Molecular Controls on Kaolinite Surface Charge

PATRICK V. BRADY,1 RANDALL T. CYGAN, AND KATHRYN L. NAGY

Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185–0750

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pH-dependent, multisite, surface charge on kaolinite can be explained by proton donor-acceptor reactions occurring simultaneously on Si and Al sites exposed on basal planes and edges. Si site Brønsted acidity at the kaolinite-solution interface differs minimally from that of pure SiO₂, whereas Al site acidity increases appreciably over that of pure Al₂O₃. Increasing temperature decreases the pK values of Al and Si proton-exchange sites. Calculated site densities indicate either an elevated participation of edges or substantial contribution from basal planes in the development of surface charge. Independent evidence from scanning force microscopy points to a higher percentage of edge surface area due to thicker particles and basal surface steps than previously assumed. Thus, no basal plane participation is required to explain the site densities determined from proton adsorption isotherms. Molecular modeling of the proton-relaxed kaolinite structure has been used to establish the elevated acidity of edge Al sites and to independently confirm the crystal-chemical controls on surface reactivity.

INTRODUCTION

A mechanistic understanding of mineral–solution interface reactions is needed to predict the extent and nature of a host of geochemical and biogeochemical processes. The origins of surface acidity are particularly important as surface charging plays a pivotal role in determining chemical transport in soils and groundwaters. By accepting or donating protons hydroxylated mineral surfaces acquire charge and the potential to control the attachment of cations or anions, bacteria, and high- and low-molecular-weight organic molecules. Surface charging reactions also modify the rates of dissolution and growth of mineral surfaces.

While the Earth’s crust consists primarily of multioxide aluminosilicates, the vast majority of experimental and theoretical attention has focused on simple (hydr)oxides of Si, Ti, Fe, and Al. Only recently has multioxide surface chemistry of primary silicates and clays been addressed in detail (1–3). Many factors obscure the crystal-chemical controls on multioxide surface charge: (1) There is no universally accepted way to sum up, or predict, the acidities of the components of a multioxide silicate. (2) Preferential leaching of components is widely observed [e.g., (4–6)], generally pH-dependent (5, 7), and therefore difficult to model. (3) Active site densities for dissolution and proton exchange are certain to be crystallographically determined [e.g., (9)], hence difficult to unravel from bulk measurements done on powders. (4) Component acidities in the multioxide phase may differ greatly from their values in the single-oxide phase due to local crystal structure. Moreover, interface-controlled electron transfer reactions can greatly complicate the surface chemistry of Fe- and Mn-containing minerals.

Here we present measured kaolinite surface charge as a function of pH and temperature and advance a model for multisite acidity. Kaolinite is uniquely suited for examining multioxide surface chemistry because (1) it contains Al in octahedral coordination and Si in tetrahedral coordination with oxygen, two of the primary metal sites exposed at clay surfaces; (2) it has no interlayer cations that can be easily leached; (3) each (hydr)oxide component exists in two distinct structural environments at the surface (i.e., basal planes, edges); and (4) there is minimal substitution of variable-valence cations, hence, minor permanent structural charge. Effects of temperature were determined from 25 to 70°C because the geologic environments in which kaolinite surface interactions are important range from weathered outcrops and soils to subsurface sedimentary basins.

EXPERIMENTAL METHODS

pH and temperature-dependent surface charge were measured on a well-crystallized kaolinite (Clay Minerals Society source clay KGal) from Washington County, Georgia, having a BET surface area of 10 to 11 m² g⁻¹ (7, 10) in a background electrolyte of 0.1 M NaCl. No washing or aging of the kaolinite was carried out. This was done to avoid potentially complicating effects of aluminum and/or silica coatings observed to form in electrokinetic studies of clay minerals (11, 12). It is, however, recognized that the bulk chemical composition of KGal kaolinite is such that a few percent of impurities may be present (10). Pruett and Schroeder (13) showed that 0 to 0.5% Fe substitution for Al in octahedral sites may occur and 1 to 4% Al substitution

1 To whom correspondence should be addressed.

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for Si in the “soft” Georgia kaolins, which include KGaI. The maximum values of these would indicate a maximum permanent charge of 35 mEq/100 g; however, the CEC for this kaolinite has been measured to be much less, 2 mEq/100 g (10) and 0.63 mEq/100 g (14), indicating minor substitution. Unpublished data of Robert Pruett (ECC, International) show that mineralogic impurities include 1.7% anatase, 0.02% Fe oxides, 0.1% micas, and trace quartz (15). The micas are predominantly muscovite about 10 to 100 μm in size. Even if we assume a maximum of 0.5% interstratified smectite based on chemistry alone and a CEC for this smectite of 100 mEq/100 g, we estimate only about 4 mEq/100 g total exchange capacity. This would correspond to a maximum CEC of 0.08 mEq/100 g. KGaI, unlike many other Georgia kaolins (16), is relatively pure and, as such, is considered of high quality for use in the paper industry.

