

Molecular simulation of humic substance–Ca–montmorillonite complexes

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Abstract

An understanding of the processes that lead to long-term stabilization of organic matter in soils is essential to the effective implementation of strategies designed to mitigate CO₂ loss from the soil carbon reservoir in temperate climatic zones. Decomposition studies indicate that montmorillonite, a smectite that often forms with interlayers rich in Ca²⁺, greatly retards the microbial mineralization of soil organic matter. We performed a series of atomistic simulations designed to identify favorable molecular-scale organo-mineral interactions within nanoscale, hydrated complexes consisting of a humic substance and Ca–montmorillonite. Both protonated and Ca-saturated forms of the model humic molecule, representing acidic and circumneutral solution conditions, respectively, were studied within the hydrated interlayer region of a rigid-atom model of Ca–montmorillonite. The protonated humic substance formed direct hydrophobic and hydrogen bonding (H-bonding) interactions with the clay mineral. A few polar organic groups adsorbed via water bridging interactions. The Ca-saturated humic substance adsorbed via numerous cation bridges, less numerous water bridges, and indirect H-bonding interactions mediated by water molecules. Application of molecular modeling techniques to this complex organo-mineral system thus allowed identification of interactions favorable to carbon sequestration under both acidic and circumneutral conditions.

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1. Introduction

Widespread adoption of land management strategies that promote soil C sequestration in temperate zones has been proposed as a means of reducing atmospheric CO₂ concentrations and mitigating climate change (Freibauer et al., 2004; Lal, 2004; Post et al., 2004). Essential to the design and implementation of these strategies is a predictive understanding of natural processes that lead to the long-term stabilization of organic matter within the soil profile.

Humic substances, perhaps best described as refractory, dark-colored, heterogeneous organic compounds produced as by-products of microbial metabolism, typically represent the oldest form of organic matter in soils, indicating their significant resistance to microbial degradation (Stevenson, 1994). However, when removed from their mineral matrices

and exposed to microbial attack, humic substances decompose rapidly (Gramss et al., 1999), revealing the fact that intimate association with soil minerals is key to their stabilization (Schulten and Leinweber, 1996; Zech et al., 1997; Baldock and Skjemstad, 2000; Laird et al., 2001). Other lines of broad evidence pointing to the importance of organo-mineral interactions for the long-term preservation of humic substances include observations of: (1) greater amounts of organic matter in fine textured, well-drained temperate soils, relative to corresponding coarse textured soils (Anderson, 1987; Oades, 1988; Stevenson, 1994; Feller and Beare, 1997), or in fine (clay and/or silt) particle size fractions relative to coarse (sand) particle size fractions (Oades, 1988; Baldock et al., 1992; Hassink, 1997; Feller and Beare, 1997; Parfitt et al., 1997); (2) greater microbial processing, as signaled by narrow C:N ratios (Baldock et al., 1992; Stevenson, 1994; Feller and Beare, 1997; Parfitt et al., 1997) and other biogeochemical indicators (Feller and Beare, 1997), experienced by organic matter within fine particle size fractions; and (3) longer mean residence times

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of organic matter associated with soil minerals (Oades, 1988; Feller and Beare, 1997; Meredith, 1997; Monreal et al., 1997; Torn et al., 1997; Baldock and Skjemstad, 2000; Eusterhues et al., 2003; Wattel-Koekkoek et al., 2003).

Explorations of the organo-mineral interactions critical to preservation of soil C must begin with a molecular-scale understanding of the adsorption of organic materials to common soil mineral surfaces. Montmorillonite, a mineral typical of well-drained, temperate soils, is a 2:1 layer-type smectite clay mineral with abundant siloxane surfaces consisting of oxygen triads that form networks of six-oxygen rings, at the center of each a distorted hexagonal (or ditrigonal) cavity. The hydrophobic nature of this siloxane surface (Bleam, 1990; Jaynes and Boyd, 1991a,b; Boyd and Jaynes, 1992; Van Oss and Giese, 1995; Giese et al., 1996; Laird, 1996; Chiou and Rutherford, 1997) is disrupted by the presence of the tetrahedral and octahedral isomorphous substitution sites within the montmorillonite, which provide the mineral's negative charge, and trigger its characteristic shrinking and swelling behavior in response to changes in relative humidity.

An examination of landscape scale trends indicates that undisturbed soils rich in montmorillonite, such as Mollisols, Alfisols, and Vertisols, typically contain large amounts of organic matter (Kern, 1994). The natural fertility of these soils results in their use for conventional agriculture, ultimately leaving them depleted in organic matter, but available for implementation of large-scale land management practices designed to sequester C (Freibauer et al., 2004; Lal, 2004; Post et al., 2004). Comparison of soils containing differing amounts of montmorillonite and other smectite minerals indicates a strong positive correlation between the percentage of silt- and clay-sized particles with either total soil organic matter (Feller and Beare, 1997) or organic matter associated with these particles (Hassink, 1997). Decomposition experiments additionally indicate that the presence of montmorillonite greatly reduces the mineralization of organic materials (Allison et al., 1949; Saggart et al., 1996). Indeed, some radiocarbon dating studies suggest that association with smectite minerals can impart mean residence times of hundreds to thousands of years to organic compounds (Anderson and Paul, 1984; Theng et al., 1992; Arai et al., 1996; Meredith, 1997; Wattel-Koekkoek et al., 2003). Furthermore, Monreal et al. (1997) reported a soil profile for which the turnover time of soil organic matter was positively correlated with the amount of associated smectite in each horizon. Thus, both landscape-scale observations and laboratory-scale experiments indicate that montmorillonite and other smectite minerals are instrumental in the long-term sequestration of soil organic matter.

Because montmorillonite minerals often form from parent materials rich in Ca^{2+} (Borchardt, 1989), it is important to determine to what extent this ubiquitous cation may affect the ability of the minerals to sequester organic matter. Addition of Ca^{2+} increases the adsorption of natural

polyanions in montmorillonite suspensions (Theng, 1979; Franchi et al., 2003), and reduces the desorption of soluble organic matter from soils (Sokoloff, 1938; Muneer and Oades, 1989a). Incubation experiments reveal that additions of Ca^{2+} increase soil retention of fresh organic matter and promote aggregate stability (Sokoloff, 1938; Muneer and Oades, 1989a,b,c). Extraction experiments that selectively remove Ca^{2+} and other multivalent cations indicate that natural organo-mineral complexes are held together by such cations (Gaiffe et al., 1984; Muneer and Oades, 1989a), especially in smectitic soils (Wattel-Koekkoek et al., 2001). When contrasting calcareous with acidic varieties of otherwise similar smectite-rich Vertisols, Holder and Griffith (1983) determined that strong organo-mineral interactions occurred in both types of soil, but that the organic matter present in the calcareous soils was especially difficult to extract. Oades (1988) observed that calcareous soils in general tend to have much more organic matter than similar noncalcareous soils, while cautioning that high base status and high clay content are strongly correlated in soils because both are traits derived primarily from parent material, such that the influence of each on organic matter retention cannot be separated causally. In addition, Ca^{2+} can influence organo-mineral interactions in less direct ways, for example, by modifying soil particle surface area and structure (Oades, 1988). These trends suggest that the presence of montmorillonite in soils, especially when in the company of Ca^{2+} , may promote the formation of larger reservoirs of soil C due to significantly reduced rates of decomposition of organic materials stabilized through the formation of organo-mineral associations. According to extraction (Wattel-Koekkoek et al., 2001) and adsorption (Chorover and Amistadi, 2001; Wang and Xing, 2005) experiments, which indicate that montmorillonite selectively adsorbs alkyl and carboxylate functional groups from humic solutions, hydrophobic and cation bridging interactions may be key mechanisms leading to the formation of these organo-mineral associations.

