Surface geochemistry of the clay minerals

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ABSTRACT Clay minerals are layer type aluminosilicates that figure in terrestrial biogeochemical cycles, in the buffering capacity of the oceans, and in the containment of toxic waste materials. They are also used as lubricants in petroleum extraction and as industrial catalysts for the synthesis of many organic compounds. These applications derive fundamentally from the colloidal size and permanent structural charge of clay mineral particles, which endow them with significant surface reactivity. Unraveling the surface geochemistry of hydrated clay minerals is an abiding, if difficult, topic in earth sciences research. Recent experimental and computational studies that take advantage of new methodologies and basic insights derived from the study of concentrated ionic solutions have begun to clarify the structure of electrical double layers formed on hydrated clay mineral surfaces, particularly those in the interlayer region of swelling 2:1 layer type clay minerals. One emerging trend is that the coordination of interlayer cations with water molecules and clay mineral surface oxygen is governed largely by cation size and charge, similarly to a concentrated ionic solution, but the location of structural charge within a clay layer and the existence of hydrophobic patches on its surface provide important modulations. The larger the interlayer cation, the greater the influence of clay mineral structure and hydrophobicity on the configurations of adsorbed water molecules. This picture extends readily to hydrophobic molecules adsorbed within an interlayer region, with important implications for clay–hydrocarbon interactions and the design of catalysts for organic synthesis.

The clay minerals are layer-type aluminosilicates, ubiquitous on our planet in geologic deposits, terrestrial weathering environments, and marine sediments (1, 2). Their name derives from the micrometer-sized particles into which they crystallize. This small particle size, in turn, endows these minerals with an important surface reactivity that plays a major role in the terrestrial biogeochemical cycling of metals, in the chemical homeostasis of the oceans, and in a broad variety of managed processes, including oil and gas production, industrial catalysis, pharmaceutical delivery, and radioactive waste disposal. Metal nutrients such as K⁺ or Ca²⁺ are retained in temperate-zone soils on negatively charged clay mineral surfaces but eventually can be released for consumption in the biosphere or for buffering these soils against excess acidity brought in by applied fertilizers or contaminated rainwater (3). Clay minerals precipitated from seawater in nearshore depositional environments can similarly influence the geochemical cycles of metal cations such as K⁺ (4), as well as the oceanic buffering of atmospheric CO₂ on a global scale (5). In engineered settings, clay mineral swelling promoted by Na⁺ adsorption plays a significant role in petroleum extraction (6) and in the construction of environmental liners (7). Major impact on industrial organic synthesis comes in the many designed catalysts developed from clay minerals with adsorbed polymeric cations (8).

Certain clay minerals are isostructural with mica (1, 2) but are not as well crystallized because of random isomorphic cation substitutions in their structure (9, 10). These cation substitutions lead to a negative net surface charge that induces an electrical double layer on clay mineral surfaces when they are exposed to aqueous electrolyte solutions (i.e., to natural waters). Water molecules can be intercalated between clay layers to create an interlayer ionic solution that causes swelling phenomena related to electrical double layer properties (3, 6, 11, 12).

The structure of the double layer that forms in swelling clay mineral interlayers has been the object of much geochemical research (12), but only in recent years, aided especially by insights gained from studies of concentrated aqueous ionic solutions (13), has the powerful tandem mix of spectroscopy and molecular modeling been able to clarify matters. Two particularly effective innovations have been isotopic-difference neutron diffraction and Monte Carlo computer simulation (13). The present article is a brief account of our own recent efforts in applying these two innovations to the hydrated clay minerals, which are of widespread importance in terrestrial surface geochemistry. The emphasis here is on a molecular picture of clay hydrate interlayer structure, particularly the issues of how similar this structure is to that in concentrated ionic solutions and how different it is from the tetrahedral hydrogen-bonded network characteristic of liquid water in bulk. This kind of fundamental understanding is essential to improved modeling of global elemental cycles and better design of engineered clay materials (5–8).