The kaolinite was characterized using TEM and SFM. TEM images were obtained using a Philips CM30 electron microscope operating at 300 kV. SFM images were obtained in air using a Park Scientific Instruments (PSI) Autoprobe LS in contact mode. A “pinch” of kaolinite was sonicated for 30 s in 3 ml of deionized water using an ultrasonicator at 50/60 Hz. We minimized the sonication time because excessive vibration has been shown to cleave kaolinite particles (17). A drop of the slurry was allowed to air-dry on a freshly cleaved muscovite mount. Images were obtained using PSI silicon Ultralevers, which have conical tips and high length-to-width aspect ratios. Ultralevers are sharper, although more delicate, than standard pyramidal Si,Ni tips and provide better resolution of step and edge features.

All solutions were made from doubly distilled water. The titrants for the adsorption measurements were 0.1 M NaOH and 0.1 M HCl (all solutions and standards were made from reagent-grade chemicals). pH electrodes (Mettler combination) were calibrated using NBS standards at the temperature of interest. Measurements were accurate to within 0.01 unit. Kaolinite (4.0 g) was titrated in 50 ml of electrolyte using a Mettler DL 12 titrator. Solutions were continuously stirred and N2 was pumped directly into the solution for 15 min before and during each titration to purge the solution of CO2. Temperature was held to ±2°C by manually adjusting a hot plate and water jacket in which the reaction vessel was immersed. Generally 1 to 5 min elapsed between titrant additions (typically 0.01 ml), allowing pH readings to stabilize within a preselected tolerance. Adsorption equilibrium was presumed to exist when the pH changed by less than ~0.01 unit per minute. After each titration the solutions were filtered and analyzed with a directly coupled plasma spectrometer for Al and Si. Dissolved levels of Al and Si were too small (<3 ppm, 1 × 10−9 mol liter−1) to significantly impact the charge balance calculations below (this assumes that the observed Al and Si levels are not the result of rapid dissolution followed by sorption).

pH-dependent surface charge was calculated at each temperature by the relation

\[ \sigma = (F/SA)(/[C_a - C_b] - [H^+] + [OH^-]), \]  

where \(\sigma\) is the proton surface charge density (coulombs m−2), \(F\) is Faraday’s constant, \(SA\) is mineral surface area (m2 liter−1), and \(C_a\) and \(C_b\) are the amounts of acid and base titrant added (mol liter−1), respectively. Note that [1] takes no account of any permanent charge arising from heterogeneous substitution (see below).

**KAOLINITE SURFACE CHEMISTRY**

Surface charge on oxide minerals arises from the adsorption of water, hydroxyls, and protons to coordinatively unsaturated bonds. Measured kaolinite surface charge is heterogeneous in that it is the net of a number of reactions occurring on a variety of crystallographically distinct sites. The kaolinite unit cell is, simplistically, a gibbsite-like sheet of octahedrally coordinated Al bound to a sheet of silica tetrahedra through shared oxygens (18). Two of three octahedral sheets are filled and the Al sheet is referred to as dioctahedral. Kaolinite layers, each comprising one octahedral and one tetrahedral sheet, are less tightly bound together in the c direction by hydrogen bonding between hydroxyl sites on the gibbsite basal plane and the highly electronegative oxygens of the silicon tetrahedral sheet (Fig. 1).

There is no universally accepted explanation for which group(s) controls pH-dependent adsorption and electrokinetic behavior in aqueous solutions. It may be the case that for different kaolinites, the predominant charged site or sites varies with bulk chemical composition or defect structure. Kaolinite surface charge has been ascribed to one, or a combination, of the following:

1. Si basal plane: Minor substitution of Al3+ or Fe3+ for Si4+ in the tetrahedral sheet would give rise to a small permanent (non-pH dependent) negative charge on the Si basal plane [e.g., (19–22)].

