MOLECULAR MODELS OF METAL SORPTION
ON CLAY MINERALS

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Chapter 4
Molecular Modeling of Clays and Mineral Surfaces
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INTRODUCTION

Containment of radionuclide and chemical wastes in the environment is linked intimately to the ability of subsurface materials to attenuate and immobilize contaminants by chemical sorption and precipitation processes. Our ability to evaluate these complex processes at the molecular scale is provided by a few experimental and analytical methods such as X-ray absorption and NMR spectroscopies. However, due to complexities in structure and composition of clays and clay minerals, and the inherent uncertainties of the experimental methods, it is critical to apply theoretical atomistic models for an improved understanding and interpretation of these phenomena. The cryptocrystalline nature of clay materials and the associated difficulty of obtaining quality X-ray structural refinements also direct a need for theoretical analysis of the bulk structure of clays. Combined with recent advances in high-performance computing, molecular modeling may help provide a sound basis for designing efficient methods for waste treatment and improved immobilization of contaminants.

Molecular modeling methods include a wide range of theoretical tools that provide a detailed probe of atomic interactions that ultimately control the crystal structure, chemical reactivity, and physical properties of materials. Their use in the study of clay mineral structures and reactivity is fairly recent due to the need for high-performance computers, yet the methods have been available for several decades. Monte Carlo and molecular dynamics methods were conceived in the 1950's using the most powerful mainframe computers of the day to simulate simple liquids (Metropolis *et al.*, 1953; Alder and Wainwright, 1957). Today, with advanced massively parallel supercomputers, it is possible to perform calculations on mixed-phase systems of over a million atoms and for simulation times that involve over a million time steps (Lin *et al.*, 1992; Lim, *et al.*, 1997). Quantum chemical calculations using various *ab initio* molecular orbital methods also have progressed with the accelerated improvement in computational power. Some Hartree-Fock calculations of simple molecules can now be performed on a personal computer. Clay minerals, represented by molecular clusters or simple periodic systems, recently have been added to the list of complex phases that can be treated by these methods. For example, the complete structure of kaolinite has been optimized with periodic molecular orbital methods (Hobbs *et al.*, 1997).

Given the burgeoning interest in computational chemistry, it is not surprising to see more researchers incorporate molecular modeling tools to evaluate the fundamental processes of clay-water interactions. Most research to date has emphasized the atomistic simulation of water in the clay interlayer to understand swelling behavior (*e.g.*, Delville, 1991; Skipper *et al.*, 1991; Boek *et al.*, 1995; Chang *et al.*, 1998). Recently, a few molecular modeling studies have investigated the external clay surfaces and their interactions with metal cations (see below). Theoretical methods offer the experimentalist a convenient means for identifying the probable sorption sites and evaluating the fundamental mechanisms of metal sorption. Therefore, molecular modeling is vital for interpreting complex experimental spectra. As a clarification, the use of the word metal in this chapter refers to the aqueous cation that interacts with the clay mineral.

This chapter provides a review of the basics of molecular modeling and a survey of recent advances in the molecular modeling of metal sorption on clay minerals. The first part of the

chapter discusses empirically-based calculations and the use of an analytical function for the energy forcefield. Functionality and parameterization of the energy terms are reviewed. Various types of energy calculations are surveyed with particular emphasis on energy minimization processes and electrostatic potential surfaces. (Details of molecular orbital methods were reviewed in Chapter 1; Monte Carlo and molecular dynamics simulations will be discussed in Chapter 3 of this volume.) The next section of this chapter summarizes the energy calculations often used to examine the bulk and surface structures of clay minerals. The final part of the chapter includes a discussion of electrostatic potential surfaces and sorption energy maps for identifying sorption sites. Examples of energy minimizations and molecular dynamics simulations are presented for the sorption of cesium and sodium ions onto surfaces of different clay minerals.

ENERGY AND INTERATOMIC FORCEFIELDS

Interatomic forcefields provide the basis for describing the fundamental interaction energies for molecular mechanics simulations. Therefore, interatomic forcefields are the key element in performing energy minimization, Monte Carlo, and molecular dynamics simulations. Essentially, the forcefield is an integrated set of analytically-based functions that describe the energy for each mode of interaction expected for an assemblage of atoms (*e.g.*, bond stretching, angle bending, Coulombic forces, and van der Waals interactions). Bond distances, bond angles, and other geometric relations, along with atomic charges, are first determined for a given atomic arrangement in a molecular system and then used to calculate the energy of the system.

The computational speed of molecular mechanics simulations is quite rapid compared to molecular orbital approaches in which the energy is determined by the computationally-intensive solution of the electron density (see Chapter 1). In contrast to the molecular orbital methods that are highly accurate and treat the chemical system as a single integrated molecular system, the empirical forcefield requires that the chemical system be broken down to a set of simple atomic interactions. In so doing, the computational effort of a forcefield-based simulation is quite straightforward and allows the computational scientist to examine fairly large chemical systems that typically can include hundreds and thousands of atoms, or even millions of atoms when a massively parallel supercomputer is available. With the recent advances in computer technology and the development of powerful workstation computers, clay minerals that can have a sizable number of atoms per unit cell are now within range for theoretical simulation. However, the calculations will only be as meaningful as the quality and validity of the forcefield.

Bonded Forcefield

Empirical forcefields usually incorporate simple analytical expressions to describe the energy for atomic interactions. Figure 1 provides a graphical representation of the various atomic interactions. The simple bonded (or valence) forcefield where bonding is defined among specific atoms is represented by the first four energy terms in the figure. Bonds are explicitly defined and can be considered to be covalent or directional in nature. The bond stretching component of the forcefield is typically defined as a simple harmonic (quadratic potential) or higher order expression (quartic potential) based on a deviation from an ideal or equilibrium bond distance. Table 1 includes the analytical expressions for this energy term as well as those for the other bonded interactions depicted in Figure 1. The bond stretch energy will increase as the distance between two bonded atoms either increases or decreases beyond an equilibrium value. More sophisticated forcefields, especially those describing organic molecular systems, rely on the more complex Morse potential (three parameter function) to describe the bond stretch energy (see Table 1). Typically, forcefields used to describe inorganic systems, including zeolites and clays, include the simpler quadratic functions. However, a Morse potential is needed to describe the hydroxyl bond in some simulations of layered silicate minerals and clays (Collins and Catlow, 1990). The Morse functionality is versatile in that it allows for dissociation of the hydroxyl bond with the energy asymptotically approaching zero at infinite atomic separation.

