

Carbon Sequestration by Smectite Clay Minerals in Soils

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Summary

Molecular simulations can be used to explore fundamental interactions that govern the formation of organo-mineral complexes in soils, complexes that in turn control the size and turnover of soil carbon pools. A suitable model organic molecule, featuring properties and behavior typical of the recalcitrant portion of soil carbon in humic substances, is needed for these simulations. The latest iteration of the Schulten model of dissolved organic matter (DOM) was simulated under both dry and hydrated conditions, and as a Na- or Ca-saturated complex, using the COMPASS force field with energy minimization and molecular dynamics algorithms. This relatively large molecule (10,419.3 Da) possesses a flexible, porous structure and a distribution of functional groups appropriate to humic substances. Simulation results for the model humic systems included such diverse molecular-scale information as an infrared spectrum, an analysis of the position of polar groups relative to the center of the molecule, an accounting of intra- and intermolecular hydrogen bonds, porosity, and cation-oxygen coordination numbers, as well as dynamic and structural cation behavior. The results indicated that the DOM molecule mimics the behavior of natural humic substances under a variety of conditions investigated and, therefore, may be suitable for use in simulations of organo-mineral complexes. Simulations of the protonated DOM molecule and its Ca-saturated complex within hydrated Ca-montmorillonite interlayers indicated that the flexibility and polarity of the organic molecule affects the interlayer environment. The protonated DOM molecule forms hydrogen bonds and engages in hydrophobic interactions with the mineral surface. Some organic hydroxyl oxygens also are attracted to cavity sites on the clay surface. The Ca-saturated complex disrupts hydrogen bonding and hydrophobic interactions, but forms cation and water bridges with the mineral surface. Our simulations suggest that application of calcium to soils containing smectites may encourage sequestration and carbon storage.

Objectives

- (1) Simulation of the DOM molecule under a variety of conditions, including dry and densely packed, hydrated, and partially deprotonated and cation-saturated.
- (2) Simulations of a fully protonated and a partially deprotonated, Ca-saturated DOM molecule in model Ca-montmorillonite interlayers.

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Approach and Procedures

The atoms in the model systems were described using the Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) force field, available as part of the Cerius² SGI modeling environment (Accelrys Inc. 2001). This force field has two principal advantages, which distinguish it from other available force fields: (a) it was designed for use with both organic and inorganic molecules and (b) it was constructed using condensed-phase data rather than gas-phase data. Two simulation algorithms were used in combination to investigate the molecular structures of each system modeled. Energy minimization (EM), i.e. geometrical optimization of a molecular structure that results in a conformation occupying a local potential energy minimum (Accelrys Inc. 2001), was often used during the initial and final stages of simulations. Intermediate-stage calculations were performed using molecular dynamics (MD), in which the Newton-Euler equations of motion are solved over very short timesteps (in the present study, 5×10^{-16} s) (Allen and Tildesley 1987). These MD calculations allow molecules to adopt new conformations closer to that corresponding to the global potential energy minimum than the conformation that results from minimization of a high-energy initial structure. In order to obtain a low-energy structure more efficiently, a series of calculations was used in which the model system was minimized, then subjected to a set of MD computations, in which the temperature was increased, then decreased in a stepwise manner over 300 - 600 K, and finally minimized again. The elevated temperatures simulated using this “annealing cycle” can encourage molecules to relax into conformations with lower potential energies more rapidly. Different sequences of EM and MD calculations were used to model the following organic and organo-mineral systems:

