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Atomic scale structures of interfaces between kaolinite edges and water

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Abstract

This paper reports the atomic scale structures of kaolinite edge surfaces in contact with water. The commonly occurring edge surfaces are investigated (i.e. (010) and (110)) by using first principles molecular dynamics (FPMD) technique. For (110)-type edge surface, there are two different surface topologies (denoted as (110)-1 and (110)-2) and they are considered separately.

By using constrained FPMD technique, the free-energy changes for the leaving processes of water ligands of O-sheet Al cations have been calculated and thus, the coordination states of those Al cations are determined. The results show that for (010) and (110)-2 edges, both the 5 and 6-fold coordination states are possible whereas for (110)-1 edges, only the 6-fold states are stable. Based on the analyses of H-bonding structures at the interfaces, the surface acid/base reactive sites are illustrated. (1) *T-sheet groups* are $\equiv\text{Si}-\text{OH}$, behaving as both proton donors and acceptors. (2) *Bridging oxygen* At (010) and (110)-2 edges, these sites are inaccessible from the water and thus, they are not effective reactive sites. At (110)-1 edges, the bridging oxygen atoms are proton accepting sites. (3) *O-sheet groups* At (010) and (110)-2 edges, for 6-fold Al cases, the active surface groups are $\equiv\text{Al}-(\text{OH})(\text{OH}_2)$ and for the 5-fold Al cases, the active surface groups are $\equiv\text{Al}-(\text{OH})$. At (110)-1 edges, the active site is $\equiv\text{Al}-\text{OH}_2$. This study provides fundamental structural properties for understanding the interface chemistry of widely occurring 1:1 type phyllosilicates.

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1. INTRODUCTION

Kaolinite is a most common member of 1:1 type phyllosilicates (Brigatti et al., 2006). It widely occurs in soils and sediments and also exists in atmospheric particles (Glaccum and Prospero, 1980). Kaolinite has wide applications in many fields, such as paper, rubber and pesticides industries (Bergaya et al., 2006). Surfaces of kaolinite can adsorb a lot

of molecules and ions via physical and chemical mechanisms, and therefore, kaolinite is very active in many natural processes, e.g. adsorption and enrichment of metals and transport of organic contaminants (Schoonheydt and Johnston, 2006). In all above processes, interfacial chemistry of kaolinite plays a central role (Schoonheydt and Johnston, 2006).

The surfaces of kaolinite can be grouped into basal surfaces and edge surfaces (White and Zelazny, 1988; Bleam, 1993). Kaolinite has two types of basal surfaces, i.e. hydroxyl and siloxane surfaces (Brigatti et al., 2006; Schoonheydt and Johnston, 2006). Their structures and

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adsorption characteristics have been widely characterized. For siloxane surfaces, surface oxygen can interact with foreign molecules through H-bonding and Si–O rings may play as adsorbing sites for some metal cations. For hydroxyl surfaces, the OH groups interact with waters and organics via H-bonding (e.g. Schoonheydt and Johnston, 2006; Vasconcelos et al., 2007). On the edge surfaces, many dangling bonds exist and thus, these surfaces are sometimes called broken surfaces. Under ambient conditions, these dangling bonds are usually saturated by chemically adsorbed water and therefore, there are abundant hydroxyl groups on edge surfaces and they can both donate and accept protons from environments. Due to this, edge surfaces are highly reactive and they are responsible for the amphotericity of kaolinite (Brady et al., 1996; Bourg et al., 2007). These surfaces are also major sites for metal complexing. The adsorption of metal cations on siloxane basal surfaces is mainly via electrostatic interactions. Not like smectites, kaolinite almost does not contain isomorphic substitutions and therefore the permanent charges are rather low. So, cations adsorption on siloxane basal surfaces is relatively weak compared with the cases of 2:1 type phyllosilicates (Vasconcelos et al., 2007). In contrast, metal cations can form strong chemical bonds with dangling sites on broken surfaces (Peacock and Sherman, 2005; Gu and Evans, 2008).