The energy function to describe angle bending, also known as a three-body term, is based on the deviation of bond angle θ from an equilibrium value. The torsion term describes the rotation about a bond and requires the measurement of a dihedral angle φ (or similar angle) for a four atom configuration. The out-of-plane stretch term of the forcefield is based on central atom displacement in a planar group of four atoms that is typical of sp^2 bonded systems, and can be described by two parameters. Simulations involving the simulation of calcite and other carbonate phases characterized by the planar CO_3^{2-} will necessarily include the out-of-plane stretch term (Pavese *et al.*, 1992; Parker *et al.* 1993; Titiloye *et al.*, 1993). Occasionally, a forcefield will include cross (or off-diagonal) terms describing the coupling between the stretching of adjacent bonds in order to accurately reproduce the experimental vibrational frequencies of molecules. Unfortunately, little is known about these complex modes of interaction in most inorganic materials including clays and therefore the cross terms are ignored. Nonetheless, some of the unknown interaction parameters (*e.g.*, partial charge and van der Waals terms) can be derived by molecular orbital calculations. This theoretical approach for obtaining the forcefield parameters was treated in greater detail in Chapter 1 and will be briefly discussed below.

The final energy term shown in Figure 1 describes the nonbonded interactions and is of most importance in simulating the sorption behavior of metals on clay minerals. Notwithstanding, the nonbond energy term is also critical in controlling the long-range nature of most periodic crystalline materials. The following expression is often used to evaluate the nonbonded energy:

$$E_{nonbond} = \sum_{i>j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{i>j}^{N} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right) \qquad (1)$$

The atomic charges are denoted by q_i and q_j while A_{ij} and B_{ij} represent the empirically-fitted parameters and N denotes the total number of atoms. Electrostatic (or Coulombic) interactions (first term of Equation (1)) dominate the nonbonded term with the energy varying as the inverse of the distance between atoms r_{ij}. This first term yields a negative potential energy when the atomic charges are of opposite sign with an attractive interaction, whereas when the charges are equivalent in sign the potential energy will be positive (repulsive). The nonbonded expression also includes a short-range overlap repulsive term (positive energy) and a van der Waals (or dispersive) attractive term (negative energy). Note that the literature will often refer to the latter two terms combined as the van der Waals energy. Equation (1) uses the standard Lennard-Jones (or 6-12) potential to describe the short range interactions although some forcefields incorporate the so-called 6-9 potential (A/r^9 - B/r^6). When incorporating the nonbonded energy expression in a bonded forcefield, it is necessary to ignore any nonbonded interactions between atoms that are implicitly accounted for by a bond stretch or angle bend term. The dominance of the electrostatic term in Equation (1) is best illustrated by an example involving the hydroxyl O-H interaction. Assuming full charges and a 1.0 Å separation, the electrostatic potential is –664 kcal/mol while the short range terms contribute only ± 10 kcal/mol.

The summations in Equation (1) are performed over all possible interatomic interactions ij (with i > j) and are typically limited by some predefined cutoff distance for molecular systems.

However, in simulating periodic systems the long-range nature of the electrostatic 1/r term will be nonconvergent. It is therefore necessary to apply the Ewald method (Ewald, 1921; Tosi, 1964) where a mathematical manipulation is used to ensure proper convergence. In this approach, the inverse distance is rewritten as its Laplace transform and then split into two rapidly convergent series, one in reciprocal space and one in real space. The reciprocal part of the electrostatic energy E_{recip} is given by Gale (1997) as:

$$E_{recip} = \frac{1}{2}\frac{4\pi}{V}\sum_G \frac{1}{G^2}\exp\left(-G^2/4\eta\right)\sum_i\sum_j q_i q_j \exp(-iGr_{ij})$$
(2)

and the real part of the electrostatic energy E_{real} is given by:

$$E_{real} = \frac{1}{2}\sum_i\sum_j q_i q_j \mathrm{erfc}(-\eta^{1/2}r_{ij})/r_{ij}$$
(3)

where G is a vector of the reciprocal lattice and η is a parameter that controls the distribution of the summation between the reciprocal and real space. In practice, the value of η is chosen to minimize the number of terms to be evaluated relative to the computational cost. Due to the substantial computational cost involved in using the Ewald summation, the literature often includes studies of crystalline systems where only direct space cutoffs for the electrostatics energy were applied. These simulations are therefore approximations and their results may be suspect.

Ionic Forcefield

An alternative to the bonded forcefield is the nonbonded or ionic forcefield that includes no predetermination of the existence of a bond between atoms. In this approximation, the forcefield incorporates only nonbonded interactions as denoted in Equation (1) and thereby drastically reduces the number of empirical parameters required. The short range interactions can be defined using a Lennard-Jones 6-12 or a 6-9 potential. More common in the simulation of oxide materials is the incorporation of a Born-Mayer potential (two parameter exponential; see Table 1) combined with the $1/r^6$ van der Waals term. In combination with the electrostatics 1/r term, this functionality is referred to as the Buckingham potential (Parker *et al.*, 1984; Catlow and Cormack, 1987; Catlow *et al.*, 1991) and is also provided in Table 1. Atoms are typically assigned their full ionic charge and are treated as rigid or more specifically as point charges. Beyond the fewer number of empirically-derived parameters, the benefits of using the ionic model include its ability to simulate glasses, melts, and other amorphous materials, and to evaluate coordination changes. Often a three-body angle bending term is incorporated into the ionic forcefield in order to describe the tetrahedral arrangement of silicon (Vessal, 1994) and aluminum (Gale and Henson, 1994). In contrast to bonded forcefields that require bonds to be preserved during the simulation, the ionic forcefield has the flexibility to simulate bond-making and bond-breaking processes resulting in the aforementioned coordination changes. However, recent efforts in the extension of bonded forcefields for simple molecules and complexes (Root *et*

al., 1993; Rappé *et al.*, 1993; Hahn *et al.*, 1997) may soon be used to examine bond rearrangement in the simulation of extended structures.