Atomistic simulations based on predetermined interatomic potentials have provided insight into the organo-mineral interactions involved in the adsorption of well-defined organic molecules, such as chlorinated organic compounds (Teppen et al., 1998; Bailey et al., 2001) and proteins (Yu et al., 2000a), to aluminosilicate surfaces. While these simulations do not have the first-principles status of quantum mechanical calculations based on the Schrödinger equation (Park and Sposito, 2004), they are capable of exploring relatively large molecular systems, providing an opportunity to assess organo-mineral interactions individually and in aggregate and contributing useful information about organic functional groups, mineral surface sites, and larger-scale structural properties of complex interacting units. Molecular simulations that allow analysis of interactions between a model humic molecule and a montmorillonite surface thus may help to further our understanding of the mechanisms of adsorption available to humic materials in soil systems.

There are few published examples of molecular simulations of the interactions of model humic materials with aluminosilicate minerals, no doubt due in part to complexities that include the design or selection of an appropriate model humic molecule that can mimic natural humic substances, and an atomistic force field that can accurately simulate both organic and mineral interactions. The utility of existing published simulations as a probe to evaluate organo-mineral interactions in natural soils has been limited by their use of inappropriate model conditions, including physically unrealistic mineral species under vacuum or without hydrating water molecules (Schulten and Leinweber, 1996, 2000; Schulten and Schnitzer, 1997; Leinweber and Schulten, 1998; Schulten et al., 1998), and unhydrated monovalent cations (Akim et al., 1998; Shevchenko and Bailey, 1998a,b; Shevchenko et al., 1999), rather than hydrated polyvalent cations, to compensate negative charge.

This paper documents molecular simulations of the interactions between hydrated Ca-montmorillonite and both protonated and Ca-saturated forms of a model humic molecule, originally developed by Schulten (1999) to portray dissolved organic matter (DOM) and subsequently modified by Sutton et al. (2005) to portray soil humic substances. With these simulations, we can observe the development of favorable organo-mineral interactions within nanoscale organo-mineral systems representing two different pH conditions. The all-atom force field COMPASS [Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, Accelrys, San Diego, CA, USA] (Sun, 1998), was used to describe these interactions. COMPASS valence parameters and atomic partial charges were derived by fitting quantum chemical data, while van der Waals parameters were determined by conducting MD simulations of molecular liquids and fitting the simulated cohesive energies and equilibrium densities to experimental data (Sun, 1998). This novel combination of parameterization techniques has resulted in a force field uniquely suited to simulation of condensed phase substances. Validation studies employing isolated molecules, molecular liquids, and molecular crystals, indicate that the COMPASS force field is capable of accurate and simultaneous prediction of structural, vibrational, and thermophysical properties for a broad range of organic and inorganic substances in isolated and condensed states (Sun, 1998).

Further research supports the accuracy of COMPASS structural predictions for diverse materials subjected to a broad range of condensed phase experimental conditions, including complex organic materials like chitosan (López-Chávez et al., 2005), eumelanin (Stark et al., 2005), and soot (Kubicki, 2006). It has also proved to be useful for simulation of interactions between water and minerals (Fleys and Thompson, 2005), further indication that it is a suitable force field for the hydrated organo-mineral systems we studied. Published research comparing simulations of complex organic materials using COMPASS and the semi-empirical quantum chemical PM3 method indicate

that the two methods can produce similar results, except where covalent interactions may develop between molecules (Kubicki and Trout, 2003). However, it is important to note that all force fields are subject to potential errors. In the case of COMPASS, intermolecular interactions between water molecules (Sutton et al., 2005), as well as interactions between water molecules and aromatic functional groups (Kubicki, 2006), are not well-represented.

Our previous work has indicated that, when simulated using the COMPASS force field, the Schulten model DOM molecule reproduces physical and chemical properties of humic substances under a range of environmental conditions that are relevant to soils (Sutton et al., 2005). The Schulten DOM molecule is one of several molecular representations of humic materials; other model humic molecules may display variation in these physical and chemical properties. The protonation states of the two forms of the DOM molecule correspond to those expected under highly acidic or circumneutral soil conditions, allowing conclusions to be drawn concerning the effect of both pH and Ca^{2+} on organo-mineral interactions. Our simulation cells consist of DOM molecules sequestered within hydrated Ca-montmorillonite interlayers. The interlayer provides a conveniently periodic system that drastically reduces computational costs. It seems likely that most soil C is not found within smectite interlayers (Baldock and Skjemstad, 2000; Laird, 2001). However, organic molecules do find their way into this region (Kodama and Schnitzer, 1971; Satoh and Yamane, 1971; Theng et al., 1986; Righi et al., 1995), where they may be protected from degradation for several thousand years (Theng et al., 1992), thus forming an extremely stable C pool.

Two simulation algorithms, energy minimization (EM) and molecular dynamics (MD), were used to explore the properties of humic substance–montmorillonite systems. Energy minimization involves geometric optimization of atomic coordinates to reduce the potential energy of a molecular system, which is calculated by summing all interaction terms described by the force field (Accelrys Inc., 2001). Minimization algorithms are independent of temperature: 0 K conditions are assumed. The optimized molecular conformation adopted after minimization is typically one of many stable states that occupy local energy minima. To move a molecule from a conformation associated with a local energy minimum to one associated with the global energy minimum, representing the most stable state, an optimized structure may be subjected to further calculations using a MD algorithm that simulates the movements of atoms as they interact with each other over time (Allen and Tildesley, 1987).

2. Methods

2.1. The Schulten DOM molecule

The Schulten DOM molecule, a particularly large and complex model of humic material, was crafted in

response to pyrolysis and other experimental studies of natural organic matter (Schulten, 1999). It consists of a Schulten model humic acid molecule, a collection of substituted aromatic and quinone structures interlinked by substituted alkyl chains, to which a hexapeptide and a trisaccharide are covalently bonded. The DOM molecule features a wealth of organic functional groups common to humic matter, including aromatic, alkyl, carboxyl, carbonyl, ketone, quinone, phenol, alcohol, ether, amine, amide, and heterocyclic N and S functional groups. It contains 1157 atoms, with the molecular formula $C_{447}H_{421}O_{272}N_{15}S_2$, and a molar mass $10,419.3 \text{ g mol}^{-1}$. Previous COMPASS force field simulations of the DOM molecule, described in detail elsewhere (Sutton et al., 2005), allowed determination of bulk characteristics of this model humic material using a dry, densely packed system, while aqueous solution characteristics were obtained through simulations representing dilute solutions under acidic (i.e. carboxyl groups) and circumneutral (i.e. carboxylate groups) conditions. To balance negative charge, deprotonated humic polyanions were saturated with hydrated Na^+ or Ca^{2+} counterions.

Physical and chemical characteristics of the model DOM molecule compared favorably with available experimental data on humic substances (Sutton et al., 2005). Relevant to the simulations presented here, deprotonation and cation-saturation of the hydrated DOM molecule led to model metal–humic structures that were more porous, had greater solvent-accessible surface areas, and formed more H-bonds with water than the protonated, hydrated DOM molecule, due to intrusion of the cation hydrates within the organic matrix (Sutton et al., 2005). Two versions of the molecule were selected for placement within montmorillonite interlayer regions, one fully protonated, the other with 76 deprotonated carboxyl groups saturated with hydrated Ca^{2+} to compensate negative charge.

2.2. Ca-montmorillonite hydrates

While the COMPASS force field produced simulations of the Schulten DOM molecule that display physicochemical qualities consistent with experimental data on humic substances (Sutton et al., 2005), its ability to model Ca-montmorillonite has not been established in any published study. Therefore, simulations of Ca-montmorillonite hydrates were performed to allow structural comparison with known properties of the interlayer region. Details of the simulations are provided in an [Electronic Annex](#). Simulations of rigid montmorillonite structures indicated that the COMPASS force field adequately captured major structural features experimentally observed in Ca-smectites (Fig. 1). Interlayer Ca^{2+} preferred midplanar positions and were hydrated by up to eight water molecules. Most water molecules were found in two layers, one adsorbed to each mineral surface, and water–mineral O H-bonds were abundant.