It can be seen that the property of edge surfaces is key for understanding interfacial chemical reactivity of kaolinite. However, up to now, the microscopic structures of edge surfaces–water interfaces have not been pictured. Using PBC (periodic bond chain) theory, White and Zelazny (1988) derived surface topologies of (010) and (110) type facets, but the details of surface hydration are still unknown. Because of the high degree heterogeneity of broken surfaces, they are quite difficult to characterize by using in situ experimental techniques such as EXAFS (extended X-ray absorption fine structure) measurement. For the titration experiments, it has been accepted that the fit “sites” can hardly be assigned to particular surface sites and it is also impossible to distinguish the contributions of different facets (e.g. Bourg et al., 2007; Gu and Evans, 2008; Gu et al., 2010).

Molecular simulation has been widely applied in the research of interface chemistry of phyllosilicates (e.g. Cygan, 2001; Bickmore et al., 2003; Cygan et al., 2004, 2009; Boulet et al., 2006; Greenwell et al., 2003, 2006; Liu and Lu, 2006; Churakov, 2006, 2007; Kubicki et al., 2007; Rotenberg et al., 2007; Liu et al., 2007, 2008a, 2008b, 2011, 2012) and has proven a powerful complement to experiments. Among various simulation techniques, quantum mechanical method is particularly strong in studying reactive processes. For kaolinite, many simulation studies have been conducted to investigate the chemistry of basal surfaces. With FPMD (first principles molecular dynamics), Tunega et al. (2004a, 2004b) studied the adsorption of water and phenoxyacetic acid herbicides on basal surfaces and they quantified the H-bonding structures. Vasconcelos et al. (2007) applied classical molecular dynamics to investigate the adsorption of metal cations on basal surfaces of kaolinite. Some studies (Hu and Michaelides, 2007a, 2007b, 2010;

Croteau et al., 2008, 2009) focused on water adsorption and ice formation on basal surfaces. With static quantum mechanical calculations, Martorell et al. (2010) investigated the structures of uranyl complexes adsorbed on basal surfaces. In contrast, there are much fewer studies on edge surfaces of kaolinite. For example, Peacock and Sherman (2005) investigated the complexing of Cu^{2+} cations on broken surfaces. In the study of Kremleva et al. (2011), they looked into uranyl complexing on the edge surfaces with static quantum mechanical methods. To the best of our knowledge, there is still no FPMD study report on aqueous interfaces of kaolinite edge surfaces.

In this study, systematic density functional theory (DFT) based FPMD simulations are performed to investigate the structures of interfaces between kaolinite edges and liquid water. Analogous to our studies on 2:1 type phyllosilicates (Liu et al., 2012), solid parts of the systems are built based on the periodic bond chain (PBC) predictions (Hartman and Perdock, 1955a, 1955b, 1955c; White and Zelazny, 1988). With FPMD method, the interfacial systems (solid + water) are treated at the same quantum-mechanical level. Free energy calculation technique was applied to explore the coordination environments of Al cations of octahedral sheet. Based on the simulations, the interfacial topologies and surface acid–base active sites are figured out. The derived interface models can be taken as the basis for future studies.

2. METHODOLOGY

2.1. Systems

The models are built based on the data of kaolinite reported by Bish (1993). The unit cell formula is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. The crystallographic parameters are: $a = 5.1535 \text{ \AA}$, $b = 8.9419 \text{ \AA}$, $c = 7.3906 \text{ \AA}$ and $\alpha = 91.926^\circ$, $\beta = 105.046^\circ$, $\gamma = 89.797^\circ$. The PBC theory predicts (010) and (110) facets are the major edge surface types of kaolinite and therefore, they are focused on in this study (White and Zelazny, 1988; Bickmore et al., 2003). The edge surfaces are cut from the unit cell and repeated along a axis and thus, the solid parts contain two unit cells (Fig. 1). Geometry optimization results of the bulk crystal show that doubling the system in c -axis does not influence the structural parameters (see the Electronic annex). The surfaces of edge models contain many dangling bonds, which are highly reactive. Under ambient conditions, they normally bind with chemically adsorbed waters. Therefore, for the initial surface models, the dangling bonds are saturated by H^+ or OH^- , that is, surface groups are $\equiv\text{Al}-\text{OH}$ and $\equiv\text{Si}-\text{OH}$. The similar saturation way has been employed in previous simulation studies of 2:1 type phyllosilicates (e.g. Churakov, 2006, 2007; Liu et al., 2008b).