- (1) *Dry, Densely Packed DOM Molecule*. A periodic system was created in which the DOM molecule was placed within a cubic cell replicated infinitely in all directions. Between annealing cycles, the dimensions of this cube were decreased in a stepwise manner, such that the density of the system increased from 0.5 g cm^{-3} to 1.25 g cm^{-3} . Afterward, a 50 ps MD calculation was performed in which cell dimensions were allowed to vary, while pressure and temperature were held at 100 kPa and 300 K, respectively. The final structure was then minimized.
- (2) *Hydrated DOM Molecule*. The DOM molecule was surrounded by a 5 Å thick layer of water molecules. This non-periodic system was subjected to a series of annealing cycles, followed by 50 ps of MD simulation under constant volume at 300 K, and finally minimized.
- (3) *Deprotonated, Cation-Saturated DOM Complexes*. Carboxyl functional groups were deprotonated in sets, starting at exterior sites and moving inward. Cations (Na^+ or Ca^{2+} , respectively) hydrated by six water molecules were added near the newly formed carboxylates, such that cation-carboxylate O distances were near 5.2 Å. After each set of carboxyls was deprotonated and cation-saturated, an annealing cycle was used to equilibrate the nonperiodic DOM structure. Once all carboxyls had been altered, the organic structure was surrounded by a 5 Å thick layer of water molecules and equilibrated via another annealing cycle. Final calculations consisted of a 50 ps MD simulation under constant volume at 300 K, followed by EM.
- (4) *Hydrated DOM-montmorillonite Interlayer Complexes*. Protonated and Ca-saturated DOM molecules were inserted into periodic Ca-montmorillonite systems with expanded interlayer

spacings. Lengthy minimizations were used to select layer spacings appropriate to each system. The remaining interlayer region was hydrated and subjected to annealing cycles and MD simulation under constant volume at 300 K, followed by EM.

Results

Although the primary goal of this project is to explore organo-mineral interactions, it is first essential to ascertain that the model organic molecule chosen as a proxy for humic substances can reproduce behavior associated with natural humic materials. A version of the DOM molecule designed by Schulten (1999) was selected to model the behavior of humic substances (*fig. 1*). This molecule was developed using information from spectroscopy, including infrared, nuclear magnetic resonance, and x-ray absorption spectroscopy, as well as from pyrolysis, electron microscopy, colloid chemistry, elemental analysis, and ecological theory. Although it features elemental ratios and functional group distributions typical of natural humic substances (Stevenson 1994), the DOM molecule may be too large according to current thinking (Burdon 2001; Piccolo 2001). The large size of the DOM molecule may, however, allow it to express behavior which corresponds to that of an association of humic molecules in soils. The presence of protein and carbohydrate structures in the DOM molecule along with alkyl-aromatic groups resembling lignin-derived moieties supports this analogy with a humic association. Thus, despite its large size, this molecule may prove to be a useful tool in the prediction of organo-mineral interactions relevant to temperate-zone soils that sequester carbon.

The dry, densely packed DOM molecule attains a final bulk density of 1.36 g cm^{-3} , which is within the experimental range of $1.2 - 1.4 \text{ g cm}^{-3}$ reported for humic substances (Diallo et al. 2001). Another means of comparing the model structure to natural humic substances is through the Hildebrand solubility parameter, a measure of the enthalpic compatibility of materials via Flory-Huggins solution theory (Diallo et al. 2001). The Hildebrand solubility parameter calculated for the model DOM molecule is $19.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$, which is slightly lower than the range of experimental estimates, $20.5 - 27.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$ (Diallo et al. 2001). A model infrared spectrum calculated for the DOM molecule (*fig. 2*) is similar to experimental spectra (Stevenson 1994). Upon hydration, the distributions of C and O atoms relative to the center of the molecule shift, indicating a concentration of oxygenated, polar functional groups in exterior positions near the water layer (data not shown). This behavior is consistent with predicted pseudomicellar structures (von Wandruszka et al. 1999). Despite this rearrangement, relatively few hydrogen bonds are seen between the organic molecule and surrounding water molecules (*table 1*).