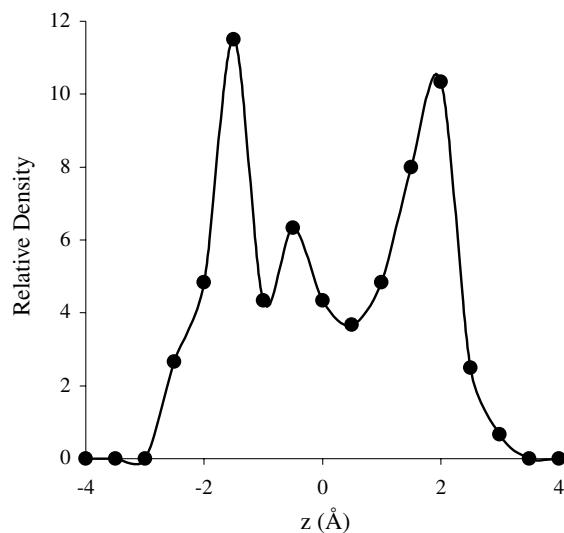


Fig. 1. Average distribution of water O along the z axis, normal to the clay layer, for the six hydrated Ca-montmorillonite systems (layer spacing 15.2 \AA) subjected to the entire cycle of EM and MD calculations. The origin represents the midplane of the interlayer.

2.3. DOM–montmorillonite complexes

Following satisfactory completion of simulations of the DOM molecule and Ca-montmorillonite using the COMPASS force field, a series of calculations to probe organo-mineral interactions between these two components was initiated. To construct the organo-mineral systems, a 32 unit cell Ca-montmorillonite clay layer was constructed from a 2×2 array of the 8 unit Ca-montmorillonite hydrate system ([Electronic Annex](#)). The lateral (xy) dimensions of the 32 unit simulation cell were $42.24 \times 36.56 \text{ \AA}$. The Ca-montmorillonite contained 24 isomorphous substitution sites (8 tetrahedral charge sites and 16 octahedral charge sites), creating a charge of $-24e$ that was balanced by 12 interlayer Ca^{2+} . These cations were surrounded by water molecules within the hydration spheres observed in the original 8 unit Ca-montmorillonite hydrate ([Electronic Annex](#)); all other interlayer water molecules were eliminated from the system. Interlayer cations and associated waters of hydration were distributed such that an equal number of cations resided near each clay surface. The initial layer spacing of the large Ca-montmorillonite simulation cell was set to 50 \AA for the protonated DOM molecule, and 55 \AA for the Ca-saturated DOM polyanion.

Initial conformations of the DOM molecules inserted into these clay interlayers came from previous calculations of these molecules using COMPASS (Sutton et al., 2005). The structure of the protonated organic molecule was taken from a simulation of DOM in a dilute aqueous solution. All water molecules were stripped from the system prior to placement within the smectite. Likewise, the structure of the Ca-saturated organic molecule was taken from a simulation of Ca-DOM in a dilute aqueous solution. Those water molecules added as part of hydrated Ca^{2+} during

the “titration” procedure used to gradually replace carboxyl groups with Ca-saturated carboxylate groups (Sutton et al., 2005) were not stripped from the structure; however, the layers of water molecules added after “titration” were removed prior to insertion within the mineral. The organic structures were pasted into the centers of interlayer regions such that the molecules were not positioned unrealistically close to other interlayer or mineral species. The initial protonated DOM–montmorillonite system consisted of a rigid, periodic 32 unit Ca-montmorillonite clay layer, 12 Ca^{2+} , 92 interlayer water molecules, and an organic molecule with the formula $\text{C}_{447}\text{H}_{421}\text{O}_{272}\text{N}_{15}\text{S}_2$. The initial Ca-saturated DOM–montmorillonite system featured a rigid, periodic 32 unit Ca-montmorillonite clay layer, 50 Ca^{2+} , 320 interlayer water molecules, and an organic polyanion with the formula $\text{C}_{447}\text{H}_{345}\text{O}_{272}\text{N}_{15}\text{S}_2^{-76}$.

To identify a layer spacing appropriate to each organo-mineral system, several sequential minimizations that included the application of pressure normal to the clay layers were performed. The use of pressure encouraged the mineral surfaces in each system to move toward each other. A typical run in this series involved application of 0.0001 GPa of pressure along the z axis of the simulation cell, and proceeded for 40,000 EM steps. Because clay layer registration is unlikely to affect systems with basal spacings greater than those observed with adsorption of a layer or two of water molecules, only the z dimensions of the systems were allowed to vary. Layer spacings and potential energies of the systems were recorded after each minimization in the sequence. Interactions making up these potential energies included those occurring among atoms within interlayer species, and between atoms of the interlayer species and atoms of the clay layer. However, they did not include interactions among the mineral atoms themselves. Although, due to their large size and complexity, the systems never reached a fully minimized state according to the high convergence criteria of the Cerius² Smart Minimizer (Accelrys Inc., 2001), when an EM calculation produced a layer spacing reduction of less than 0.1 Å (Ca-saturated DOM–montmorillonite), or produced a slightly increased layer spacing (protonated DOM–montmorillonite), this was considered to indicate minimization sufficient for development of a suitable layer spacing for the organo-mineral systems. Layer spacings were fixed at 30.53 Å for the protonated DOM–montmorillonite system, and 33.32 Å for the Ca-saturated DOM–montmorillonite system.

Water molecules were added to fully hydrate the interlayer region using the InsightII v2000.1 software package (Accelrys Inc.). 451 water molecules were added to the interlayer containing the protonated DOM molecule, bringing the total number of interlayer water molecules to 543, while 400 water molecules were added to the interlayer region containing the Ca-saturated DOM polyanion, for a total of 720 interlayer water molecules. The hydrated organo-montmorillonite interlayer systems were minimized, then subjected to annealing MD runs as described

in the [Electronic Annex](#). Further minimization of each annealed structure was followed by a 10 ps MD computation at 300 K. Afterward, InsightII (Accelrys Inc.) was used again to add more water molecules to the interlayer. The protonated DOM–montmorillonite system was unable to accommodate more water, while the Ca-saturated DOM–montmorillonite system adsorbed 132 additional water molecules, for a total of 852. The densities of the organo-mineral systems, as well as the hydrated interlayer regions, were calculated at this point.

Minimization of the Ca-saturated DOM–montmorillonite system was followed by an annealing MD run for both organo-mineral structures, as described in the [Electronic Annex](#). Each temperature in the annealing cycle was held for 10 ps. The annealed structures were minimized, then subjected to 20 ps of MD calculations at 300 K. A final minimization of each system resulted in hydrated organo-mineral complexes free of physically unrealistic configurations, and likely associated with the global energy minimum for each DOM–montmorillonite cell. Potential energy distributions were calculated for the two systems in their final conformations, as well as for periodic representations of the protonated and Ca-saturated DOM molecules without clay and water molecules. A lower limit for the molar cohesive energy, or intermolecular potential energy, of water can be calculated by subtracting the cohesive energy of the periodic DOM molecule and four times the dry Ca-montmorillonite potential energy calculated in the [Electronic Annex](#) from the cohesive energy for each organo-mineral complex, then dividing the value obtained by the number of water molecules in each system.

Structural analysis of the organo-montmorillonite systems began with visual examination of the protonated and Ca-saturated DOM molecules apart from their hydrated interlayer environments, and calculation of their solvent-accessible Connolly surface areas (solvent molecule radius 1.4 Å) and molecular volumes (Accelrys Inc., 2001). Inspection of interlayer cations included calculation of Ca–O radial distribution functions (RDFs) and coordination numbers (CNs), as described in the [Electronic Annex](#), and examination of the local structure around each individual Ca^{2+} . The H-bonds occurring within the DOM molecules, and between organic and water atoms, organic and clay atoms, and clay and water atoms, were identified and counted as described in the [Electronic Annex](#). This was followed by individual analysis of each organo-mineral interaction occurring within the DOM–montmorillonite systems.

3. Results and discussion

Visualizations of the final structures of the acidic (protonated) and circumneutral (Ca-saturated) organo-mineral systems (Fig. 2) provide a means to evaluate qualitatively the different organo-mineral interactions that formed under the two pH regimes. As well, the conformational differences between the two systems have energetic consequences.