These solid models are placed in 3D periodically repeated boxes (Fig. 1). These boxes have a solution space of about $20 \text{ \AA}$ in the direction vertical to the edge surface (by taking surface protons as the starting point). The solution region contains 45 water molecules and this approximately reproduces the bulk water density under ambient conditions.

Fig. 1. The used systems for (010) and (110) type interfaces of kaolinite. O = red, H = white, Si = yellow and Al = purple. A: (010); B: (110). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(010) edge surface has symmetric frameworks (excluding OH and OH₂ ligands). As shown in Fig. 1A, the edge Al atoms at the right hand side of the solid part are 6-fold coordinated, i.e. $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$. Al atoms at the left hand are left 5-fold, i.e. $\equiv\text{Al}-(\text{OH})$. (110) edge model has two different surface topologies (Fig. 1B). The left and right type edges are denoted as (110)-1 and (110)-2, respectively. Therefore, totally three edge surfaces are looked into. Thanks to the periodic boundary condition, the same system is used to investigate (110)-1 and (110)-2.

2.2. Car–Parrinello MD

FPMD simulations are carried out with CPMD package (Car and Parrinello, 1985). DFT is used to calculate the electronic structures with the BLYP functional (Becke, 1988; Lee et al., 1988). BLYP functional has been shown to be able to accurately describe the behaviors of water and protons (e.g. Laasonen, 1993; Marx et al., 1999). This functional can also nicely predict free energy changes of proton transfer processes in aqueous systems (e.g. Sprik, 2000; Sulpizi and Sprik, 2008; Liu et al., 2010). BLYP has been widely employed in simulation studies of silicates, e.g. in our previous study on phyllosilicates (Liu et al., 2008b), it is shown that the agreement of structures between BLYP and PBE is within 2.0%. For kaolinite, BLYP accurately reproduces the structures (see the Electronic annex).

In the calculations, norm-conserving Martins–Trouillier pseudopotentials (Trouillier and Martins, 1991) and the Kleinman–Bylander scheme (Kleinman and Bylander, 1982) are used to describe the interactions between the valence and the core states. The orbitals are expanded in plane wave basis sets with a kinetic energy cutoff of 70 Ry.

In the simulations, all hydrogen atoms are assigned a mass of deuterium. The fictitious electronic mass is set to 800 a.u. and the equation of motion is integrated every 0.144 fs. These settings maintain the adiabatic conditions of CPMD method. The temperature is controlled at 300 K by using the Nosé–Hoover chain thermostat (Marx and Hutter, 2009).

In the simulation of (110)-2 system (Section 3.2), desorption of the coordinated water would happen very

fast. In order to reach reasonable equilibrations, this system is equilibrated while constraining coordination numbers of central Al atoms to prevent the reactions to happen and in the production stages, the constraints are removed.

In each unconstrained MD simulation, the equilibration step lasts over 12 ps and the production step is over 50 ps. Each constrained MD simulation includes a prior equilibration run for at least 3 ps and a production stage for over 15 ps. The results are recorded every 5 steps.

2.3. Free energy calculation

In order to explore the coordination states of surface Al cations, constrained FPMD simulations are employed to enforce $\equiv\text{Al}-\text{OH}_2$ bonds to break and free energy changes are derived via the thermodynamic integration technique (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 Al cations with respect to water oxygen is taken as the reaction coordinate (Q) to represent the reaction progress.