2. Edges: Exposed Al and Si centers at kaolinite edges are terminated by hydroxyls (19, 20), which, in the case of the alumino, can accept or donate protons. Because alumina surfaces are generally positively charged at pH < 8.7 [e.g., (23)], whereas silica mineral surfaces are anionic down to pH 2 to 3 [e.g., (24)], positive edge charge is attributed most reasonably to gibbsite-like edge sites (25). Negative surface charge is dominated at high pH (pH > 9) by the contribution of silanol groups (25–27). Lewis acid sites also form due to the adsorption of water onto alumino sites (28).

3. Basal plane hydroxyl groups: Hydroxyl groups on the octahedral plane are coordinated to two underlying alumino atoms, and are thought to be appreciably less reactive.
than edge aluminols and silanols (28). Hydroxyl groups may exist locally on the silicon tetrahedral sheet as well [e.g., (1)]. Zhou and Gunter (29) have recently compared measured kaolinite surface charge with that of the constituent oxides SiO$_2$ and Al$_2$O$_3$ to argue for considerable ionization of basal planes.

4. Interlayer cations: Kaolinites often contain interstratified smectite layers that have interlayer cations (16, 30). These interlayer cations can easily be exchanged for protons in solution. The extent of smectite interstratification appears to be a function of the kaolinite’s origin, although exact controls are unknown.

A variety of surface complexation models have been used to explain pH-dependent charge and the electrokinetic behavior of the kaolinite surface. Surface acidity and cation adsorption have been explained using the constant capacitance model (2, 31–33), the triple-layer model (26, 34), and semiempirical power-exchange functions (26).

**MODELING APPROACH**

Because the cation-exchange capacity of kaolinite is minimal at mildly acidic pH (26) we neglect any permanent, pH-independent, negative charge on the silicon tetrahedral face. This is consistent with the ion-exchange results of Ferris and Jepson (25). By neglecting permanent charge we are in effect examining kaolinite surface acidity solely by modeling the amphoteric properties of aluminol and silanol sites on the edges and basal planes.

The inclusion of basal planes in the model is required by the conclusion of Zhou and Gunter (29) that at best only a tenth of the pH-dependent surface charge can be fit onto kaolinite edges, assuming that edges contribute no more than 14% of the total kaolinite surface area. In other words, basal planes must possess pH-dependent negative surface charge as well. This points out the essence of the problem: if the acidity of the edges is appreciably different from that of basal planes, the areal distribution of the two must be known to accurately model total surface charge. Historically, the two types of acidity have been treated as one (26, 31, 32). Two exceptions are the studies by Zhou and Gunter (29) and Wieland and Stumm (2) in which the contributions of edges and basal planes were explicitly considered.

Our modeling strategy is three-pronged. We combined calculated charge distribution from potentiometric titration data, measured proportions of edge and basal surface area from SFM images, and modeled surface charge density using an atomistic approach to arrive at a consistent picture of the actual metal sites and locations that control surface charge development on kaolinite. The model is constrained by the conclusions we derived from the above studies, i.e., the permanent structural charge is small and charge on edges and basal surfaces is distinct.
The program FITEQ (35) was used to regress proton surface charge density measurements (calculated from Equation [1]) and provide best-fit values of surface site acidity constants as well as total site density, $S$. The latter was calculated using a relative error of 0.01 unit for pH ($=0.02303$ for [H$^+$]). FITEQ iteratively performs a nonlinear least-squares optimization calculation using an assumed chemical model of the solid solution interface. A constant capacitance model [e.g., (36, 37)] was used to link surface charge, $\sigma$, and surface potential, $\psi$. The capacitance was set to 4.0 F m$^{-2}$. This value was chosen to minimize the variance in the model fit to the data at 25°C.

Because the kaolinite surface is composed of Al and Si sites, a two-site model was used to fit the data. A four-site model (Al$_\text{edge}$ + Al$_\text{basal}$ + Si$_\text{edge}$ + Si$_\text{basal}$) gave no discernible improvement in fit over the two-site model. In other words, the acidities of the edges and basal planes could not be differentiated on the basis of our experimental data. Therefore, as an initial hypothesis, we modeled surface charge development through reactions that were assumed to occur equivalently on edges and basal planes.