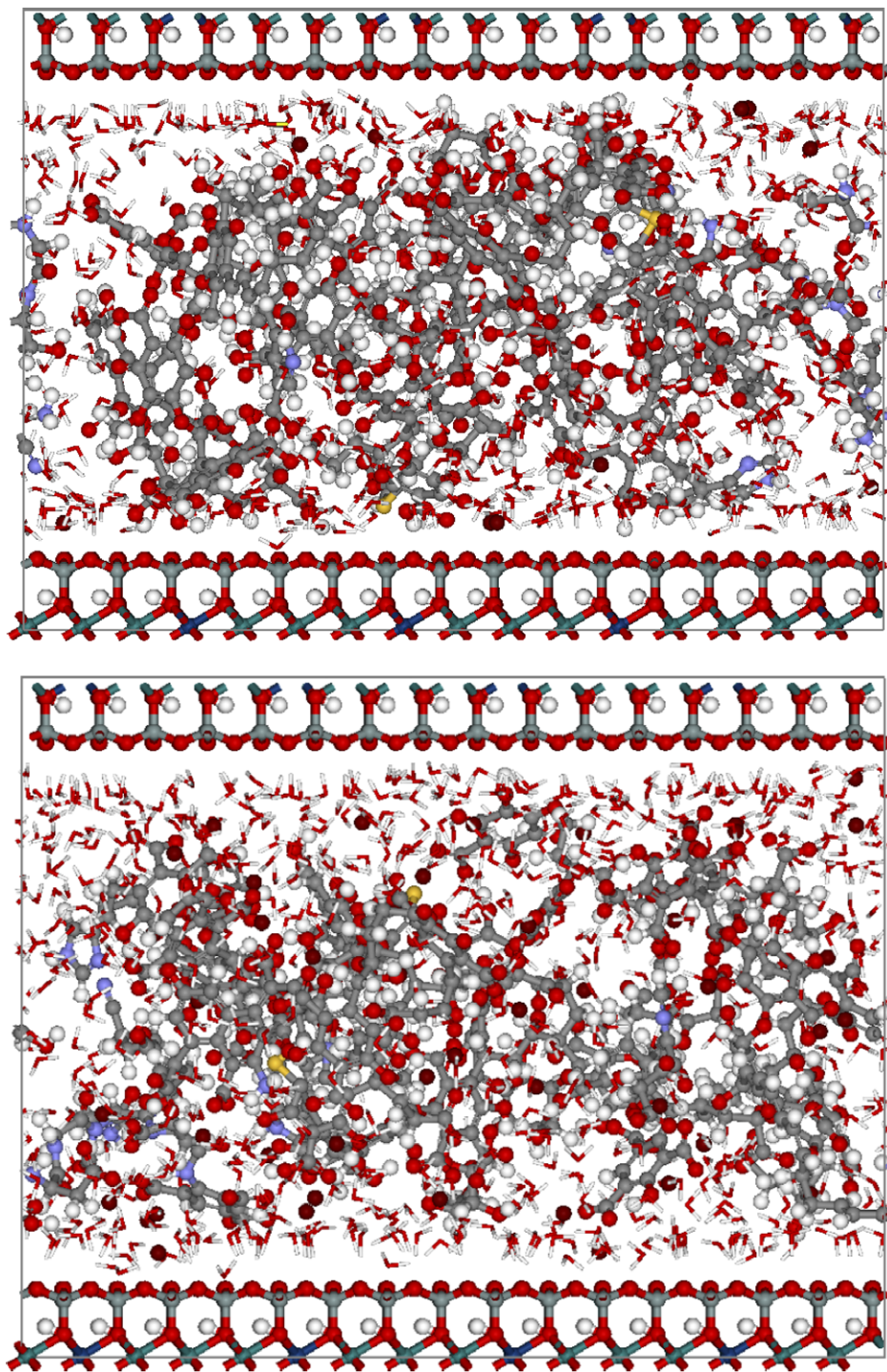


Fig. 2. Views of the protonated (top) and Ca-saturated (bottom) DOM–montmorillonite systems. Water molecules are represented using cylinders to reduce visual clutter, while DOM and clay molecules are represented in the ball and stick style. Grey denotes C, red denotes O, white denotes H, N and S are blue and yellow, respectively, and Ca^{2+} is brown. Within the clay layer, grey spheres represent Si, blue-green spheres represent Al, and blue spheres represent Mg.

Though these simulations were not designed to provide accurate thermodynamic quantities that could be related to natural systems, comparison of calculated energies can highlight the presence of contrasting chemical properties. The total potential energies of the protonated and Ca-saturated DOM–montmorillonite interlayer assemblies were

-7.537×10^4 and -1.696×10^5 kJ mol^{-1} , respectively (where “mole” refers to a mole of the organo-mineral simulation cell). The cohesive energies of these hydrated organo-mineral systems, or the energies derived from nonbond (electrostatic and van der Waals) contributions, were -7.199×10^4 and -1.673×10^5 kJ mol^{-1} , respectively.

Evidently, the interaction of numerous electrostatic charges, made possible by the deprotonation and Ca-saturation of carboxylate groups, created opportunities for intra- and intermolecular interactions that lowered the potential energy of both the polyanion and the circumneutral organo-mineral system, relative to the protonated counterparts. The total potential energies of the protonated and Ca-saturated DOM molecules isolated from their acidic and circumneutral interlayer environments were -1.543×10^4 and -7.721×10^4 kJ mol⁻¹, and the corresponding cohesive energy values were -1.059×10^4 and -7.221×10^4 kJ mol⁻¹, respectively.

Changes in the protonation state, and the corresponding hydrophobicity, of the DOM molecule in response to acidic and circumneutral conditions led to complex and contrasting structural properties in dilute aqueous solutions (Sutton et al., 2005). The chemically active mineral surfaces defining the Ca-montmorillonite interlayer region simulated in the present study modified the pH-dependent behavior exhibited by these model humic molecules, and resulted in the creation of a variety of organo-mineral interactions, including hydrophobic interactions, direct and indirect H-bonding interactions, and cation and water bridging interactions.

3.1. Hydrophobic interactions

The basis of the hydrophobic interaction is the inability of nonpolar molecules to support H-bonds, which, for isolated nonpolar molecules, will necessarily lead to the formation of cagelike structures of H-bonded water molecules around them and the creation of solvent-excluding surface area (Israelachvili, 1991). The Gibbs energy cost of these cagelike structures is high, since they are unlike the normal structure found in bulk liquid water. Thus Gibbs energy is minimized by reducing the combined size of all cagelike structures, which is the same as reducing the total solvent-excluding surface area. This kind of reduction occurs if two nonpolar molecules are brought into close contact as opposed to being separated by large (molecular-scale) distances. Thus hydrophobic interactions are the result of minimizing the solvent-excluding area of the nonpolar molecules in an aqueous solution.

Hydrophobic interactions were common in the protonated organo-mineral system, and absent from the deprotonated, Ca-saturated system. These hydrophobic interactions took place between organic moieties, typically substituted alkyl chains, located close to and parallel with mineral surfaces (Fig. 3). The C atoms involved were about 4 Å from the montmorillonite surface, and water molecules were excluded from these hydrophobic regions.