Crystal Structures of Clay Minerals. Clay minerals are stacked, polymeric sandwiches of tetrahedral and octahedral sheet structures (3, 9–12). They are classified first into “layer types,” differentiated by the number of tetrahedral and octahedral sheets that have combined, and then into “groups,” differentiated by the kinds of isomorphic cation substitution that have occurred (10). Layer types are sketched in Fig. 1A, and the groups are identified in Table 1. The 1:1 layer type consists of one tetrahedral sheet fused to an octahedral sheet. It is represented in Table 1 by the kaolinite group, whose generic chemical formula is

\[ [\text{Si}_{n_1}\text{Al}_{n_2-n_1}]\text{Al}_{n_1+n_2}4\text{Fe(III)}_2\text{O}_10(\text{OH})_8 \cdot n\text{H}_2\text{O} \]

where cations enclosed in square brackets are located in the tetrahedral sheet, and the stoichiometric coefficients (\(n_1, i = \ldots\))

Abbreviation: MC, Monte Carlo.

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where charge and mass balance constraints again appear in Table 1. The symbol \( C_x \) represents \( x \) moles of monovalent cation charge that balances negative structural charge created by isomorphic replacement of tetrahedral Si by Al; dioctahedral Al by Mg, Fe(II); or trioctahedral Mg by the unspecified structural cation M (for example, Li in the trioctahedral mineral hectorite). The layer charge \( x \) is thus the number of moles of excess electron charge per chemical formula unit that is produced by isomorphic cation substitutions (Table 1). It is balanced by cations adsorbed on or near the basal plane of a tetrahedral sheet.

The three 2:1 groups are differentiated in two principal ways. As indicated in Table 1, the layer charge generally decreases in the order illite \( \rightarrow \) vermiculite \( \rightarrow \) smectite. The vermiculite group is further distinguished from the smectite group by a much greater degree of isomorphic substitution in the tetrahedral sheet (9, 10). Among dioctahedral smectites, those for which substitution of Al for Si in the tetrahedral sheet exceeds that of Fe(II) or Mg for Al in the octahedral sheet are called beidellite, and those for which the reverse is true are called montmorillonite (11). The emphasis in the present article will be on vermiculite and smectite clay minerals because of their importance in terrestrial weathering processes and designed industrial applications (5–8).

**Siloxane Surface Reactivity.** The plane of oxygen ions bounding each side of a 2:1 clay mineral layer (i.e., the basal plane of a tetrahedral sheet) is called a siloxane surface (12). A reactive site associated with this surface is the hexagonal cavity formed by the bases of six corner-sharing Si tetrahedra (Fig. 1B). It has a diameter of \( \approx 0.26 \text{ nm} \) and is bordered by six oxygen ions, with a hydroxyl group rooted at the bottom in the octahedral sheet. In dioctahedral clay minerals, this hydroxyl group points toward the empty metal site in the octahedral sheet whereas, in trioctahedral clay minerals, it points perpendicularly to the siloxane surface (9).

The reactivity of the siloxane surface depends on the nature of the local charge distribution in the clay layer (12). In the absence of nearby isomorphic cation substitutions that create negative charge, a siloxane surface functions only as a mild charge donor. If isomorphic substitution of Al by Fe(II) or Mg occurs in the octahedral sheet, the resulting excess negative charge makes it possible for the surface to form reasonably strong adsorption complexes with cations and water molecules. If isomorphic substitution of Si by Al occurs in the tetrahedral sheet, with the excess negative charge thereby localized much nearer to the siloxane surface, much stronger adsorption complexes with cations and stronger hydrogen bonds to vicinal water molecules become possible. Charged sites also exist on the edges of clay mineral crystallites (12). Their role in clay mineral surface geochemistry ranges from critical to subordinate as the layer type shifts from 1:1 to 2:1 (9, 11, 12).

Cation adsorption complexes can be classified as either inner-sphere or outer-sphere (3). An inner-sphere surface complex has no water molecule interposed between the surface functional group and the small cation or molecule it binds whereas an outer-sphere surface complex has at least one such interposed water molecule. Outer-sphere surface complexes thus comprise solvated adsorbed cations. Surface complexes involving metal cations are illustrated in Fig. 2 for a 2:1 layer type clay mineral.

Ions bound in surface complexes are distinguished from those adsorbed in the diffuse portion of the electrical double layer (also illustrated in Fig. 2) because the former species remain immobilized on a siloxane surface over molecular time scales that are long when compared with, for example, the 4–10 ps required for a single diffusive step by a solvated ion in aqueous solution (13). The well known outer-sphere surface complex formed by bivalent metal cations (for example, \( \text{Ca}^{2+} \)) in the interlayer region of montmorillonite (compare the left
side of Fig. 2) is immobile on the molecular time scale of \( \approx 100 \) ps probed by electron spin resonance spectroscopy and by quasielastic neutron scattering (14, 15). These three types of clay mineral surface species—inner sphere complex, outer-sphere complex, and diffuse-layer—represent different modes of adsorption of aqueous cations that contribute to the formation of an electrical double layer on charged siloxane surfaces (3).