A significant refinement of the ionic forcefield is the inclusion of a shell-model in the potentials (Dick and Overhauser, 1958). The shell allows the introduction of electronic polarization by coupling an ion core to a shell that has no mass by a harmonic spring (Figure 2). The shell simulates the polarizable valence electrons. The displacement of the shell from the core of the ion is a measure of the polarization relaxation of the ion to form a dipole. Essentially, the shell model allows the valence electrons to shift toward other ions to simulate a covalent-like bond that is explicitly defined in a bonded forcefield. Large polarizable anions such as oxygen and fluorine, and cations such as lithium, nickel, and barium are best simulated as shell ions. The shell model refinement to the ionic forcefield provides a robust methodology that is not limited to calculations of bulk structures. Surfaces, point defects, diffusion, elastic constants, dielectric behavior, and other material properties can be accurately simulated, and necessarily require the inclusion of a polarization energy. The polarization energy can also be treated by a polarizability term for each ion as done by Rustad *et al.* (1996a, 1996b) and Wasserman *et al.* (1997) in their theoretical analysis of oxide and oxyhydroxide surfaces. Lasaga and Cygan (1982) complied and discussed polarizabilities appropriate for the simulation of silicate minerals.

Parameterization of Forcefields

The success of any empirically-based molecular model will be highly dependent on the quality of the forcefield utilized. Parameterization can be accomplished by a statistical fitting of the desired parameters to achieve the best possible agreement between calculated and observed structures. Both molecular geometries and crystalline structures are used for the parameterization. Typically, the structures of simple binary oxide compounds are used to derive the interatomic potentials for the metal-oxygen interactions. Also, various spectroscopic techniques, in particular, XAFS or XANES (O'Day *et al.*, 1994; Brown *et al.*, 1995), can provide structural information for parameterization. In applying empirical forcefields to examine complex materials such as clays, it is assumed that the different interactions can be directly combined to describe ternary or higher order oxides. Only metal-oxygen, hydrogen-oxygen, and oxygen-oxygen parameters are needed in the simulations of clays. As with most materials simulations, metal-metal short range interactions are ignored.

Theoretical methods also are convenient for determining forcefield parameters, especially when suitable model compounds are unavailable. A theoretical approach has the advantage over experimental methods in providing a wide range of interatomic dimensions for which the energies can be evaluated and then fit to the appropriate forcefield expression. The electron-gas model of Jackson and Gordon (1988) can be helpful in this approach, as well as the more sophisticated molecular orbital methods. Lasaga and Gibbs (1987) successfully used Hartree-Fock *ab initio* methods to derive potential energy surfaces and an ionic model for the Si-O bond in silicate minerals. Semi-empirical molecular orbital methods were used by Delville (1991) to obtain clay-water parameters. Empirically-based methods such as the free energy perturbation technique have also been used to derive potentials for metal-oxygen interactions (Aqvist, 1990). The forcefield parameters obtained from theoretical methods can be used alone or in conjunction

with those obtained from experimental data. For example, several experimentally-derived metal-oxygen interactions can be incorporated with an oxygen-oxygen potential derived from a Hartree-Fock calculation in the simulation of a ternary silicate phase.

Bonded forcefields require parameters for the atomic charges that significantly influence the contribution of the electrostatic nonbonded component to the total energy (Equation (1)). The partial charges can be calculated in one of several ways. Typically, high-level molecular orbital calculations are performed on small cluster molecules representing the appropriate metal coordination. The resulting electrostatic potentials are then used in a least-squared fit to obtain the optimum atomic charges that reproduce the electrostatic potential outside the molecule. The CHELPG method (Chirlian and Francl, 1987, Breneman and Wiberg, 1990) is helpful in this approach. Atomic charges can be obtained from the molecular orbital calculations using a Mulliken electron population analysis (Mulliken, 1955), although this and other related analyses of the wavefunction are less sophisticated and occasionally lead to ambiguous charge assignments. Rappé and Goddard (1991) have developed a general charge prediction scheme QEq based on the geometry and electronegativities of the various atoms. Deformation electron densities derived from X-ray diffraction experiments on oxide crystals can also be used to derive atomic charges as was done recently by Teppen *et al.* (1997) for silicon and aluminum in silicates. Alternatively, empirical methods can be used in which coordination, connectivity, and bond order are used to assign atomic charges. No matter how the partial charges are obtained in the parameterization of the forcefield, it is important to recognize that partial charges are an integral part of the forcefield and cannot be arbitrarily transferred to another forcefield.

Shell models require second derivative properties to be reproduced by the parameterization of the forcefield. The second derivative of the energy with respect to the spatial coordinates for a chemical system, also known as the Hessian matrix, is directly related to the dielectric properties (static and high frequency values) and elastic constants of the solid. Provided these experimental values are known for model compounds, it is possible to include more constraints on the parameterization. The harmonic potential that represents the core-shell coupling (Figure 2) can be obtained from the high frequency dielectric constant or refractive index of the model compound. Additionally, the Hessian matrix includes the vibrational force constants that are critical in the evaluation of vibrational spectra and thermodynamic properties of the material. Gale (1996, 1997) has developed a general lattice energy code GULP that simplifies the derivation of these forcefield parameters.

Selected Forcefields

The choice of a forcefield is crucial in obtaining accurate and reliable results from the energy calculations. Often the forcefield is developed by the individual computational scientist for a specific chemical system and modeling problem. However, with the availability of more general molecular modeling software for workstation environments and recently for personal computer systems, there is a need for more generalized and integrated forcefields. Several general forcefields are typically included with commercial software packages and provide a convenient means of testing the validity of a molecular model and comparing different forcefields.

Most of the general forcefields have traditionally been developed for the analysis of organic molecules with particular application to the pharmaceutical industry and the development of new drug compounds. Fortunately, the functionality of these forcefields is quite general and has been readily adapted for application to materials with particular emphasis on the simulation of zeolites for the catalysis industry. The CVFF (consistent valence forcefield of Dauber-Osguthorpe *et al.*, 1988) and CFF91 (consistent forcefield of Maple *et al.*, 1994) are two bonded forcefields that have been widely used in this effort. The CFF91 forcefield, as extended by Hill and Sauer (1994, 1995) using Hartree-Fock molecular orbital calculations on quartz and zeolites, provides a general method of examining aluminum substitution in the zeolite framework. The Universal forcefield (UFF of Rappé *et al.*, 1992) has been parameterized for the complete periodic table based on a set of rules for element type, hybridization, and connectivity. This bonded forcefield has been successfully used for modeling organic molecules, metal complexes, oxides, and zeolites, but to date has not been fully tested for clay minerals. The Dreiding forcefield (Mayo *et al.*, 1990) is a more specialized bonded forcefield designed for the structure prediction of organic, biological, and some inorganic molecules. Numerous other specialized forcefields have been developed and published in the literature but typically are restricted to specific chemical systems and a particular type of energy calculation.

