the free-energy profile for the leaving process of one H_2O ligand for $\equiv\text{Mg}-(\text{H}_2\text{O})_2$. One can see that the loss of one H_2O is thermodynamically unfavorable and only the 6-fold Mg state is stable at that interface.

4. SUMMARY

With FPMD, we investigate the microscopic structures of phyllosilicate edges in contact with water. The interface topologies and hydration structures are revealed for the commonly occurring (010) and (110) edge surfaces. These atomic-level pictures can be used as the basis for understanding relevant interfacial characteristics such as acid/base properties and cation complexation. The models and the free-energy values are summarized in Fig. 20 and Table 1, respectively. The following conclusions are drawn.

- (1) Coordination environments of O-sheet cations (i.e., Al/Mg) are determined through free-energy calculations.

Fig. 15. RDFs and running CNs for (A) water O around Mg and (B) water H around O of $\equiv\text{Mg}-\text{O}-\text{Si}\equiv$ site.

Fig. 16. Snapshots of proton-transfer (PT) events occurring at an Mg-substituted (010) interface. Left: the initial structure; middle: the intermediate structure after the first PT; right: the final structure. Some atoms have been removed for clarity. O = red, H = white, Si = gray, Mg = green and Al = cyan. The blue arrows denote the directions of PTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 17. RDFs and running CNs for (A) water O around H of $\equiv\text{Mg}-(\text{OH})_2$ group and (B) water H around O of $\equiv\text{Al}-(\text{OH})_2$ group at Mg-substituted (010) interface.

Fig. 18. Snapshot of (010) system with 6-fold coordinated Mg. For clarity, the other water molecules and some framework atoms have been removed. O = red, H = white, Si = gray, Mg = green and Al = cyan. The green numbers denote the H-bond lengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 19. Free-energy profile calculated for the leaving process of H_2O ligand of $\equiv\text{Mg}-(\text{OH})_2$ at Mg-substituted (010) interface. The curve is shown to ease visualization.

(010) edges. For Al, both the 5- and 6-fold coordination states are possible, whereas only the 5-fold coordination is stable for Mg.

(110) edges. For Al, only the 6-fold coordination states are stable. For Mg cations, both the 5- and 6-fold coordination states are stable, and the transi-

tion between the two is barrier free. In the 5-fold case, the solvent waters form H-bonds with the bridging oxygen (i.e., O of $\equiv\text{Mg}-\text{O}-\text{Si}\equiv$).

From Table 1, it is clear that all of the stable 5-fold states have slightly higher free-energy values (2–3 kcal/mol) than their respective 6-fold states. This indicates that the 6-fold states are only slightly more probable than the 5-fold. Therefore, at aqueous interfaces, there should be a considerable number of 5-fold octahedral sites. Furthermore, the barriers are slightly higher than the thermal energy (2–5 kcal/mol and 2–3 kcal/mol for desorption and adsorption, respectively), which implies that water-exchange events actually occur frequently.

- (2) Acid/base reactive sites have been determined based on H-bonding analyses.

Bridging oxygen sites. At (010) edges, these atoms are not in contact with the solvent; therefore, they are not effective proton-accepting sites. At (110) edges, for the neutral and octahedrally substituted frameworks, those atoms (i.e., $\equiv\text{M}-\text{O}-\text{Si}\equiv$) are proton-accepting sites. For the T-sheet substituted case, the bridging site becomes a proton-donating group (i.e., $\equiv\text{Al}-\text{OH}-\text{Si}\equiv$) by capturing a proton.

T-sheet groups. All T-sheet edge groups are $\equiv\text{M}-\text{OH}$ ($\text{M}=\text{Si}/\text{Al}$), which can act as both proton donors and acceptors.

O-sheet groups. At (010) edges with 6-fold Al, the active surface groups include $\equiv\text{Al}-(\text{OH})(\text{H}_2\text{O})$ and $\equiv\text{Al}-(\text{OH})_2$, whereas for Mg cations, the edge group is $\equiv\text{Mg}-(\text{OH})_2$. In the 5-fold coordination scenario, the active groups are $\equiv\text{Al}-\text{OH}$. At (110) edges, $\equiv\text{Al}-\text{OH}$, $\equiv\text{Al}-\text{OH}_2$ and $\equiv\text{Mg}-\text{OH}_2$ groups are the proton-donating sites.

- (3) It is shown that isomorphic substitutions significantly influence edge–water interfacial structures. Many other metal cations, such as Ti(IV), Mn(III), Fe(II/III), and Li(I), also occur in phyllosilicates in nature and in the laboratory (Bergaya et al., 2006). It can be expected that those cations also lead to different interface structures. Such issues should also be addressed. The acidity constants of edge groups are

Fig. 20. Topologies of (010)- and (110)-type edge surfaces of phyllosilicates.

Table 1

Free-energy values (in kcal/mol) for the 5-fold Al states and the barriers for the dissociation processes of H₂O ligands at 2:1-type phyllosilicate-edge–water interfaces. The free energy of the respective 6-fold state is taken as the reference energy.

	5-fold	Barrier (6 → 5)
Non-sub (010)	3.0 ± 0.9	5.0 ± 0.6
Non-sub (110)	unstable	3.8 ± 0.3
T-sub (010)	2.8 ± 0.9	4.0 ± 0.8
T-sub (110)	–	–
O-sub (010)	unstable	7.5 ± 0.6
O-sub (110)	2.1 ± 0.9	2.6 ± 0.7

necessary for determining the protonation states at certain pH levels. Previous studies have proved that acidity values can be predicted accurately with FPMD (e.g., Sulpizi and Sprik, 2008; Liu et al., 2010, 2011); thus, these calculations will be performed in future studies.

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