Interlayer Surface Structure by Neutron Diffraction. The surface species “cartooned” in Fig. 2 emerged conceptually from the results of in situ spectroscopic studies (14, 15). The consensus of these studies is that hydrated smectite and vermiculite interlayers are in many ways similar in structure to a concentrated ionic solution (14). Aqueous solution molecular structure, in turn, has been explored especially well over the same time-period by isotopic-difference neutron diffraction (13, 16). In this methodology, isotopic substitution of one or more diffracting atoms is performed (for example, substitution of hydrogen by deuterium in interlayer water) to create differences in coherent neutron scattering cross section that facilitate locating the atom accurately in relation to its diffracting neighbors (13, 16). Isotopic-difference neutron diffraction methods are reviewed concisely by Skipper et al. (17) for hydrated 2:1 clay minerals. Neutron diffraction studies of the interlayers in these systems have already provided valuable insight as to molecular structure in the electrical double layer formed on siloxane surfaces (17–19).

Fig. 3 is a visualization of the arrangement of water molecules around Ca\(^{2+}\) adsorbed in the interlayer region of the two-layer hydrate of trioctahedral vermiculite, based on the results of H/D isotopic-difference neutron diffraction experiments (18). Because the water protons could be identified separately from those in the clay mineral structure and were distinguishable from other interlayer atoms, it was possible to show rather clearly that the Ca\(^{2+}\) are octahedrally coordinated to their nearest-neighbor water molecules, as also occurs in concentrated, as opposed to dilute, aqueous solutions of CaCl\(_2\) (13, 18). Moreover, four of the solvating water molecules form hydrogen bonds with the siloxane surfaces, as expected for clay minerals with isomorphic substitutions only in the tetrahedral sheets (12). Because the two-layer hydrate of vermiculite has about eight water molecules per Ca\(^{2+}\) in the interlayer region.

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**Table 1. Some clay mineral groups**

<table>
<thead>
<tr>
<th>Group</th>
<th>Layer type</th>
<th>Layer charge, ( x )</th>
<th>Structural charge balance*</th>
<th>Structural mass balance*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>1:1</td>
<td>(&lt;0.01)</td>
<td>( x = 4 - n1)(^\dagger)</td>
<td>( \sum_{i=1}^{6} n_i = 8)(^\dagger)</td>
</tr>
<tr>
<td>Illite</td>
<td>2:1</td>
<td>(1.4–2.0)</td>
<td>( x = 8 - n1 + n4 + n5 + n6)(^\dagger)</td>
<td>( \sum_{i=1}^{6} n_i = 12)(^\dagger)</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>2:1</td>
<td>(1.2–1.8)</td>
<td>( x = 8 - n1 + n4 + n5 + n6)(^\dagger)</td>
<td>( \sum_{i=1}^{6} n_i = 12)(^\dagger)</td>
</tr>
<tr>
<td>Smectite</td>
<td>2:1</td>
<td>(0.5–1.2)</td>
<td>( x = 8 - n1 + n4 + n5 + n6)(^\dagger)</td>
<td>( \sum_{i=1}^{6} n_i = 12)(^\dagger)</td>
</tr>
</tbody>
</table>

*Based on an \( O^{\dagger}(OH)_6 \) (1:1) or \( O^{\dagger}\text{H}(OH)_4 \) (2:1) unit cell formula.

\(^\dagger\)See text for definitions of \( n_i (i = 1, \ldots , 6) \).

\(^\ddagger\)The formulas given are dioctahedral clay minerals with bivalent M in the octahedral sheet. For trioctahedral smectite and vermiculite with monovalent M in the octahedral sheet, \( x = 2(8 - n1) - n2 - n3 + n6 \) and \( \sum_{i=1}^{6} n_i = 14 \).
An essay on hydrated clay minerals, detailing the interactions of water molecules with different clay minerals. The essay discusses the results of neutron-scattering and electron spin resonance studies, indicating the presence of water molecules in the interlayer region of Ca-vermiculite. Monte Carlo simulations are used to explore the structural inferences of these clay minerals, particularly Wyoming montmorillonite. The essay also delves into the properties of water molecules, specifically those that are solvated or desolvated within the clay mineral structure. A diagram of a Ca$^{2+}$ solvation complex with water molecules is included, highlighting the importance of these complexes in understanding the behavior of hydrated clay minerals. The essay concludes with a discussion on the application of these findings to fundamental geochemical research.
FIG. 4. Visualization of Na$^+$ bound in an outer-sphere surface complex in the interlayer region of Wyoming montmorillonite, based on MC simulation. A portion of the siloxane surface structure also is shown.