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

$$n_{\text{O}} = \sum_{i=1}^{N_{\text{O}}} S(|r_{\text{O}_i} - r_{\text{M}}|) \quad (2)$$

The function $S(r)$ weights the contributions of all H₂O oxygen with Fermi function (Sprik, 1998, 2000),

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

Here r , κ and r_c stand for the distance between Al and water O, inversion of the width and the cutoff, respectively. In our calculations, 0.2 and 2.8 Å are used for κ and r_c , respectively. With the computational settings described above, the mean forces can reach a reasonable convergence of 0.0025 Hartree. Based on this, the uncertainty of

free-energy values is estimated to have an upper limit of about 1.8 kcal/mol. This error is similar to those in our previous studies (Liu et al., 2010, 2011a, 2011b).

3. RESULTS AND DISCUSSIONS

3.1. (110)-1

As shown by the free-energy profile (Fig. 2), the leaving process of H₂O ligand is thermodynamically unfavorable and the 5-fold does not occur as a stable state. Therefore, at this interface, Al atoms are 6-fold coordinated, i.e. they all have a H₂O ligand (Fig. 3).

From the collected trajectory, radial distribution functions (RDF) and running coordination numbers (CN) are derived to represent the correlations between atomic species (Allen and Tildesley, 1987). For the Al site, one H of the H₂O ligand performs as a proton donor (marked in the snapshot in Fig. 3). As shown in Fig. 4, the peak ranging from 1.4 to 2.4 Å indicates the H-bond between that H and water O. That peak amounts to about 1 on the running coordination number curve. It shows that this H-bond always hold during the simulation period. In contrast, the other OH of the H₂O ligand always has an orientation approximately perpendicular to the basal surface and never changes (denoted with green lines in Fig. 3). Therefore, this OH group should not be considered as an effective proton donor.

As shown in Fig. 5, an H-bond exists between water H and the O of ≡Al–O–Si≡ site, which ranges 1.4–2.2 Å (see the snapshot in Fig. 4). It indicates that this site behaves as a basic group. This is very similar to ≡Al–O–Si≡ sites on (110) interface of 2:1 phyllosilicates (Churakov, 2007; Liu et al., 2012). The O of ≡Al–O–Si≡ group directly contacts with water and it can serve as an important metal complexing site.

≡Si–OH group performs as both proton donor and acceptor, which is similar to the case in 2:1-type phyllosilicates (Bickmore et al., 2003; Liu et al., 2012). As the RDFs and running CNs curves show (Fig. 6), the H of ≡Si–OH donates an H-bond to water and at the same time the O accepts an H-bond from water.

Fig. 2. Free energy profile calculated for the leaving process of H₂O ligand of Al atom at (110)-1 interface. The curve is used to guide eyes.

Fig. 3. The snapshot for kaolinite (110)-1 interface. Blue lines show H-bonds and blue numbers denote the bond lengths. Green lines denote the H atoms of ≡Al–OH₂ sites, which do not donate H-bonds to water. O = red, H = white, Si = yellow and Al = purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. RDFs and running CNs for water O around one H of ≡Al–OH₂ group at (110)-1 interface.

Fig. 5. RDFs and running CNs for water H around the O of ≡Al–O–Si≡ group at (110)-1 interface.

3.2. (110)-2 interface

For this interface, the free-energy profile indicates that both the 6- and 5-fold states are stable (Fig. 7). The 5-fold state has a slightly lower free energy than the 6-fold by 2.7 kcal/mol. The barrier for the leaving process of water ligand is only 2 kcal/mol, which indicates that the water can leave very easily. In the unconstrained MD simulation, the spontaneous desorption of that water ligand is observed, as shown by the trajectory in Fig. 8. After the dissociation, that water forms an H-bond with the OH ligand of ≡Al–OH.

Fig. 6. RDFs and running CNs for (A) water O around H of $\equiv\text{Si-OH}$ and (B) water H around O of $\equiv\text{Si-OH}$ group at (110)-1 interface.

Fig. 7. Free energy profile calculated for the leaving process of H_2O ligand of Al atom at (110)-2 interface. The curve is used to guide eyes.

Fig. 8. Trajectory of $\equiv\text{Al-OH}_2$ distances during the simulation of kaolinite (110)-2 edge interface.

After the water ligand leaves, the OH group uplifts and finally becomes almost parallel to the basal surface (marked with a green line in Fig. 9). This orientation is quite similar to the 5-fold scenario observed in (110) interface of 2:1 type phyllosilicates (Liu et al., 2012).