For aluminol groups,
\[
\text{Al} - \text{O} - \text{H}_2 ^+ \leftrightarrow \text{Al} - \text{O} - \text{H} + \text{H}^+ ,
\]
\[
K_{\text{Al,1}} = (\text{Al} - \text{O} - \text{H}) \exp(\psi / RT) ,
\]
\[
d_{\text{Al,1}} / (\text{Al} - \text{O} - \text{H}_2 ^+ ) .
\]
\[
\text{Al} - \text{O} - \text{H} \rightarrow \text{Al} - \text{O} + \text{H}^+ ,
\]
\[
K_{\text{Al,2}} = (\text{Al} - \text{O} - \text{H}) \exp(-\psi / RT) d_{\text{Al,2}} / (\text{Al} - \text{O} - \text{H}) .
\]

For silanol groups,
\[
\text{Si} - \text{O} - \text{H} \leftrightarrow \text{Si} - \text{O} - \text{H} ^+ ,
\]
\[
K_{\text{Si,2}} = (\text{Si} - \text{O} - \text{H}) \exp(-\psi / RT) d_{\text{Si,2}} / (\text{Si} - \text{O} - \text{H}) .
\]
TABLE 1
Model Fit Parameters

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>pK_{Al,1}</th>
<th>pK_{Al,2}</th>
<th>pK_{Si,2}</th>
<th>[Al—O—H]²⁻</th>
<th>[Si—O—H]²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.33 (0.060)ᵇ</td>
<td>5.28 (0.014)</td>
<td>8.23 (0.064)</td>
<td>1.1 (0.02)</td>
<td>1.9 (0.01)</td>
</tr>
<tr>
<td>50</td>
<td>2.54 (0.056)ᵇ</td>
<td>4.20 (0.028)</td>
<td>7.98 (0.152)</td>
<td>1.6 (0.04)</td>
<td>6.2 (1.75)</td>
</tr>
<tr>
<td>70</td>
<td>2.43 (0.076)ᵇ</td>
<td>3.80 (0.030)</td>
<td>6.75 (0.050)</td>
<td>1.4 (0.03)</td>
<td>2.2 (0.09)</td>
</tr>
</tbody>
</table>

ᵇ In parentheses are calculated 2σ values.

that edge site density is 8 sites nm⁻², as determined by Sposito (28). Our SFM results show that KGa1 kaolinite easily contains this much edge surface area, based on examining only a few particles. The data also support site densities of up to ~3 sites nm⁻² if we assume an average edge surface area of ~40%. Recently, Zhou and Maurice (39) reported on their SFM morphological characterization of KGa2 and KGa1-b kaolinites from Georgia. Their results support our data on KGa1 and suggest that, in general, edge surface areas assumed in previous studies (2, 29) have been somewhat underestimated. SFM analysis therefore indicates that basal surfaces need not be considered in modeling charge site densities on kaolinite, consistent with the concept of these surfaces behaving in a hydrophobic manner. Recent measurements of asphaltene adsorption onto kaolinite (40) point to 25 to 28% of the surface as being hydrophilic, supporting our hypothesis that edge sites make a larger contribution than most researchers have previously thought.

The results in Fig. 2 are consistent with previous measurements of kaolinite surface charge. Our measured 25°C zpc (pH 3.9 ± 4.3) is slightly lower, yet similar to those measured by Riese (26) (pH 4.6) and Motta and Miranda (32) (pH 4.5). Also, fitting the 25°C data with the one-site model thickness to diameter, or aspect, ratio. If only edges participate in proton adsorption, then at most 1.6 sites nm⁻² are needed on the basal surfaces to account for all of the proton charge density measured (assuming that edges constitute 20% of the overall surface area). This presents somewhat of a dilemma, because it is generally considered that both the silicon tetrahedral and gibbsitic surfaces of kaolinite are relatively hydrophobic given that no bonds other than weak hydrogen bonds are broken when two kaolinite layers are separated. Therefore, we must find another way to account for the site densities observed from coulometric titration data. One reasonable explanation is that previous estimates of edge surface area are in error. For example, steps and ledges exposed on basal planes may provide additional edge sites that cannot be identified by geometric characterization of kaolinite particles from scanning or transmission electron photomicrographs.