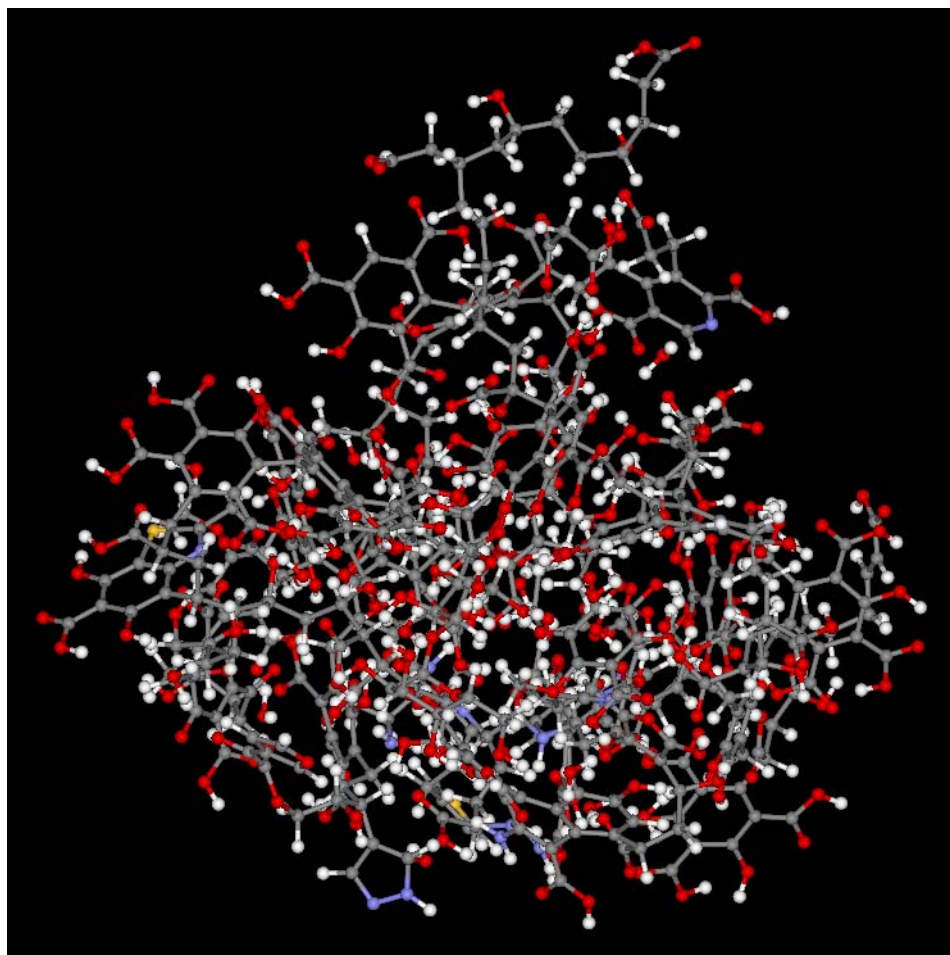


Figure 1. Visualization of the model humic molecule described by Schulten (1999), including associated trisaccharides, polypeptides, and water molecules. Grey spheres represent C, red spheres represent O, white spheres represent H, and N and S are blue and yellow, respectively.

Table 1. Structural information concerning both protonated and metal cation-saturated DOM.

	Na-DOM	Ca-DOM	DOM hydrate
solvent accessible surface area (\AA^2)	5731.4	5638.6	4415.4
porosity	0.815	0.753	0.637
cation-O coordination number (CN)	2.66	4.15	
cation-carboxylate O CN	0.65	1.29	
cation-water O CN	1.84	2.7	
DOM-DOM H-bonds	20	17	15
DOM-water H-bonds	89	44	13