The hydrophobic nature of the protonated DOM molecule, and its close proximity to the mineral surface, promoted the formation of hydrophobic interactions. Minimum molar potential energies for water molecules, -59.2 kJ mol⁻¹ for the protonated DOM–montmorillonite system, and -77 kJ mol⁻¹ for the Ca-saturated DOM–

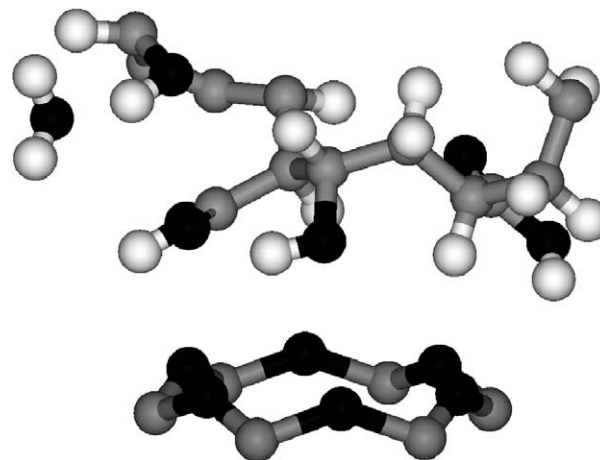


Fig. 3. A portion of the protonated DOM–montmorillonite system displaying a typical hydrophobic organo-mineral interaction, as well as the attraction of an organic O to a six-oxygen cavity. For the interlayer components, grey spheres represent C, black spheres represent O, white spheres represent H. For the mineral surface, black spheres represent O and grey spheres represent Si.

montmorillonite system (Table 1), indicate that the interlayer of the protonated DOM–montmorillonite was more hydrophobic than that of hydrated Ca-montmorillonite (-62.2 kJ mol⁻¹) due to the presence of neutral organic material typical of acidic conditions. The reduced water content and interlayer density of the acidic interlayer system, relative to its circumneutral, Ca-saturated counterpart, reflects this hydrophobicity. The density of the interlayer region of the protonated DOM–montmorillonite complex, with a layer spacing of 30.53 Å and a total of 543 water molecules, was 1.06 g cm⁻³ (Table 1). In contrast, the deprotonated, cation-saturated DOM–montmorillonite complex, with a layer spacing of 33.32 Å and a total of 852 water molecules, had an interlayer density of 1.26 g cm⁻³ (Table 1).

Rearrangement of the organic molecule to facilitate formation of hydrophobic interactions resulted in a more diffuse organic structure and an expanded solvent accessible surface area, relative to that measured for the protonated

Table 1
Thermodynamic properties of model organo-mineral systems

	Protonated DOM–montmorillonite	Ca-saturated DOM–montmorillonite
Surface area of organic molecule ^a (Å ²)	4951.9	5558.4
Volume of organic molecule ^a (Å ³)	8253.7	7918.4
Interlayer density (g cm ⁻³)	1.06	1.26
Minimum water potential energy (kJ mol ⁻¹)	-56.5	-74.1

^a Surface area and volume measurements exclude contributions from the Ca²⁺ associated with the Ca-saturated DOM molecule.

molecule simulated within a dilute aqueous solution (Sutton et al., 2005). The solvent accessible surface area of the deprotonated DOM molecule within the smectite interlayer was 5558.4 \AA^2 , similar to the surface area obtained from a simulation of DOM within a dilute, circumneutral pH aqueous solution (5638.6 \AA^2 ; Sutton et al., 2005) (Table 1). However, the solvent accessible surface area for the protonated DOM molecule within the interlayer was 4951.9 \AA^2 , 12% greater than the value obtained from a simulation representing the same molecule within a dilute, acidic aqueous solution (4415.4 \AA^2 ; Sutton et al., 2005). The protonated DOM molecule is larger than the corresponding Ca-saturated molecule in the z dimension, maximizing contact with the mineral surface (Fig. 2). In contrast, the Ca-saturated DOM configuration exhibits extensive spreading along the xy plane (Fig. 4), and dimin-

ished contact with the mineral surface (Fig. 2). The protonated and deprotonated DOM molecules within the smectite interlayers had molecular volumes of 8253.7 and 7918.4 \AA^3 , respectively, similar to those measured for the molecules under dilute acidic and circumneutral aqueous conditions (8233.9 and 8037.1 \AA^3 , respectively; Sutton et al., 2005) (Table 1).

Few portions of the Ca-saturated DOM molecule were close enough to the clay to take part in hydrophobic interactions. The deprotonated DOM polyanion, appropriate to circumneutral pH conditions, would be repelled from the negatively charged montmorillonite surface if not for the presence of numerous Ca^{2+} within the interlayer solution. Thus the presence of hydrated, charge screening cations between organic and mineral components of the Ca-saturated DOM–montmorillonite system (Fig. 2), similar to that observed experimentally between the natural organic matter adsorbed to a mica surface using surface X-ray reflectivity measurements (Nagy et al., 2001), impeded the formation of direct hydrophobic interactions between nonpolar moieties simply by preventing close contact between the organic and mineral molecules. This distance between organic and mineral materials resulted in a larger interlayer spacing, relative to that of the acidic organo-mineral system.

Published simulations between another model humic molecule and hydrated siloxane surfaces indicate that when such molecules are fully protonated, hydrophobic (Akim et al., 1998; Shevchenko and Bailey, 1998a,b) interactions are common, while when partial deprotonation results in the formation of carboxylate groups, other interactions prevail (Akim et al., 1998; Shevchenko and Bailey, 1998a; Shevchenko et al., 1999). Simulations of a variety of organic materials near smectite and other siloxane surfaces under dry conditions frequently suggest that organic molecules prefer to maximize contact with the mineral, promoting hydrophobic interaction (Shevchenko and Bailey, 1998a,b; Teppen et al., 1998, 2002; Haberhauer et al., 2001; Yu et al., 2000a,b, 2001, 2003). Upon hydration, many small, nonpolar organic molecules partially or fully desorb from the mineral surface, in response both to competition from water molecules for mineral surface sites, as well as to the availability of a hydrophilic environment attractive to these organic materials (Teppen et al., 1998, 2002; Yu et al., 2003). However, hydration does not hinder the formation of hydrophobic organo-mineral interactions involving molecules with reduced polarity, such as methane (Titiloye and Skipper, 2000; Park and Sposito, 2003; Cygan et al., 2004) and carbazole (Van Duin and Larter, 2001). Evidently the hydrophobicity of alkyl chains near the mineral surfaces within the protonated DOM–montmorillonite system is sufficient to allow the formation and maintenance of hydrophobic organo-mineral interactions despite hydration.

Experimental adsorption and desorption studies on smectites indicate that hydrophobic microsites far from clay charge sites are capable of strongly adsorbing small organic

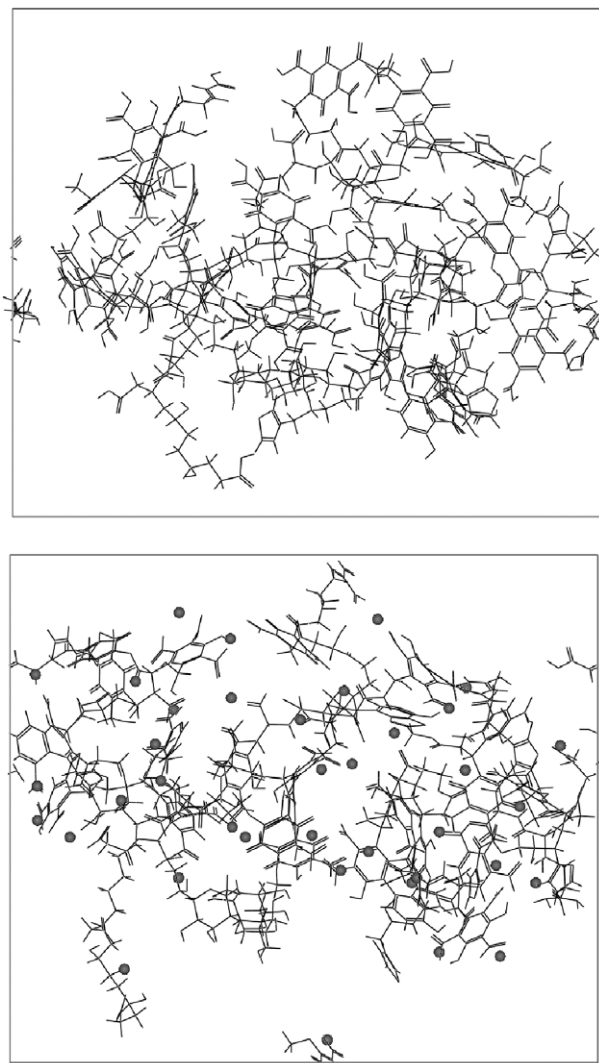


Fig. 4. View of protonated (top) and Ca-saturated (bottom) DOM molecules within interlayers of hydrated Ca-montmorillonite in the XY (or top-down) plane (water and clay molecules removed from the images to improve visibility). Grey lines represent the organic structures, while grey spheres represent Ca^{2+} . The grey box outlining the views indicates the dimensions of the simulation cell.