To better quantify the amount of edge surface area, we determined geometric edge and basal surface areas of KGa1 particles from SFM images (Fig. 3). We found that the aspect ratio of this kaolinite ranges from 2:1 to 10:1. Interestingly, the particles tend to be thicker on average than previous estimates. In addition, the basal surfaces often contain steps that range from 1 to 30 unit cells high. For particularly rough particles (e.g., particle C in Fig. 3), the additional contribution from basal plane step edges approaches 5% of the particle’s total geometric surface area. The percentage edge surface area ranges approximately from 10 to 50% of the total surface area. (In Fig. 3, we assumed that the underlying basal surfaces were perfectly flat; however, they too probably contain some basal step structure.) To explain the observed proton charge density of 2.2 to 2.7 sites nm⁻² (again, excluding the 50°C value) we need from 27 to 34% edges, respectively, assuming

![FIG. 3. Atomic force microscopy image of KGa-1 kaolinite particles.](image)
used by Motta and Miranda (32) gives values $pK$ similar
to those observed by the latter authors at 25°C.

Using a triple-layer model, but an otherwise identical
approach to ours, Riese (26) argued for silanol group control
over pH-dependent surface charge at acid to neutral pH and
aluminocharge predominance at higher pH. Our model
points in the opposite direction, namely, alumino
groups are proposed to control kaolinite surface charge at neutral
and acidic pH values, with silanol groups contributing only
under alkaline conditions. The potentiometric titration data
allow either interpretation. Control over negative surface
charge by Al sites at pH < 7 is hypothesized for a number
of reasons. The value of $\Delta pK = pK_2 - pK_1$ for Al$_2$O$_3$ is
relatively small [ ~4 (41)], whereas the $\Delta pK$ for SiO$_2$ is
much larger [ ~7 (42)]. Assuming the same trend holds for
the Al and Si sites on the kaolinite structure suggests that
the lowest $pK_2$ belongs to the Al site (to give a $\Delta pK$ of
~3) and that the Al site dominates overall deprotonation at
pH < 7. The minimal temperature dependence observed for
$pK_1$ is similar to that observed for Al oxide (43), pointing
to Al control of positive surface charge. Schindler et al. (31)
identified Al sites on kaolinite as the primary destination for
sorbing Cu, Cd, and Pb from pH 4 to 7. At the same time
XAS analysis of Co adsorption onto kaolinite (44) points
to greater reactivity of Al sites (Al–O–H edge sites and
bridging Al–O–Si sites) relative to Si–O–H sites. In general,
surface charge becomes more negative with increasing
temperature, and there is an increasing affinity of the kaolinitic
surface for cations.

Al sites at the kaolinite surface are appreciably more
acidic than in pure alumina. The pH of zero charge for the
Al sites on kaolinite is ~3.8 at 25°C, compared with pH
8.55 for Al$_2$O$_3$ (42) and pH 8.9 for $\alpha$-Al$_2$O$_3$ (45). Silanol
sites, on the other hand, are only slightly less favored proton
donors at the kaolinite surface relative to a pure silica phase,
as $pK_{SiO_2}$ is similar to the same quantity measured on pure
SiO$_2$. The dependence of individual site acidity on the local
crystal structure emphasizes the point that surface reactivity
depends critically on interactions occurring at the molecular
level.

To unravel the specific controls of site acidity at the kaolinite–water interface we used an atomistic approach based
on the distribution of atomic charges and the observed crys-
tallographic structure of kaolinite. A molecular representa-
tion of kaolinite including the basal and edge surfaces was
constructed to perform these calculations. This form of mo-
olecular modeling relies on the net summation of charges at
a given distance from a distribution of point charges to pro-
vide a molecular electrostatic potential (MEP) surface. The
MEP calculation generates a solid surface about the kaolinite
molecule using the van der Waals radii of the atoms. The
surface is triangulated and the electrostatic potential $V$
is evaluated at each vertex $R$ of the polygonal surface:

$$V = \sum_{i=1}^{n} q(i)/|R - r(i)|,$$

where $n$ is the total number of atoms (ions), $q(i)$ is the
charge of the $ith$ atom, and $r(i)$ is the location of the $ith$
atom relative to $R$. The MEP surface provides an indication
of the electrostatic potential at the van der Waals surface as
limited by the assumption of the point charge model. The
point charge approximation may not be accurate if the elec-
tron density cannot be described as a spherical distribution
about the atom; however, this is less a concern for silicate
minerals with their predominantly ionic bonding component
as compared with organic systems with significant covalent
bonding. In essence, the MEP calculation provides the sur-
face expression of the internal distribution of ionic charges
associated with the molecule. The strength of the MEP sur-
face calculation is in predicting the most favorable site on
a molecular surface for a reaction that is initially driven
by relatively long-range electrostatic forces, for example,
sorption of solution ions and ionic complexes onto mineral
surfaces.