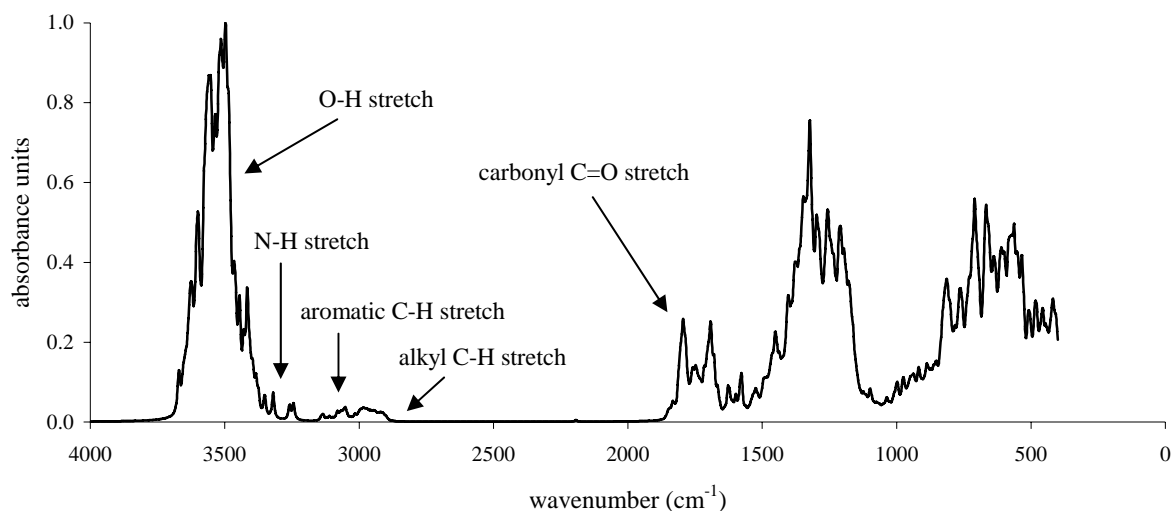


Figure 2. Predicted infrared spectrum of the dry, densely packed model DOM molecule.

Humic molecules are not fully protonated under the pH conditions in most soils, so any exploration of humic behavior must include observations of the DOM molecule in a partially deprotonated state. Cations added to balance the resulting negative charge were placed in a hydrated state near the newly formed carboxylate groups, rather than in a diffuse layer surrounding the organic molecule. The model metal-humic complexes simulated were more porous and formed more H-bonds with water than the protonated, hydrated DOM molecule, due to intrusion of the cation hydrates (*table 1*). Coordination numbers indicate that, relative to Na⁺, Ca²⁺ is both more strongly bound to carboxylate groups and more fully hydrated, an effect of the higher charge of the bivalent cation (*table 1*). While over half the Na⁺ exhibit exchange reactions that leave them far from the carboxylate group near which they were placed, and some move to positions so far from the organic molecule that they can be considered to reside within the hydration shell, i.e. as members of the diffuse ion swarm surrounding the organic polyanion, relatively few Ca²⁺ show exchange behavior and none moves into the hydration shell. The tight binding of Ca²⁺ is reflected as well in the greater proportion of bidentate inner sphere Ca-carboxylate interactions formed relative to those in the Na-DOM complex (*fig. 3*). The predicted behavior of these two cations agrees well with experimental studies (van den Hoop et al. 1990; Bonn and Fish 1993). The Ca-DOM complex also features fewer hydrogen bonds than the Na-DOM complex, perhaps due to reduced orientational freedom of both the organic moieties and the water molecules after interaction with Ca²⁺. Differences in the number of hydrogen bonds in the Na-DOM and Ca-DOM complexes indicate that the identity of the counterions associated with humic substances may affect their ability to sorb and retain xenobiotic organic molecules via these bonds, as also suggested by recent experimental results (Yuan and Xing 2001).