molecules (Laird et al., 1992; Barriuso et al., 1994; Ghosh and Keinath, 1994; Laird, 1996; Celis et al., 1997; Laird and Fleming, 1999) and larger organic polymers (Theng, 1979, 1982) through hydrophobic interactions with interlayer and external surfaces. When exposed to solutions of natural organic matter, smectite minerals selectively adsorb large amounts of alkyl C functional groups (Chorover and Amistadi, 2001; Wang and Xing, 2005). Studies of natural soils indicate that alkyl C is preferentially preserved, especially in clay size fractions, which are often enriched in smectite minerals (Oades, 1988; Baldock et al., 1992; Ristori et al., 1992; Leinweber et al., 1999; Baldock and Skjemstad, 2000; Chen and Chiu, 2003). ^{13}C CP/MAS NMR spectra of smectitic soils are dominated by alkyl signals (Wattel-Koekkoek et al., 2001), and radiocarbon dating of such soils reveals that the C can be highly recalcitrant (Wattel-Koekkoek et al., 2003). An examination of the chemical composition of the few natural organo-smectite interlayer complexes recovered from soils indicates that the organic material retained in these interlayers is primarily alkyl (Theng et al., 1986; Schnitzer et al., 1988; Schulten et al., 1996) or alkylaromatic (Righi et al., 1995), suggesting that hydrophobic interactions may play a large role in the formation of these organo-mineral complexes. Soils containing smectites with intercalated organic material are typically acidic ($\text{pH} \leq 5$). This collection of laboratory and field evidence suggests that hydrophobic interactions may play an important role in sequestration of organic matter in soils, especially under acidic conditions.

3.2. Direct and indirect H-bonding interactions

The protonation state of the DOM molecule influenced the type of H-bonding interactions that formed between protonated functional groups and electronegative atoms within the organo-mineral systems. The final configuration of the protonated DOM–montmorillonite simulation system contained multiple direct organo-mineral H-bonds, while the Ca-saturated system contained none (Table 2). Flexible portions of the protonated DOM molecule moved to positions near the montmorillonite surface, where organic alcohol or carboxyl protons formed H-bonds with mineral O atoms (Fig. 5). Four of the six organo-mineral

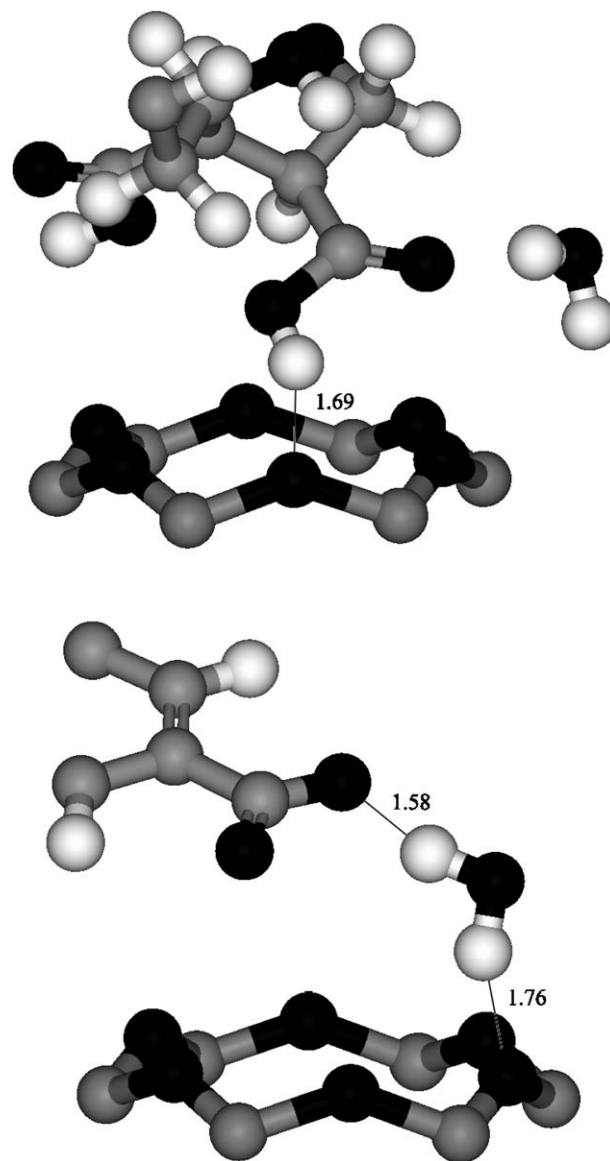


Fig. 5. Examples of H-bonding interactions found in the organo-mineral systems include a direct organo-mineral H-bond (top) taken from the protonated system (O–O distance 2.58 Å, O–H–O angle 149.3°), and an indirect organo-mineral H-bonded structure (bottom) taken from the Ca-saturated system (O–O distances 2.53 and 2.68 Å, O–H–O angles 161.4° and 157.3° for upper and lower H-bonds, respectively). Atoms are color-coded by element as described in Fig. 3. Selected distance measurements are provided in Ångstroms.

Table 2
Number of H-bonds within DOM–montmorillonite interlayer regions

H-bonds	Protonated DOM–montmorillonite	Ca-saturated DOM–montmorillonite
<i>Intramolecular</i>		
DOM	37	43
<i>Intermolecular</i>		
DOM–DOM	0	0
DOM–water	60	152
DOM–mineral	6	0
Water–mineral	84	97
Water–water	17	33

H-bonds occurred near octahedral charge sites abandoned by interlayer cations.

Published studies of the interactions of earlier iterations of this model humic substance with siloxane surfaces also indicate that when the organic molecule is fully protonated, organo-mineral H-bonds form frequently (Schulten and Leinweber, 1996, 2000; Schulten and Schnitzer, 1997; Leinweber and Schulten, 1998; Schulten et al., 1998). A broad range of organo-mineral simulations, ranging from atomistic EM and MD calculations of montmorillonite and model silicate minerals with amino acids (Newman et al., 2002) or proteins (Yu et al., 2000a), to quantum chemical analyses

of the interactions of molecular clusters of aluminosilicates with simple organic molecules such as acetic acid (Kubicki et al., 1997; Haberhauer et al., 2001; Tunega et al., 2002), also feature such H-bonds. Experimental evidence for the existence of weak organo-mineral H-bonds frequently takes the form of infrared spectra that indicate shifts in key vibrational frequencies of organic molecules upon introduction into the mineral matrix (Theng, 1979; Mortland, 1986; Ristori et al., 1992).

Also evident in the protonated system were organo-mineral interactions derived from electrostatic attraction of negatively charged portions of polar organic moieties for the mineral hydroxyl functional group located near the six-oxygen surface cavities covering the montmorillonite surface. Some organic functional groups adopted positions in which the organic O atoms were just 2 or 3 Å from six-oxygen cavities, while the organic O-H bond was roughly parallel to the clay surface (Fig. 3). This organo-mineral interaction might have resulted in the formation of more H-bonds, if the mineral hydroxyl groups located within these cavities were allowed to move. Hydroxyl groups within a flexible montmorillonite structure could respond to the presence of a nearby organic O atom by adopting a configuration more perpendicular to the mineral surface, possibly allowing the interior proton to form a H-bond with the organic functional group. This interaction was absent from the Ca-saturated system due to the rigid nature of the montmorillonite mineral.

The Ca-saturated DOM molecule, excluded from positions near the mineral surface due to the arrangement of hydrated Ca^{2+} around the exterior of the DOM molecule and near each of the mineral surfaces, and featuring far fewer protonated functional groups, took part in a less direct organo-mineral interaction mediated by H-bonds. Several water molecules formed H-bonds with organic and mineral constituents simultaneously, creating a series of indirect H-bonded structures in this system (Fig. 5). Few such indirect H-bonded structures were present in the protonated system, as the reduced polarity and neutral charge of this organic molecule led to reduced formation of H-bonds with water molecules (Table 2), and even the exclusion of water molecules from sites near the mineral surface. A MD simulation of amino acids between montmorillonite layers featured such indirect H-bonds (Newman et al., 2002), as did a quantum chemical simulation of nitrobenzene near a montmorillonite surface (Gorb et al., 2000). It seems unlikely that current spectroscopic techniques would be able to identify indirect organo-mineral H-bonding structures mediated by ubiquitous water molecules. This weak potential interaction can be explored only through molecular modeling methods at this point.