The MEP calculation was performed on a UNIX worksta-


Molecular electrostatic potential (MEP) surface (right) and corresponding structure (left) for a hydrated crystallite of kaolinite (silicon: yellow, aluminum: magenta, oxygen: red, hydrogen: white). Oblique view is approximately normal to the (010) surface of kaolinite; (001) basal surface is on top.

Fig. 4. Molecular electrostatic potential (MEP) surface (right) and corresponding structure (left) for a hydrated crystallite of kaolinite (silicon: yellow, aluminum: magenta, oxygen: red, hydrogen: white). Oblique view is approximately normal to the (010) surface of kaolinite; (001) basal surface is on top.

The results of the MEP calculation indicate a significant difference between the edge and basal surfaces in their potential for surface reaction (Fig. 4). The (010) edge sites exhibit an extreme electrostatic potential that is approximately $-0.9$ charge/Å, whereas the (001) surface is characterized by an extreme value of $-0.3$ charge/Å. This sizable difference in electrostatic potential between the two kaolinite surfaces is related to the sheet structure of kaolinite and the net modification of the electrostatic potential by the spatial distribution of point charges. The MEP surface for the (010) surface of kaolinite exhibits the most negative potential at the aluminum octahedral layer between two of the upper protonated oxygens. This firmly suggests a stronger Lewis base behavior of these aluminum sites relative to the (001) basal aluminum and hydroxyl groups. The silicon tetrahedral layer exhibits a negative net MEP charge smaller in absolute value ($-0.6$ charge/Å) than that observed for the aluminum sites. The differences in potential exhibited in the MEP surface underscore the relative affinity of the different kaolinite surfaces and surface sites for subsequent reaction with an aqueous cation or positively charged complex. The spatial distribution of charge on the kaolinite surface will direct the initial approach of these species as influenced by long-range Coulombic forces.

Asymmetries in the MEP surface are related to crystallographic differences among the cleaved surfaces and to edge effects that result from limitations in the size of the kaolinite crystallite that is practical for the computational effort. Additionally, the surface hydrogen positions determined by the energy-minimization calculations are controlled by hydrogen bonding with oxygens between the aluminum and silicon layers and between kaolinite layers. The lack of long-range forces in these calculations emphasizes the influence of edge effects on these results.

**DISCUSSION AND CONCLUSIONS**

We had two primary conclusions:

1. Edge sites contribute more to kaolinite surface area
and charge development than has been assumed. One result of this is that basal plane ionization is not needed to account for measured proton adsorption.

2. Al sites at the kaolinite surface are significantly more acidic than are the same sites on the pure Al oxide, or Al hydroxide. Approaches that rely on simple addition of oxide components to understand multioxide surface charge (2, 7, 27, 33, 48, 49) are probably unrealistic at the molecular level, at least below pH 7. Nevertheless, the fact that Si site deprotonation is roughly the same for the kaolinite surface as the pure oxide suggests that at pH > 7, where Si surface charge is most important, the approximation may be more accurate.

Understanding proton adsorption is a necessary first step to unraveling the affinity of clay mineral surfaces for both inorganic and organic (biological and xenobiotic) species. The kaolinite results presented above suggest that the most important tools for understanding proton adsorption on clays are (1) analytical approaches for accurately quantifying the edge/basal plane ratio and (2) methods for quantifying the surface acidity shift of the non-Si oxides from the pure state to that in the clay lattice structure, as a function of mineral composition.

We have shown that scanning force microscopy is an effective solution for the first problem. Molecular modeling, as we have applied it to a fairly large molecular representation of a crystalline material, is uniquely suited for the second.

It is reasonable to apply the results obtained for the 1:1 layer phase kaolinite to examination of surface charge on the more complex 2:1 layer clays. In the latter, substitution of trivalent cations (primarily Fe and Al) into Si sites imparts a net negative charge to the basal plane which is satisfied by interlayer cations. The relative affinity of the basal plane for various cations reflects the interplay between electrostatic interaction and hydration effects (50). As a first approximation we would expect the same to hold true for cation interaction with heterovalently substituted sites at clay edges. Proton affinity for edge sites will ultimately depend on the radial distribution of charge among metal site, the adjacent basal planes, and the solution. A promising way to examine more complex clays, therefore, may be through the application of MEP calculations to establish charge distribution on these sites.

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REFERENCES