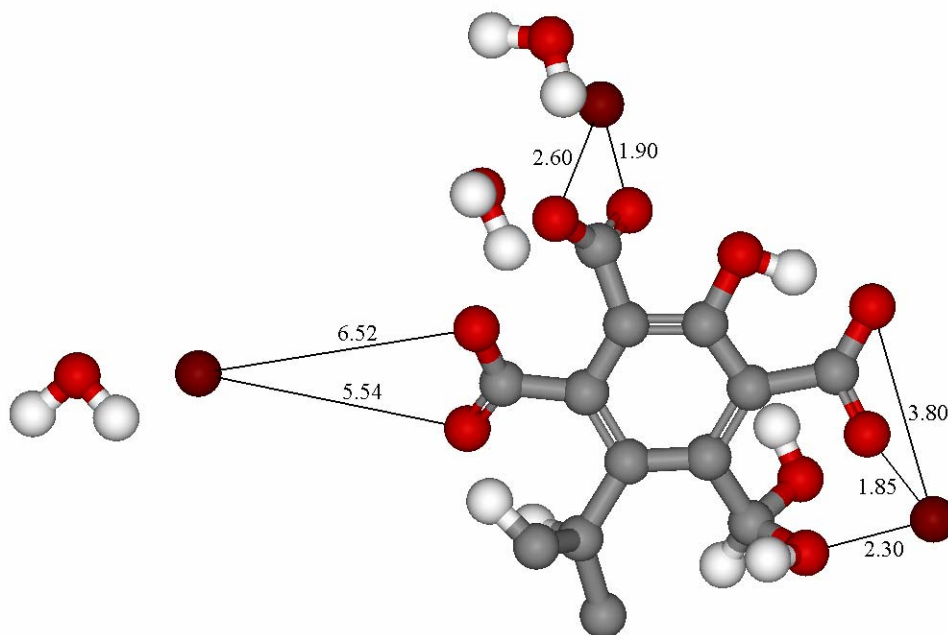


Figure 3. A portion of the Na-DOM structure, featuring three types of cation-carboxylate complex: (left) an outer sphere Na-carboxylate complex; (top) a bidentate inner sphere Na-carboxylate complex; and (right) a monodentate inner sphere Na-carboxylate complex—which also happens to possess inner sphere coordination with an alcohol group. Atoms are color-coded as described in Figure 1, with brown spheres representing Na^+ .

The simulation data indicate that the Schulten DOM molecule mimics satisfactorily the properties of natural humic substances under a variety of experimental conditions. Protonated or deprotonated, Ca-saturated DOM molecules were then inserted into Ca-montmorillonite interlayers, and minimization was used to establish the layer spacing for each system. The protonated DOM-montmorillonite complex had a layer spacing of 30.53 Å. The density of the fully hydrated interlayer region, containing a total of 543 water molecules, is 1.06 g cm⁻³. On the other hand, the deprotonated, cation-saturated DOM-montmorillonite complex had a layer spacing of 33.32 Å, and an interlayer featuring 852 water molecules with a density of 1.26 g cm⁻³. The protonated DOM molecule is more flexible, which allows the clay layers to come closer together. However, the hydrophobic nature of the protonated humic molecule reduces the amount of water that can enter the interlayer region. The deprotonated, Ca-saturated humic polyanion, however, is extremely polar and facilitates the entry of more water molecules through DOM-water interactions as well as through the larger resultant layer spacing. It is not surprising, given both the larger water content and more polar environment, that the Ca-saturated DOM-montmorillonite features a greater number of hydrogen bonding interactions for all types of hydrogen bond pairs, with one notable exception (*table 2*).

Table 2. Hydrogen bonding within the DOM-montmorillonite interlayer complexes.

H-bonds	Protonated DOM	Ca-saturated DOM
<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

Hydrogen bonding proves to be an important organo-mineral interaction within the protonated DOM-montmorillonite system, whereas it is completely absent from the Ca-saturated DOM-montmorillonite system (*fig. 4a*). The flexibility of the protonated organic molecule allows fragments to move to positions near the clay mineral, while the presence of numerous protonated carboxyl and alcohol functional groups on these fragments facilitates hydrogen bonding with the oxygen surface. Hydrogen bonding is common near the montmorillonite octahedral charge sites which lack a nearby charge-compensating interlayer cation. Whereas mineral surface oxygens can attract the hydrogens of organic hydroxyl groups to form hydrogen bonds, the hydroxyl groups found at the bottom of the surface cavities can attract the oxygens of other organic hydroxyl groups (*fig. 4b*), just as they can attract the oxygens of interlayer water molecules in the same system. A hydroxyl oxygen so attracted can be found hovering near the center of a six-oxygen cavity, about 2 - 3 Å away from the mineral surface. The hydrogen of the organic hydroxyl group is oriented such that the O-H bond is roughly parallel to the clay surface. Another important organo-mineral interaction observed in the protonated DOM-montmorillonite complex is hydrophobic interaction (*fig. 4b*). Typically, a flexible alkyl group adopts a position parallel to and approximately 4 Å away from the mineral surface. No water molecules are found between the organic and mineral constituents in this hydrophobic interaction.

A very different set of organo-mineral interactions dominates the Ca-saturated DOM-montmorillonite system. Most notable are cation bridges, in which Ca^{2+} is typically inner sphere coordinated to an organic carboxylate and outer sphere coordinated to the mineral surface (*fig. 5a*). Such cation bridges are thought to play a significant role in the storage of carbon in Mollisols and other Ca^{2+} - and clay-rich soils (Oades 1988). Several water bridges can be observed in the model Ca-saturated DOM-montmorillonite system as well, in which a water molecule simultaneously hydrogen-bonds to an organic functional group and the mineral surface (*fig. 5b*). Water bridging is rare in the protonated DOM-montmorillonite system. Few hydrophobic interactions can be identified in the Ca-saturated DOM-montmorillonite system.