It is important to highlight two general forcefields that have been designed specifically for the simulation of clay minerals. The bonded forcefield of Teppen *et al.* (1997) is based on the functionality of the CFF91 forcefield and has been parameterized for aluminous dioctahedral clays. Unique in the forcefield is the inclusion of a bending potential for octahedral O-Al-O angles that is characterized by a double-well potential with minima at both 90° and 180°; other general forcefields only allow aluminum to be treated in tetrahedral coordination. The Teppen *et al.* (1997) forcefield refines some of the Hill and Sauer (1994, 1995) modifications of CFF91 by incorporating Hartree-Fock molecular orbital calculations performed at the MP2 level to account for electron correlation effects. The success of this forcefield is demonstrated by the accurate molecular dynamics simulation of the dioctahedral structures of gibbsite, kaolinite, and pyrophyllite (Teppen *et al.*, 1997); structural parameters were reproduced to within 1% of the experimental values. Nonbonded parameters for interlayer sodium and calcium ions were also derived and incorporated in the successful simulation of a dry beidellite smectite clay. This research group is continuing its development of new potentials for clay simulations, and is currently developing CFF91 parameters for magnesium and other atoms needed to model trioctahedral clays.

The second useful forcefield for modeling clay minerals is the nonbonded version of the CVFF forcefield called CVFF_aug (Vessal, unpublished data). This forcefield relies on a Lennard-Jones 6-12 potential to describe the short-range interactions associated with the major atoms in clay minerals, and includes aluminum in tetrahedral and octahedral coordinations. No valence bonds between atoms are required in this forcefield. Potentials for octahedral magnesium, iron, and titanium and various interlayer metal ions are included. The parameters were derived using experimental structural data for simple oxides, muscovite, and several model clay minerals in combination with the parameter-fitting capabilities of the program GULP (Gale, 1997). The CVFF_aug parameters were derived for periodic assemblies and require full ionic charges. Although somewhat simpler in form than the bonded forcefields, CVFF_aug forcefield produces relatively accurate structures for clay minerals (see below). The CVFF_aug forcefield is distributed by Molecular Simulations Inc. (San Diego).

THEORETICAL METHODS AND MODELING TOOLS

Molecular Orbital Methods

The accuracy of energy calculations obtained by molecular modeling simulations ultimately relies on the quality of match of the calculated energy to the exact potential energy surface of a chemical system. The latter is best described by the exact solution to the Schrödinger equation, and is obviously a daunting task and well beyond standard computational means for even the simplest molecules. Nonetheless, molecular orbital calculations provide a useful tool in this effort and have been used to describe the geometries and energies of simple representations of aluminosilicates (*e.g.*, Lasaga and Gibbs, 1987; Teppen *et al.*, 1994). Among the molecular orbital approaches are semi-empirical techniques, Hartree-Fock *ab initio* methods, and density functional theory (DFT) models. These are discussed in some detail in Chapter 1 and by Hehre *et al.* (1986). It is noteworthy that with the recent advances in computational power it is now possible to obtain optimized molecular orbital structures of clays as demonstrated in the calculations of Hess and Saunders (1992) and Hobbs *et al.* (1997) on kaolinite.

Energy Minimization

Energy minimization (or geometry optimization) methods based on a molecular mechanics approach are a convenient and rapid alternative to the sophisticated molecular orbital methods. Assuming that the empirical forcefield provides the best possible fit to the true potential energy surface, it is possible to evaluate the total potential energy for various configurations of the chemical system. The goal is to locate the points on the potential energy surface where the lowest energy occurs or where the net force on each atom is zero. In the energy minimization procedure, it is first necessary to evaluate the energy of the molecule or crystal for a given starting configuration. The configuration is then adjusted using appropriate algorithms to lower the value of the total energy. This process is repeated until a particular tolerance (usually measured as a root-mean-square derivative of the energy) is achieved for the difference in energy between successive steps, and results in a minimized configuration. Obviously, the number of iterations may be quite small or may number in the thousands depending on the efficiency of the minimization algorithm, the energy tolerance, the number of atoms and bonds, and how far the initial configuration is away from the equilibrium geometry.

Energy minimizations are technically 0 K simulations since kinetic energy and thermal vibrations are ignored (*i.e.*, no entropic energy). However, parameterization of the forcefield often incorporates experimental data obtained at room-temperature, and therefore allows the implicit incorporation of temperature effects. External energy constraints such as hydrostatic pressure and axial stresses, can be imposed during the energy minimization of systems comprised of periodic cells. This requires the optimization of cell parameters (all or selected cell dimensions and angles). Constant volume minimizations constrain the cell parameters to fixed values and may often lead to the buildup of net forces on the atoms and cell faces, especially if the values are far from equilibrium. However, this minimization approach provides a method of incorporating thermal effects by constraining the cell parameters to those values obtained from

experimental crystal refinements for diffraction data collected at a particular temperature. Additionally, selected atoms or subsets of a molecule can be fixed during a minimization, or selected geometries (*e.g.*, bond angles) can be constrained to particular values. The former approach is particularly helpful in examining clay structures where appropriate forcefield parameters are lacking or where only hydrogen atom positions are to be optimized (*e.g.*, Giese and Datta, 1973; Giese, 1982; Collins and Catlow, 1991).

Figure 3 provides a schematic representation of how the different energy components of a simple two-atom (uncharged) system are combined to obtain a minimum for the total energy. In this example, a Lennard-Jones potential is used to describe the short range repulsive energy and longer range van der Waals attractive energy; electrostatic energy is nonexistent. The equilibrium separation distance for the atoms is indicated by the minimum in the total energy curve. The same minimization concept applies in multi-atom and periodic systems where now the total energy for the iteration is evaluated for all possible atomic interactions described by the forcefield. The curvature and depth of the total energy minimum will vary from system to system, and often will be masked by local minima and metastable molecular configurations (or conformations). Therefore, it is critical that the entire potential energy surface be mapped by performing numerous minimizations using different initial configurations to ensure that the true global minimum has been attained.