3.3. Cation and water bridging interactions

Cations played a role in the formation of organo-mineral complexes in both systems. The Ca–O RDFs calculated for both organo-mineral models (Fig. 6) indicated inner

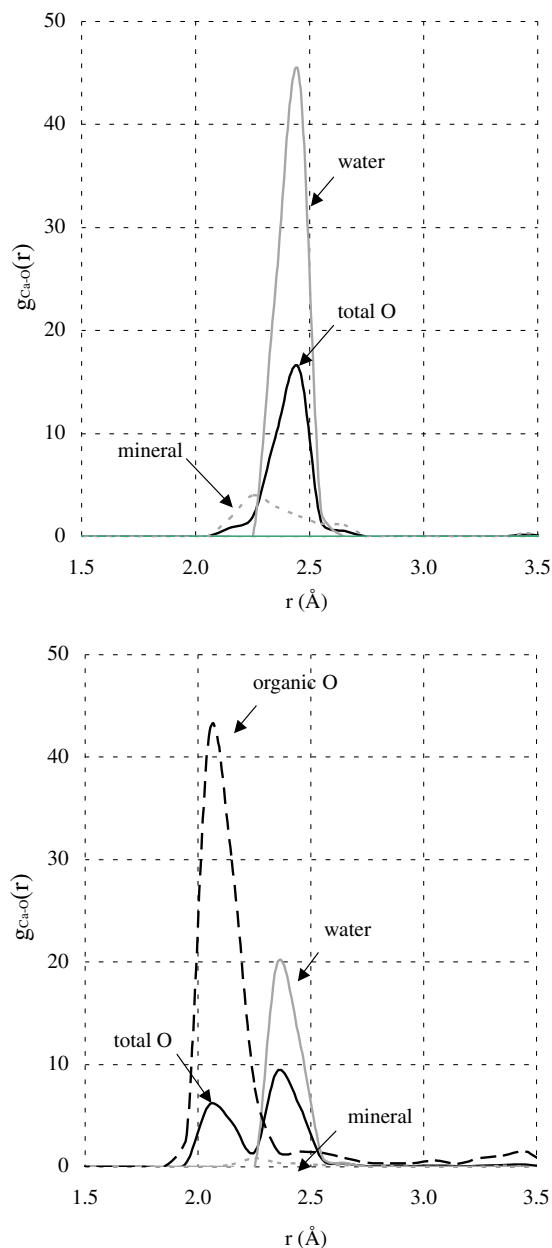


Fig. 6. Ca–O radial distribution functions for the protonated (top) and Ca-saturated (bottom) DOM–montmorillonite systems.

sphere coordination of Ca^{2+} occurred within a radius (ρ) of 2.75 Å. Inner sphere complexes between cations and polar organic functional groups, essential for the formation of cation bridging organo-mineral interactions, were not observed in the protonated system (Table 3). Only outer sphere complexes, or water bridges (Fig. 7), formed between organic moieties including carboxyl and alcohol groups and the interlayer cations, which remained close to the mineral surface (Fig. 2), preferring positions near tetrahedral charge sites and above surface O triads. Direct cation bridging ion–dipole interactions are observed in many model organo-smectite interlayers under dehydrated conditions (Bujdák et al., 2000; Hackett et al., 2000; Pintore et al., 2001; Pospíšil et al., 2002; Boulet et al.,

Table 3

Ca–O coordination numbers for protonated and Ca-saturated DOM–montmorillonite systems, calculated using a maximum radius of 2.75 Å

Ca–O pairs	Protonated DOM	Ca-saturated DOM
Ca–O _{total}	7.58	6.91
Ca–O _{water}	6.08	4.02
Ca–O _{mineral}	1.50	0.22
Ca–O _{organic}	0	2.67
Ca–O _{carboxylate}		2.45
Ca–O _{other organic}		0.22

2003; Gaudel-Siri et al., 2003; Kuppa and Manias, 2003), but these interactions are rarely preserved upon hydration because water molecules replace the polar organic groups occupying positions near cations, creating water bridges (Bujdák et al., 2000; Hackett et al., 2000; Boulet et al., 2003). While some experimental studies suggest the significance of direct ion–dipole interactions as a mechanism for adsorption of organic materials to minerals (Dios Cancela et al., 1996, 2000), much of this work is conducted under dehydrated conditions. In an environment that includes water, ions with large hydration energies like Ca^{2+} must form water bridges with polar organic functional groups (Theng, 1979).

Early definitions of the water bridging interaction suggested that the water molecule hydrating a cation also must take part in a H-bond with the organic functional group (Theng, 1979; Mortland, 1986). Although several outer sphere Ca–DOM complexes can be identified in the protonated DOM–montmorillonite system, the lack of H-bonds between hydrating water molecules and organic functional groups means that this type of water bridge is absent. Only two water bridging interactions including such H-bonds are observed in the Ca-saturated system. Apparently, Ca^{2+} exerts such a strong influence over the position and orientation of hydrating water molecules within these simulations that their ability to form secondary H-bonds with organic molecules is hampered. Experimental data including the removal of significant levels of clay-adsorbed organic molecules through washes with water (Theng, 1974, 1979; Theng and Scharpenseel, 1975; Mirabella et al., 1996), the trend observed in montmorillonite suspensions of increasing organic adsorption with increasing cation charge to radius ratio (Theng and Scharpenseel, 1975), and distinctive shifts, or lack thereof, in infrared signals (Theng, 1974, 1979; Bosetto et al., 1994), are interpreted to be evidence of adsorption through water bridges. None of these experimental observations provides compelling evidence that the water molecule between cation and organic is H-bonded to the organic functional group. Based on the modeling data presented here, it appears that a water bridge structure that includes a H-bond with the organic functional group is not common.

Cation bridges were the dominant organo-mineral adsorption complex present in the Ca-saturated DOM–montmorillonite system, though they were completely absent in the protonated system. In the Ca-saturated system, numerous inner sphere Ca–carboxylate complexes formed,

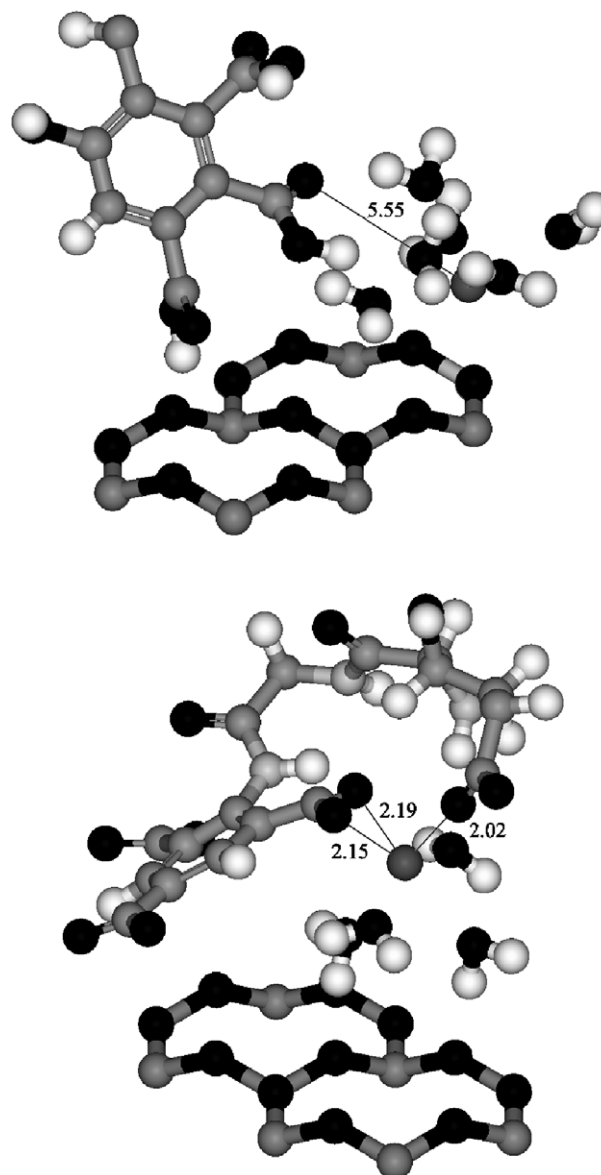


Fig. 7. Examples of bridging interactions found in the organo-mineral systems include a water bridge (top) taken from the protonated system, and featuring outer sphere complexation between Ca^{2+} and a carboxyl O atom marked by a black line, and inner sphere coordination with the mineral surface, and a cation bridge (bottom) taken from the Ca-saturated system, and featuring inner sphere complexation between Ca^{2+} and carboxylate groups marked by black lines, and outer sphere coordination to the mineral surface. Atoms are color-coded by element as described in Fig. 3, with the addition of pale grey spheres representing N in the organic fragment, large grey spheres representing Ca^{2+} in solution, and a light grey sphere (partially hidden by an O) representing Al substituted for Si in the mineral surface. Selected distance measurements are provided in Angstroms.