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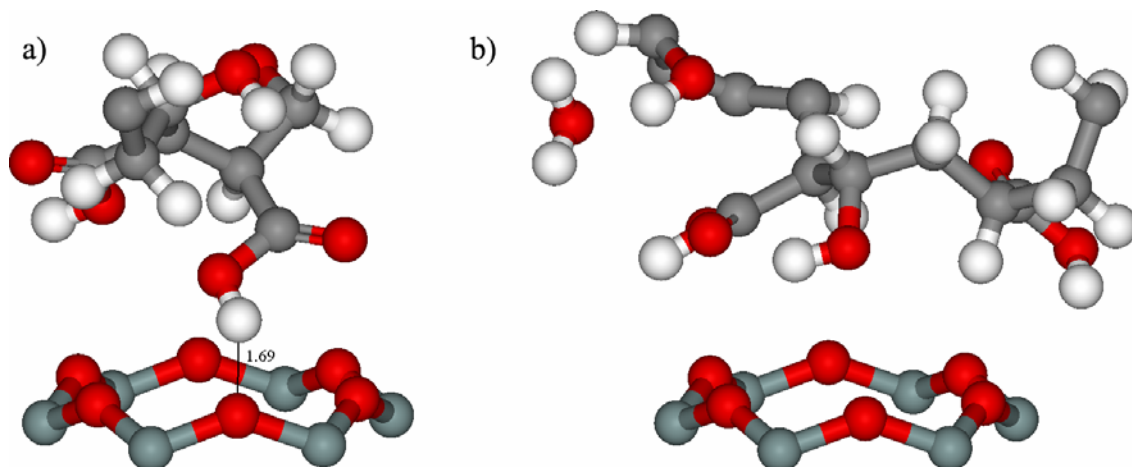


Figure 4. Organo-mineral interactions typical of the protonated DOM-montmorillonite system include (a) hydrogen bonds between organic protons and surface oxygens, (b) attraction of organic oxygens toward mineral surface cavities and hydrophobic interactions, often a result of positioning a flexible alkyl chain about 4 Å from the mineral surface, such that water molecules are excluded from the space between organic and mineral molecules. Atoms are color-coded as described in Figures 1 and 3.