Various minimization algorithms are available for obtaining the geometry-optimized lowest energy structure of a molecule. These range from fairly crude methods such as line searches and steepest-descents methods to the sophisticated Newton-Raphson method. In practice, no one search method is used exclusively; rather, a combination of algorithms is incorporated to first approach the minimum configuration and then refine the calculation to the true minimum. The steepest descents method performs a line search defined along the direction of the local negative energy gradient. The method is relatively slow but is very robust in finding a general minimum when configurations are far from being minimized. The conjugate gradient method, however, can correct for any path deviations away from the minimum and provide a more efficient minimization. The Newton-Raphson method evaluates both first and second derivatives of the energy to efficiently identify a search path and locate the minimum. Unfortunately, the initial configuration must be near the minimum for this method to be suitable; it is also computationally expensive for systems having a large number of atoms. However, the cost of calculating the Hessian (second derivative) matrix may be reduced significantly if there are any symmetry constraints that can be identified in the molecule or periodic cell.

Monte Carlo Methods and Molecular Dynamics

The use of Monte Carlo methods, as the name implies, in molecular modeling requires the iterative random sampling of a simulation volume to sample a range of configurations and potential energies. This approach has been conveniently used to examine the swelling properties and the structure of water and ions in the interlayer of montmorillonite (Delville, 1991, 1992; Skipper *et al.*, 1991, 1995a, 1995b; Boek *et al.*, 1995). The attainment of equilibrium in these simulations often required over one million configurations in order to provide interlayer spacings as a function of the number and orientation of water molecules. Molecular dynamics simulations

are often used in conjunction with Monte Carlo simulations in order to examine the time evolution of a system and to incorporate temperature effects. Velocities, as defined by a Boltzmann distribution of thermal energy, are initially imparted onto all or a subset of the atoms contained in the simulation cell of the clay. Molecular dynamics then involves solving the classical equations of motion for the assemblage of atoms. Iterative time steps on the order of a femtosecond (10^{-15} s) are used to obtain trajectories of atomic motion for simulation times up to several hundred picoseconds (10^{-12} s). Karaborni *et al.* (1996) combined a grand-canonical (constant chemical potential) Monte Carlo approach with molecular dynamics to examine the hydration of montmorillonite. Similarly, Chang *et al.* (1995, 1997, 1998) and Greathouse and Sposito (1998) simulated the interlayer environment in montmorillonite and in some cases derived self-diffusion coefficients for water and the interlayer ions at various water contents. Recently, de Siqueira *et al.* (1997) used a Monte Carlo approach to simulate the dehydration of montmorillonite at elevated pressures and temperatures in order to examine the release of interlayer waters and the formation of illite. In all of these studies of water in smectite clay, the simulations were performed with rigid clay layers; only the interlayer waters and ions were allowed to freely translate while monitoring the contraction or expansion of the interlayer spacing. Details of Monte Carlo and molecular dynamics techniques are provided in Allen and Tildesley (1989), Frenkel and Smit (1997), and Chapter 3 of this volume.

Electrostatic Potential Surfaces

A convenient modeling tool for examining the surface environment of molecules and crystals is the calculation of electrostatic potential maps. These maps are especially helpful in determining sites for metal sorption onto clay surfaces because the electrostatic component of the nonbonded energy makes up a significant part of the sorption energy. As noted above, the electrostatic potential determined in a molecular orbital calculation is often used to derive atomic charges used in a forcefield. Conversely, the atomic charges can be used to determine the electrostatic potential for a molecule or a molecular configuration representing a surface. This approach allows for the determination of electrostatic potentials for large assemblies and various configurations of atoms that would otherwise be treated by molecular orbital methods.

The molecular electrostatic potential (MEP) calculation generates a solid surface about a molecule using the van der Waals radii of the atoms. The surface is triangulated into numerous sections where the electrostatic potential V is evaluated at each vertex R for each surface section:

$$V = \sum_i \frac{q_i}{\left| R - r_i \right|} \tag{4}$$

The summation is performed over all atoms of the molecule where q_i is the atomic charge and r_i is the location of the atom relative to R. The MEP surface calculation is limited by the assumption of the point charge model and may not be accurate if the electron density cannot be described as a spherical distribution about the atom. This is less a concern for most silicate systems that are predominantly ionic in contrast to organic molecules with significant covalent bonding. Given this limitation, the MEP calculation can generate a graphical representation of how the surface may control sorption. It provides the surface expression of the internal

distribution of atomic charges associated with the molecule. The MEP surface can be used to predict the most favorable site on a surface for a reaction that is initially driven by long-range electrostatic forces as in the sorption of metal ions from solution onto the clay surface (Brady *et al.*, 1996). Electrostatic potential maps derived by molecular orbital calculations (Bleam, 1990) also have been used to assess the nature of the distortions of the basal (001) surface of talc and pyrophyllite.

A significant refinement of the MEP method is the addition of the short range repulsion and van der Waals energies to obtain the total energy for a particular surface region and sorption site. This method employs the calculation of a large docking grid about the mineral surface and can be computationally intensive according to the size of the molecular cluster chosen to represent the clay surface. This method will be reviewed later in the chapter. The next section provides a discussion of molecular models for the simulation of bulk and surface structures of clay minerals.

CLAY MINERAL STRUCTURES

Bulk Structures

Molecular modeling methods provide a unique and convenient approach for examining the bulk structures of minerals. The methods are especially attractive for analyzing clay minerals where there is a paucity of experimental diffraction data and structural refinements, in part due to the cryptocrystalline nature of clays, the lack of quality single crystals, complex substitutions in tetrahedral and octahedral sites, and stacking disorder. Recent studies using periodic molecular orbital methods for sheet silicate minerals, such as the Hartree-Fock analysis of lizardite (Smrcok and Benco, 1996) and the density functional theory approach for optimizing talc and pyrophyllite (Bridgeman *et al.*, 1996) and kaolinite (Hobbs *et al.*, 1997), may eventually be used to routinely predict clay structures. However, until the computational costs of these calculations are significantly reduced, most theoretical clay structure analyses will rely on the molecular mechanics approach.