Fig. 10 shows the H-bonding between $\equiv\text{Al-(OH)}_2(\text{OH})$ site and water. The H_2O ligand forms H-bond with waters (Fig. 10A and snapshot in Fig. 9), which is indicated by the 2nd RDF peak (centered 1.65 Å and ranging 1.3–2.1 Å). The OH of $\equiv\text{Al-(OH)}_2(\text{OH})$ not only donates but also accepts H-bonds from water (Fig. 10BC). Fig. 10B shows the

Fig. 9. Snapshot for kaolinite (110)-2 interface. Blue lines show H-bonds and blue numbers denote the bond lengths. Green line and green number denote the 5-fold Al atom. O = red, H = white, Si = yellow and Al = purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

H-bond donated by $\equiv\text{Al-(OH)}$ is centered around 2.0 Å and ranging 1.5–2.5 Å. The comparison with that of $\equiv\text{Al-(OH)}_2$ implies OH group is less acidic than OH_2 ligand.

As can be seen on the snapshot (Fig. 9), the $\equiv\text{Al-O-Si}\equiv$ site at this interface is hidden from the water and thus, it should not be considered as an effective reactive group.

The role that the H of $\equiv\text{Si-OH}$ plays depends on the coordination state of the adjacent edge Al atom. At the interface with 6-fold Al (i.e. $\equiv\text{Al-(OH)}_2(\text{OH})$), $\equiv\text{Si-OH}$ often donates H-bond to the O of $\equiv\text{Al-OH}$ (Fig. 11A and snapshot in Fig. 9) and therefore in this case, it is not an effective proton donating site. With the 5-fold Al (i.e. $\equiv\text{Al-OH}$) (Fig. 11B and snapshot in Fig. 9), $\equiv\text{Si-OH}$ donates H-bond to a solvent water and it indeed acts as a proton donor to solutions.

For the case having the 5-fold Al, $\equiv\text{Al-OH}$ is approximately parallel to the basal surfaces and it plays as both proton donor and acceptor. This is shown by the structural analyses in Fig. 12AB. The peak for water O around H of $\equiv\text{Al-OH}$ ranges 1.6–2.5 Å. Therefore, qualitatively it is less acidic than $\equiv\text{Al-OH}_2$ site in the 6-fold case.

3.3. (010) interface

For (010) interface, the free-energy curve shows that both the 6-fold and the 5-fold are stable (Fig. 13). The

Fig. 10. The RDFs and running CNs between waters and the groups of $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$ at kaolinite (110)-2 interface.

Fig. 11. RDFs and running CNs for H of $\equiv\text{Si}-\text{OH}$ around water O at the (110)-right interfaces with (A) 6-fold Al and (B) 5-fold Al.

Fig. 12. RDFs and running CNs for (A) O_{water} around H of $\equiv\text{Al}-\text{OH}$ and (B) H_{water} around O of $\equiv\text{Al}-\text{OH}$ at the (110)-2 interfaces with 5-fold Al.

Fig. 13. Free energy profile calculated for the leaving process of H_2O ligand of Al atom at (010) interface. The curve is used to guide eyes.

5-fold is only about 2 kcal/mol higher than the 6-fold. This small free-energy difference indicates that the 6-fold is slightly more probable than the 5-fold state.

At this interface, the potential acidic sites include the OHs of $\equiv\text{Si}-\text{OH}$ and $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$ sites, and the basic sites include the O atoms of $\equiv\text{Si}-\text{OH}$ and of the OH of $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$.

The structural analyses shown in Fig. 15 indicate that the OH_2 ligand of $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$ donate one H-bond to solvent waters (Fig. 15A and snapshot in Fig. 14). In contrast, the OH ligand does not and therefore, it is not an effective proton donating site (Fig. 15B). The O of the OH ligands accepts H-bond from waters and thus performs as a basic site (Fig. 15C).