FIG. 5. Visualization of K$^+$ bound in an inner-sphere surface complex in the interlayer region of Wyoming montmorillonite, based on MC simulation. Green lines extend from K$^+$ (black sphere) to nearest-neighbor O in the surface complex. Dashed lines indicate hydrogen bonds between water molecules. Portions of the opposing two siloxane surfaces also are shown, with the beige sphere at the bottom of the figure (center) indicating a site of Al$^{3+}$ substitution for Si$^{4+}$. 

solution (≈18.5 molal). Fig. 6 conforms to the trend expected for small interlayer cations, in that only outer-sphere surface complexes have formed, comprising just two solvating water molecules, in agreement with the average hydration number of 2.3 found in isotopic-difference neutron diffraction studies of very concentrated LiCl solutions (16). The nonsolvating water molecules have keyed themselves into the hexagonal cavities of the siloxane surface (one such molecule is at the center of the simulation cell), reminiscent of the situation in trioctahedral vermiculite (17–19).

Much experimental and theoretical information points to an inherent hydrophobicity of the siloxane surface [see, for example, the summary by Jaynes and Boyd (36)] were it not for the presence of layer charge. Pyrophyllite, the uncharged analog of montmorillonite, and talc, the uncharged analog of vermiculite, both have hydrophobic siloxane surfaces (36, 37). Studies of the effect of layer charge on the adsorption of both water and hydrocarbon molecules by smectites (36, 38) indeed show that surface hydrophobicity increases as the layer charge decreases. Recent molecular dynamics simulations of ion solvation and mobility in aqueous solution (39, 40) suggest that large cations like K$^+$ tend to interact with water molecules not only through their positive charge but also through solvent cage formation, which is just what hydrocarbon molecules do (41–43). This hydrophobic tendency may be the basis for K$^+$ associating directly with clay mineral O (Fig. 5) instead of forming a well organized solvation complex near octahedral charge sites, as does Na$^+$ in Fig. 4. Fig. 7 exposes the inherent hydrophobicity of the siloxane surface even more directly through a MC snapshot of a methane molecule adsorbed in the interlayer region of the three-layer hydrate of Na-montmoril-
lonite (H₂O/CH₄ = 23). The well known 20-fold coordination cage induced by CH₄ in bulk water (41, 42) was reproduced successfully by the CH₄-O potential function used in the MC simulation (43). In the interlayer of a Na-montmorillonite hydrate, however, methane coordinates to eight clay mineral O and approximately a dozen water molecule O to form this cage in a highly distorted coordination structure. This kind of hydrophobic association, which may be favored for CH₄ over a purely solvent-based arrangement of neighboring O atoms, could play an important role in the chemical evolution of organic molecules as mediated by clay minerals (44).

The multifaceted nature of interactions within clay mineral interlayers leads necessarily to complexity in the structure of adsorbed water. This complexity is well illustrated by a consideration of water molecule orientations in the two-layer hydrate of Na-montmorillonite as revealed by MC simulation (29). Sodium–water molecule interactions in this system produce a local coordination structure like that in concentrated aqueous solutions of NaCl (13, 29), but Na⁺ interactions with tetrahedral charge sites are still strong enough to allow inner-sphere complex formation with oxygen ions in the siloxane surface. The configuration of water molecules differs between inner-sphere and outer-sphere surface complexes. When these two species are forced to cohabit within the constrained spatial domain that exists in an interlayer region, disorder in the water network is likely, with distorted H-bonds and an array of water dipole orientations taking on almost every possible direction (29). This disorder is enhanced by an evident attraction between water molecules and the cavities in the siloxane surface, which gives rise to nonsolvating water molecules keyed into these holes irrespective of the type of adsorbed cation (6, 18, 19, 29–31, 33). The characteristics of adsorbed water on 2:1 clay minerals also reveal the competition between interlayer cations and clay mineral structure for intercalated water molecules, as well as that between hydrophilic and hydrophobic interactions. This competition produces a complex electrical double layer structure whose origins and behavior are beginning to be understood at a fundamental level as the basis for progress toward improved design in applications (7, 8) that provide palpable benefits for human-kind.

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