Kaolinite ($Al_2Si_2O_5(OH)_4$) provides an excellent example of the use of forcefield methods for obtaining theoretical bulk structures (Cygan *et al.*, 1997). The experimental crystal structure recently was obtained by Bish (1993) based on the refinement of the neutron diffraction data of Young and Hewat (1988) obtained at 1.5 K. Energy minimization methods were used to calculate the 0 K optimized structures for kaolinite based on the bonded forcefield of Teppen *et al.* (1997) and an ionic forcefield using a shell model. The calculations were performed with periodic boundary conditions and a unit cell comprised of 34 atoms that were all allowed to freely translate during the minimization (*i.e.*, P1 symmetry). By allowing the periodic cell to have P1 symmetry (no symmetry constraints), there is no prejudicial choice for the space group of kaolinite. Additionally, Ewald summations were used and all six cell parameters were allowed to optimize to simulate constant pressure conditions. The observed kaolinite structure of Bish (1993) was used for the initial configuration. The shell model uses the Buckingham potentials and spring constants derived by Sanders *et al.* (1984) and Jackson and Catlow (1988), and requires a Morse potential to describe the hydroxyl bonds (Collins and Catlow, 1990).

Figure 4 shows a comparison of the two energy-minimized crystal structures of kaolinite with the experimental kaolinite structure from Bish (1993). Both theoretical models have cell parameters that are in excellent agreement (approximately 1%) of the observed values (a = 5.1535 Å, b = 8.9419 Å, c = 7.3906 Å, α = 91.926º , β = 105.046º, and γ = 89.797º). The shell model is characterized by slightly tilted silicon tetrahedra and inner hydroxyls that are influenced by the vacant octahedral sites but are directed downward toward the silicon sheet. The positions of the interlayer hydroxyls are in good agreement with the observed structure; however, both types of O-H bond distances are underpredicted by approximately 10%. The bonded model has inner hydroxyls that are appropriately positioned sub-parallel to the ab plane, but several of the interlayer hydrogens are significantly displaced from the observed position and are not involved in the hydrogen bonding across the interlayer. Both models favorably predict the Al-O bond distances; however, the bonded model overpredicts the apical and basal Si-O bond distances (bonded: 1.632 Å and 1.641 Å; shell: 1.625 Å and 1.619 Å; experimental: 1.618 Å and 1.616 Å).

A symmetry analysis of the atomic positions in the energy-optimized structures indicates that both kaolinite models possess a face-centered symmetry in the ab plane that verify C1 symmetry for the unit cell. These results support the conclusions of Bish (1993) in his reanalysis of the kaolinite diffraction data that were originally interpreted as P1 triclinic symmetry by Young and Hewat (1988).

Energy minimization is typically used prior to performing molecular dynamics simulations. The dynamics calculation includes temperature effects which provide a means of surpassing small energy barriers (on the order of kT) that may limit the sampling of potentially lower energy surfaces. In developing the extension of the CFF91 forcefield for clay minerals, Teppen *et al.* (1997) tested the feasibility of the new forcefield parameters by performing molecular dynamics simulations of the bulk structure of kaolinite, gibbsite, and pyrophyllite. They obtained equilibrium structures and stabilization of potential energy within 5 to 20 psec of simulation time. Mean values obtained from the equilibrated portion of the trajectories (atomic path histories) give cell parameters and bond distances that are consistent with the energy-minimized structure discussed previously. Although the dynamics simulations were at 298 K, no expansion of the structure was noted in comparison with the 0 K minimized result. In contrast to previous molecular dynamics simulations of clays in which the clay layers were rigid, this dynamics study provided the first fully-relaxed structural analysis.

The results of a theoretical analysis of the bulk structure of a trioctahedral smectite clay (Na-hectorite) is presented in Figure 5. The figure shows the optimized structure from a constant pressure energy minimization of a supercell (eight unit cells) of hectorite having P1 symmetry. All atoms are allowed to freely translate in the simulation. The starting structure was obtained by first converting a model clay structure (montmorillonite from Tsipursky and Drits, 1984) to a trioctahedral clay with magnesium and lithium filling all octahedral sites and including three hexahydrate complexes of sodium ion in the interlayer. The tetrahedral layers are comprised of all silicons so that the layer charge is generated by the three lithiums in the octahedral layer. The ionic forcefield CVFF_aug was used in conjunction with the Discover energy program (Molecular Simulations Inc., San Diego); covalent bonds between atoms do not exist in the clay structure using this forcefield and are only provided in Figure 5 for visualization purposes. Water molecules are flexible and have bonds described by the potentials from the CVFF forcefield.

The energy-optimized structure of hectorite shows the interlayer sodium ions positioned over or near the ditrigonal cavities (hexagonal holes) of the silicon tetrahedral sheet. The ions maintain their hydration sphere within the interlayer although there exists some deflection of water molecules near the cavities. Most of the hydroxyls associated with the octahedral sheet of hectorite point toward the interlayer and are normal to the ab plane. However, when situated near the lithium site, the hydroxyls are angled slightly upward. X-ray diffraction analysis of the energy-optimized structure of hectorite produces a d-spacing of 12.57 Å for the (001) basal reflection.

A molecular dynamics simulation at 298 K and 1 bar pressure (NPT ensemble; constant number of atoms, pressure, and temperature) was performed on hectorite starting with the energy-minimized structure and allowing all atoms to move according to the forcefield derivatives. The duration of the simulation was 30 psec using a time step of 0.5 fsec; the structure equilibrates within the first 10 psec of simulation time. Note that due to the nature of the forcefield parameters in describing hydrogen and the hydroxyl bonds in clay minerals, it is often necessary to decrease the time step of a molecular dynamics simulation to fairly short times (less than 1 fsec) in order to ensure stability of the fully-relaxed calculation with no constraints. Alternatively, all or part of the geometry of the water molecules can be constrained using the RATTLE algorithm (Anderson, 1983) to allow the use of larger time steps (up to 4 fsec). The dynamics simulation provides a mean basal d-spacing of 11.99 Å for the equilibrated Na-hectorite. The shortening of this d-spacing is related to the slight collapse of the interlayer as the waters conform about the sodium ions and siloxane surfaces to form a monohydrate structure. The theoretical d-spacing values for 18 interlayer water molecules (0.106 g H_2O/g clay) are in fairly good agreement with those experimentally observed by Chipera, Carey, and Bish. (unpublished data) for two sodium-exchanged smectites (11.28 Å for SWy at 0.074 g H_2O/g clay and 12.55 Å for SAz at 0.149 g H_2O/g clay). Similar molecular dynamics simulations of interlayer calcium ion and europium ion in the interlayer of hectorite produced expanded basal d-spacings of 14.18 Å and 13.96 Å., respectively, for water contents of 0.136 g H_2O/g clay. These values are consistent with the increase of ionic size and charge effects expected for these ions (Brindley and Brown, 1980; Sato *et al.*, 1992).