For the interface having the 5-fold Al, $\equiv\text{Al}-\text{OH}$ site performs as both proton donor and acceptor. As shown

Fig. 14. The snapshot for kaolinite (010) interface. Blue lines show H-bonds and blue numbers denote the bond lengths. Green lines denote the H atoms of $\equiv\text{Al}-\text{OH}_2$ sites, which do not donate H-bonds to water. O = red, H = white, Si = yellow and Al = purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

by the RDF and running CN, H-bond exists between the H of $\equiv\text{Al}-\text{OH}$ and water O (Fig. 16A). Fig. 16B illustrates that on average there are 1.7 H-bonds between O of $\equiv\text{Al}-\text{OH}$ and water H. By comparing these curves with those in the 6-fold case, one can see that in the 5-fold case, there are more chances for $\equiv\text{Al}-\text{OH}$ to act as reactive sites. Similar to $\equiv\text{Al}-\text{OH}$ site on (110)-2 interface, this group is less acidic than $\equiv\text{Al}-\text{OH}_2$ site.

$\equiv\text{Si}-\text{OH}$ group donates an H-bond to water (Fig. 17A) and the O atom accepts an H-bond from waters. Therefore, this $\equiv\text{Si}-\text{OH}$ group also performs as both acidic and basic site.

At this interface, O atoms of $\equiv\text{Al}-\text{O}-\text{Si}\equiv$ sites are inaccessible from the solvent (see the snapshot in Fig. 14), and therefore, these O should not be considered as effective reactive sites.

Fig. 15. RDFs and running CNs between the groups of $\equiv\text{Al}-(\text{OH}_2)(\text{OH})$ and waters at kaolinite (010) interface.

Fig. 16. RDFs and running CNs for (A) O_{water} around H of ≡Al–OH and (B) H_{water} around O of ≡Al–OH at the (010) interfaces with 5-fold Al.

Fig. 17. RDFs and running CNs between waters and ≡Si–OH at kaolinite (010) interface.

4. SUMMARY

In summary, the microscopic structures of kaolinite edges-water interfaces are figured out by using FPMD simulations. Fig. 18 illustrates the derived topologies. These fundamental properties provide physical basis for understanding the interfacial chemistry of 1:1 type phyllosilicates. The following points are concluded.

Firstly, coordination states of Al cations are determined using free energy calculations. For (010) and (110)-2 edges, both the 5- and 6-fold coordination states are possible. For (110)-1 edges, only the 6-fold states are stable.

Secondly, interfacial acid/base reactive sites are illustrated with H-bonding analyses.

Bridging oxygen At (010) and (110)-2 edges, these sites are inaccessible from the solvent and thus, they are not effective reactive sites. At (110)-1 edges, the bridging oxygen atoms are proton accepting sites.

T-sheet groups T-sheet edge groups, i.e. ≡Si–OH, generally perform as both proton donors and acceptors. But at (110)-2 interface having 6-fold Al, ≡Si–OH usually donates H-bond to the adjacent ≡Al–OH sites rather than to waters.

O-sheet groups At (010) and (110)-2 edges, for 6-fold Al cases, the active surface groups are ≡Al–(OH)(OH₂) and for the 5-fold Al cases, the active surface groups are ≡Al–(OH). In the 5-fold case, ≡Al–(OH) group has an orientation approximately parallel to the basal surface, which is quite similar with that in 2:1 phyllosilicates systems (Liu et al., 2012). At (110)-1 edges, ≡Al–OH₂ is the active

Fig. 18. Topologies of kaolinite edge surfaces in water.

surface group. $\equiv\text{Al}-\text{OH}_2$ performs as proton donor and it is more acidic than $\equiv\text{Al}-\text{OH}$ that can act as both proton donor and acceptor.

The derived interface structures and active sites can be used as the basis for understanding interfacial phenomena of 1:1 phyllosilicates, for example, implications are provided for complexation modeling (Bourg et al., 2007), e.g. in defining surface sites and estimating densities of sites. Our results also show the constraints of crystallography on interfacial chemistry like in the systems of 2:1-type phyllosilicates and therefore, the contributions of different facets should be taken into account.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2012.06.008>.

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