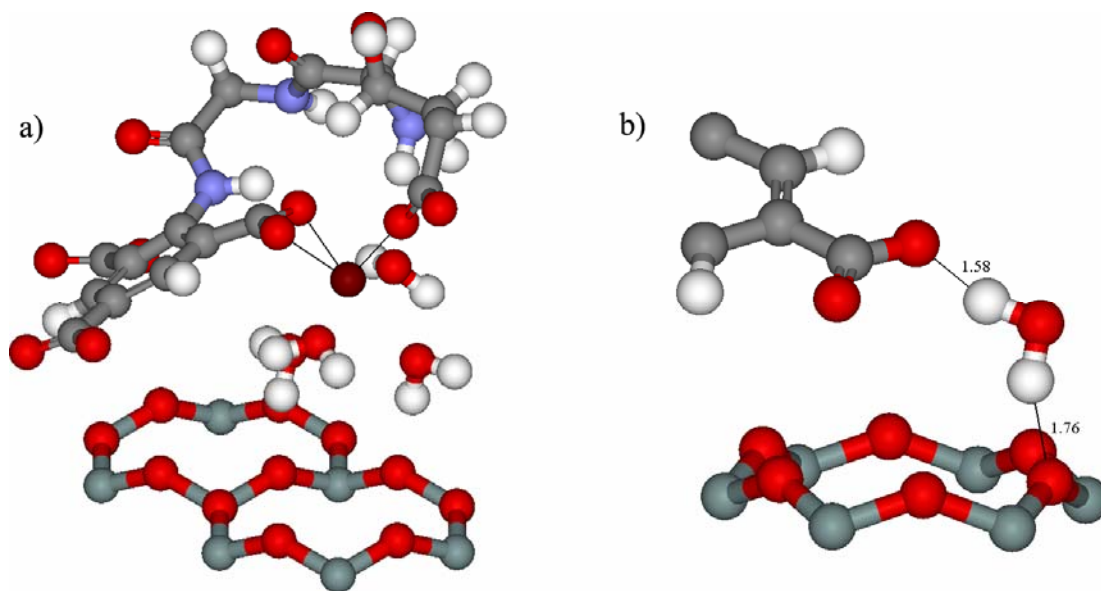


Figure 5. Organo-mineral interactions typical of the Ca-saturated DOM-montmorillonite system include (a) cation bridges, consisting usually of Ca^{2+} inner sphere coordinated to carboxylate groups and outer sphere coordinated to the mineral surface, and (b) water bridges, in which a water molecule is simultaneously hydrogen-bonded to the organic and mineral molecules. Atoms are color-coded as described in Figures 1 and 3.

Discussion

The simulation results indicate that, for soils strongly influenced by Ca-smectite clay minerals, cation bridging is the dominant mechanism of stabilization of natural organic materials. Although the Ca-saturated DOM-montmorillonite system studied here is that of the smectite interlayer region, which provides a convenient three-dimensional periodic simulation system, these conclusions apply readily to more accessible external clay mineral surfaces. The prevalence of Ca^{2+} cation bridges is in keeping with a variety of observed landscape-scale trends and experimental evidence that point to the importance of this type of interaction in soils. Higher organic matter contents are observed in calcareous soils as compared to noncalcareous soils (Oades 1988). The removal of Ca^{2+} from soils frees humic substances for laboratory extraction and stimulates the decomposition of organic matter, whereas its addition enhances retention of organic materials and stabilizes soil structure (Oades 1988). Thus a supply of dissolved Ca^{2+} appears to be an essential component for the sequestration of soil organic matter.

Perhaps more surprising is the observation that, where cation bridging interactions dominate, hydrogen bonding interactions are absent. Because the Ca-saturated DOM molecule still contains numerous protonated alcohol functional groups capable of producing hydrogen bonding interactions, a lack of appropriate organic functional groups does not explain fully this observation. It would appear that the presence of bivalent cations produces a more polar, highly organized Ca-saturated DOM structure surrounded by partially hydrated Ca^{2+} ions. Associated cations and water molecules thus shield the organic material from direct contact with the mineral surface, eliminating organo-mineral hydrogen bonds and drastically reducing hydrophobic interactions. Although the dominance of cation bridge interactions in the Ca-saturated DOM-montmorillonite system suggests that land management techniques to optimize soil carbon storage may require additions of dissolved Ca^{2+} , the exclusion of hydrogen bonding in the same system suggests the possibility that creating favorable conditions for one type of organo-mineral interaction could result in the release of organic materials held in place by other interactions that become inhibited by the new conditions.

Although we can assume that 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? Organic molecules tucked within a clay interlayer would be protected from microbial degradation, potentially forming a very stable and long-lived pool of soil carbon. Organic materials have been found within the interlayers of smectite minerals obtained from a few different soil ecosystems (Kodama and Schnitzer 1971; Satoh and Yamane 1971; Theng et al. 1986; Righi et al. 1995). Radiocarbon dating performed on one of these samples indicated the interlayer organic substance was thousands of years old (Theng et al. 1992). Acidic solutions of humic fractions have been shown to penetrate montmorillonite interlayers when in the presence of Ca^{2+} , but such interlayer complexation is virtually absent above pH 5 (Schnitzer and Kodama 1966; Martinez and Rodriguez 1969). Although the Ca-saturated DOM-montmorillonite model system examined in our study indicates that, once within the interlayer, a humic substance in the presence of sufficient Ca^{2+} takes part in cation bridges with the mineral surface, it does not address the mechanism of initial entry into the clay interlayer region. Simulation of the interactions between a realistically sized model humic

molecule and the edge sites of Ca-montmorillonite is necessary to ascertain the feasibility of interlayer complexation of organic materials under typical soil conditions.

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