Most of the recent work in developing forcefields for clay minerals and in simulating the bulk structures of clays has been geared toward validation. In order to have predictive capability, these simulation tools and forcefields must be proven worthy in accurately reproducing the structure and physical properties of simple clay systems. The above examples provide some of this validation and proof for extending the use of the simulation tools to more sophisticated applications. In particular, there is a great need with regard to environmental licensing and protection concerns to understand mechanisms of radionuclide (Cygan *et al.*, 1998) and organic compound (Johnston, 1996) sorption on clay minerals. An example of the latter is given by Teppen *et al.* (1997) in their molecular dynamics simulation of the sorption of hexadecyltrimethylammonium ion (HDTMA$^+$) in the interlayer of the dioctahedral clay beidellite.

Surface Structures

Although details of the sorption and exchange of metal cations within the interlayer of clay minerals has been a main thrust of clay mineralogy research for many years and is well documented (*e.g.*, Brindley and Brown, 1980; Sposito, 1984, 1989), there is significantly less known about the mechanisms of metal sorption on external surfaces. Jenne (1998) includes a recent review of the status of this research area and how experimental techniques are being developed to distinguish between interlayer and surface sorption. Appropriately, empirically-based molecular modeling methods recently have been used to provide an atomistic description of metal sorption on these surfaces (Purton *et al.*, 1997; Cygan *et al.*, 1998). Molecular orbital

calculations of mineral surfaces, however, have been limited to relatively simple mineral oxides and sulfides (Tossell, 1995).

The contribution of external clay mineral surfaces to sorption relies significantly on the number and type edge sites with broken bonds that are exposed to solution. The reactivity of these sites is controlled by the local crystal structure and any isomorphic substitutions among the sites. Other external surfaces of clays such as the siloxane basal (001) surface are considered hydrophobic and have low sorption affinity, unless significant isomorphic substitutions are present to increase the local negative charge. The isomorphic substitutions may occur in either the octahedral sheet (*e.g.*, Mg^{2+} for Al^{3+}) or the tetrahedral sheet (usually Al^{3+} for Si^{4+}) and are common in most illite and smectite clays. Additionally, the external surfaces of natural clays in soils and subsurface environments are often coated with organic material that will affect sorption properties.

The nature of broken edge sites in clay minerals is primarily controlled by the equilibrium established between the silanol and aluminol groups of the clay and the aqueous solution that they are exposed to. Water molecules will react with the broken edge sites to quickly establish an equilibrium that is dependent on the pH of the solution and the point of zero charge (PZC) of the clay (Sposito, 1984; Stumm, 1992). At pH values below the PZC, the silicon and aluminum edge sites develop a positive charge due to the surplus of adsorbed protons. Anions can be readily sorbed from solution under these conditions. As the pH increases, protons will begin to desorb and reduce the anion sorption capacity of the clay surface until the PZC is attained, beyond which the surface will become negative and begin to adsorb cations. Surface titration experiments on kaolinite (Brady *et al.*, 1996) have determined that the PZC at 25ºC is approximately 4 and that complete deprotonation of the edge aluminols occurs at a pH value of 5.3. The silanol groups are not fully deprotonated until the pH exceeds a value of 8.3. Metal cation sorption will therefore be most enhanced at the highest pH values. The cation exchange capacity for kaolinite is controlled exclusively by this process due the lack of isomorphic substitution and interlayer sites (Brady *et al.*, 1996, 1998). The crystal structure of kaolinite showing the edge aluminols and silanols for a (010) surface at pH4 and 25ºC is presented in Figure 6.

Particle size and shape will strongly control the overall cation exchange capacity of kaolinite. Because the neutral siloxane surface has negligible sorption capacity, the edges associated with the (100), (010), and (110) growth surfaces will control most of the sorption. Additionally, as particle size decreases, the contribution of these sorption sites becomes increasingly important. A recent atomic force microscopy (AFM) examination of kaolinite (Nagy, 1995) has shown that the edges of kaolinite particles can contribute up to 50% of the total surface area of the mineral. The relative edge surface area of kaolinite is substantial in comparison to the edges of illites and smectites that make up only about 10% of the total surface area (Jenne, 1998). An electrostatic potential calculation for the basal (001) aluminol surface of kaolinite indicates much less sorption capacity than the edge surfaces (see below).

An atomistic description of the external clay surface requires some approximation in order for the complex features of natural clays to be amenable to molecular modeling methods. The

cleavage of a crystalline material to create a surface will result in the relaxation of surface atoms in response to losing half of their coordination. The cleaved surface must also be void of dipoles in order to remain stable and, therefore, electronic polarization plays a significant role in the relaxation of the surface atoms to stabilize the crystal face (Tasker, 1979). Empirically-based molecular modeling programs such as MARVIN (Gay and Rohl, 1994) are available to examine surfaces and growth morphologies. However, these models have been successfully applied only to simple halides and oxides; attempts at modeling the relaxation of clay mineral surfaces have been less favorable. A recent study by Bleam *et al.* (1993) included the development of a structural model for various surfaces of pyrophyllite in order to map out the electrostatic and crystal-chemical control for water sorption. Although this study examined only the Coulombic energy and limited structural relaxation, their results suggest a cleavage stabilization of the (010) and (110) surfaces relative to the (100) and (130) surfaces. The addition of protons and oxygens to each surface indicates an additional stabilization preferred by the (110) surface.

The difficulty in modeling the surface structure of clays ultimately lies in the lack of appropriate forcefield parameters that account for electronic polarization. Of course, in applying a bonded forcefield to the simulation of a surface, there is no guarantee that the parameters derived from normal bonding environments in the bulk solid are transferable to the lower coordination sites on surfaces. In these cases, the forcefields may require derivation directly from accurate molecular orbital methods. Nonetheless, molecular models can be developed that treat the surface as a rigid or fixed substrate for sorption. The pH-dependence of the surface structure can be treated by constructing molecular cluster or periodic cell models of the clay mineral with the appropriate protonation state for the aluminol and silanol edge sites based on experimental data. All heavy atoms of the structure can be fixed while allowing the surface hydrogens (or internal hydrogens) to freely translate and relax during an energy minimization or molecular dynamics simulation. The surface hydrogens will behave differently for simulations of a surface exposed to vacuum compared to one exposed to solution (water molecules with or without ions). These and other methods that treat ionic sorption on mineral surfaces are discussed in more detail in the next section.