along with a few inner sphere complexes between Ca^{2+} and other organic functional groups. The Ca–carboxylate complexes typically featured smaller Ca–O distances than found in hydrated Ca^{2+} (Fig. 6). Typical cation bridges in this system involved a cation directly coordinated to carboxylate groups and outer sphere coordinated to the mineral surface (Fig. 7). Cations participating in these

interactions frequently occupied positions near octahedral charge sites, while cations involved in the occasional water bridge, or far from organic moieties, preferred locations near tetrahedral charge sites. Perhaps the recessed position of the octahedral charge allowed carboxylate functional groups to exert a stronger competing pull on nearby cations, such that cation-organic inner sphere complexes became favorable. The reduced CN of cations present in the Ca-saturated system, especially with respect to waters of hydration (Table 3), is likely due to restrictions to the stereochemical environment caused by the presence of organic moieties within the coordination spheres of Ca^{2+} near the DOM polyanion, as organic structures attached to coordinating organic O would block water molecules from fully hydrating the cation (Sutton et al., 2005).

While other simulations have indicated the importance of cation bridging in the adsorption of polyanions to negatively charged aluminosilicates (Akim et al., 1998; Shevchenko and Bailey, 1998a,b; Shevchenko et al., 1999; Bailey et al., 2001; Yu et al., 2003), no previous study has begun with fully hydrated cations as found in the solution state. By not accounting for cation hydration in this way, earlier models may have contained a strong inherent bias favoring the formation of cation bridges. Previous work also involved the use of monovalent cations, although in natural soil environments it is expected that multivalent cations such as Ca^{2+} are necessary to the formation of strong organo-mineral cation bridges (Theng, 1979; Oades, 1988, 1995; Baldock and Skjemstad, 2000). The simulations presented in this paper provide molecular modeling evidence that Ca^{2+} can form cation bridges between negatively charged organic functional groups and the mineral surface, even when the cation is introduced to the system in a fully hydrated form.

While we can assume that such DOM–montmorillonite cation bridging interactions are able to form on external mineral surfaces, is it possible that they can occur within the smectite interlayer region, the specific system modeled in this study? Acidic solutions of humic fractions have been shown to penetrate montmorillonite interlayers when in the presence of Ca^{2+} (Mirabella et al., 1996), but such interlayer complexation is virtually absent above pH 5 (Schnitzer and Kodama, 1966; Martín Martínez and Perez Rodríguez, 1969). The few natural organo-smectite interlayer complexes described in the literature were all recovered from acidic soils (Kodama and Schnitzer, 1971; Satoh and Yamane, 1971; Theng et al., 1986; Righi et al., 1995). The protonated DOM molecule might represent better the organic material present under such acidic soil conditions. Although the Ca-saturated DOM–montmorillonite system indicates that once within the interlayer, a partially deprotonated humic substance in the presence of sufficient Ca^{2+} takes part in cation bridges with the mineral surface, producing potential energies suggesting greater stability than evident in the protonated DOM–montmorillonite system, the models examined here do not address the mechanism of entry into the clay interlayer region. Simulation of the interactions of a model

humic molecule with appropriately protonated broken edge sites of a flexible Ca-montmorillonite would be necessary to ascertain the feasibility of interlayer complexation of organic materials under a range of typical soil pH conditions. Nonetheless, observations of organo-mineral interactions taking place within the computationally convenient montmorillonite interlayer region can provide insight regarding the mechanism of adsorption of humic materials to external mineral surfaces and more accessible mesopores.

The appearance of a few physically unrealistic cation-mineral complexes within the organo-mineral systems indicated that the results presented here may contain artifacts particular to the methodology used. Some of the Ca^{2+} in the protonated DOM–montmorillonite system were not fully hydrated because they formed inner sphere complexes with the mineral surface (Fig. 3). The mineral surface contributed 1.50 O to the Ca–O_{total} CN of 7.58 in the protonated organo-mineral system (Table 3). Inner sphere Ca-montmorillonite complexes were seen in the Ca-saturated DOM–montmorillonite system as well, although to a lesser extent (Fig. 3). The mineral contribution (0.22) to the Ca–O_{total} CN of 6.91 was reduced in part due to the greater number of cations present, relative to the protonated system (Table 3). A single inner sphere Ca-montmorillonite complex was produced in one of the many simulation systems representing hydrated Ca-montmorillonite, consistent with the suggestion that the partial charge on the montmorillonite O atoms in these simulations may be excessively attractive to positively charged moieties. Such inner sphere Ca-montmorillonite complexes would not be expected based on the large hydration energy of Ca^{2+} , and have not been observed in previous studies on Ca-montmorillonite hydrates conducted using both modeling (Chávez-Páez et al., 2001; Greathouse and Storm, 2002) and experimental (Hall, 1982; Slade et al., 1985; Cases et al., 1997) methods. These unusual complexes formed during the annealing stage of the present simulations, an indication that the use of high temperature to hasten the adoption of low potential energy configurations resulted in cation hydrate structures inappropriate to clay hydrates at 300 K.

If the annealing procedure employed here encouraged the formation of unrealistic inner sphere complexes at the mineral surface, it may have produced an excessive number of inner sphere complexes with organic functional groups as well. While the exact number of inner sphere complexes that formed in the DOM–montmorillonite systems may be elevated due to this simulation artifact, it is still possible to gain insight through observation of the pH-dependent behavior of the systems relative to one another (Sutton et al., 2005). Similarly, the proportional increase in prevalence of inner sphere Ca-montmorillonite complexes in the organo-montmorillonite systems relative to the montmorillonite hydrate, even after identical annealing time periods, implies that the presence of organic matter in the interlayer may disrupt sufficiently the structure of interlayer water molecules to weaken the level of hydration seen around counterions.

4. Conclusions

Simulations of a model humic molecule in protonated and Ca-saturated forms within a hydrated Ca-montmorillonite interlayer were conducted to improve understanding of the mechanisms of organic matter stabilization within soils. The COMPASS force field, designed for condensed phase organic and mineral systems, was not equipped to simulate a flexible montmorillonite, so a rigid mineral layer with partial charges taken from Skipper et al. (1995a,b) was used. The protonated DOM–montmorillonite system featured significant direct hydrophobic and H-bonding interactions between organic and mineral components. No direct ion–dipole interactions were observed; instead, polar organic functional groups formed water bridging complexes with nearby Ca^{2+} . Some cations formed inner sphere complexes with the mineral surface, their hydration shells stripped away after annealing calculations, perhaps partially in response to the disruption of water structure created by large organic molecules. The Ca-saturated DOM–montmorillonite system exhibited organo-mineral cation bridges, as well as a few water bridges and an indirect form of H-bonding mediated by water molecules. Application of molecular modeling techniques to this complex organo-mineral system allowed identification of favorable interactions between humic substances and mineral surfaces under acidic and circumneutral pH conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2006.04.032](https://doi.org/10.1016/j.gca.2006.04.032).

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