ATOMISTIC MODELS OF METAL SORPTION ON CLAYS

Molecular Electrostatic Potential Surface of Kaolinite

A molecular electrostatic potential model of kaolinite was used by Brady *et al.* (1996) to evaluate the crystallographic control of surface charge and metal sorption. A molecular cluster model of kaolinite comprised of approximately ten unit cells was constructed based on the refinement structure of Bish (1993). The molecule was created with dangling oxygen bonds on the (100) and (010) surfaces that were subsequently protonated to simulate a pH value just above the PZC for kaolinite. The (001) surfaces were terminated below the basal oxygens of the siloxane sheet and above the basal aluminols of the interlayer. Atomic charges were assigned using those obtained by a Mulliken analysis and periodic Hartree-Fock calculations of kaolinite by Hess and Saunders (1992). Silicon has a charge of 2.5, aluminum 2.1, oxygen -1.2, and hydrogen 0.56. The partial charge for the edge protons is assumed to be identical to that of the inner and basal hydrogens.

All hydrogen positions were energy-optimized using the Discover energy program and the CVFF forcefield while constraining the heavy atomic positions to those determined by Bish (1993). The resulting molecular structure was then used for the MEP surface calculation based on Equation (4) (Figure 7). The results of the MEP calculation indicate a significantly greater electrostatic potential on the edge surfaces than on the aluminol basal surface. This difference is related to the sheet structure of kaolinite and the effective screening of charge by the basal aluminols. The MEP surfaces for the (010) and (100) faces exhibit the most negative potential at the aluminum octahedral layer between two of the upper protonated oxygens. This suggests a stronger Lewis base behavior of these aluminols relative to the basal aluminol sites. Silanol sites associated with the siloxane sheet in the center of the molecule exhibit a more positive potential than that observed for the aluminols. The differences in electrostatic potential exhibited in the MEP surface emphasize the relative propensity of the different kaolinite surfaces and surface sites for subsequent reaction with a solution cation or positively charged complex. Asymmetries in the MEP surface are related to crystallographic differences among the cleavage surfaces and to edge effects of the molecular cluster. A necessary refinement of this calculation would be the incorporation of long-range electrostatics based on a periodic crystal.

Surface Energy Maps for Metal Sorption

A significant extension of the MEP calculation is the inclusion of short range repulsion and van der Waals energies to obtain the total energy for a particular surface region and sorption site. This method employs the calculation scheme of Pattabiraman *et al.*, (1985) to generate a large docking grid about the mineral surface based on the nonbonded energy. It was originally designed for interactively manipulating molecules for locating optimum docking sites in drug development, but has been applied successfully to the sorption of metals onto molecular cluster representations of clay surfaces. The procedure involves decoupling the energy terms for the substrate and metal by using a forcefield in which the nonbonded A_{ij} and B_{ij} parameters of Equation (1) are calculated as the geometric mean of individual atomic values (*i.e.*, $A_{ij} = (A_i A_j)^{1/2}$ and $B_{ij} = (B_i B_j)^{1/2}$). Equation (1) can then be rewritten as:

$$E_{nonbond} = \sum_{j} q_j \sum_{i} q_i / r_{ij} + \sum_{j} \sqrt{A_j} \sum_{i} \sqrt{A_i} / r_{ij}^{12} - \sum_{j} \sqrt{B_j} \sum_{i} \sqrt{B_i} / r_{ij}^{6} \qquad (5)$$

The docking grid is based on calculating the second summation of each term (i sums for the substrate) for each point on a finely-spaced (usually less than 1 Å) three dimensional grid that encloses the substrate molecule. The resulting energy values are independent of the sorbing species (or metal cation) and represent the relative energy values for the interaction with a fictitious point charge. In this formalism, a negative energy value denotes a site favorable for cation sorption whereas a positive value represents a site for anion sorption. Large molecular clusters that may include several hundred atoms to represent a particular surface may require tens of thousands of grid points to be evaluated.

Sorption map calculations for kaolinite were performed on a molecular cluster comprised of 450 atoms (ten unit cells) using the CVFF forcefield and the Discover energy program. The cleavage surfaces were first protonated to represent conditions for pH values of 4, 8, and 10, and then the hydrogens were allowed to energy minimize for each structure as done similarly in the previous MEP calculation on kaolinite. The resulting sorption maps are presented in Figure 8 where the most negative energy contour is plotted for each of the three kaolinite clusters. Note that the contours are concentrated for all three calculations to the front left side of the (100) surface, which corresponds to an exposed edge for the triclinic shape of the molecular cluster. This optimum binding region for cations is controlled by a number of crystallographic features including the type of cleavage surface, the octahedral vacancy, and the protonation state of the surface oxygens. No significant sorption sites exist on the basal (001) surfaces. The contour for pH 4 extends from the lower aluminol sites, across the interlayer, to the upper aluminol sites and the upper edge of the cluster. The width of the contour is restricted to the region between the optimized hydrogens on the silanol and aluminol sites. The results for the intermediate pH show a low energy contour that crosses the interlayer and includes the lower aluminol site and upper silanol site. The aluminol site broadens now that the aluminol protons are no longer present. The contour for the high pH sorption map occurs entirely in the interlayer region where the upper layer silanols are deprotonated. The minimum energy values for each contour map show a steady increase in relative sorption energy as the pH increases and the cluster surface charge becomes more negative.

Energy grids were calculated for an illite molecular cluster using an idealized structure of paragonite ($NaAl_2(Si_3Al)O_{10}(OH)_2$) as a proxy. Isomorphic substitution of aluminum on the silicon sheet was performed randomly to maintain aluminum avoidance. Surfaces were protonated for pH values of 6, 8, and 10 and atomic charges assigned using the same values as those used in the MEP and sorption map calculations for kaolinite; the interlayer sodium ions were assigned their full formal charge. Each illite model was comprised of approximately 660 atoms (twelve unit cells); hydrogen positions were optimized prior to the energy grid calculation. Approximately 60,000 points at a resolution of 0.67 Å were used in the calculation of each energy grid.

Figure 9 presents two energy slices determined from the energy grid calculation for the illite cluster that represents the lowest pH condition. The sorption maps are keyed to an energy spectrum that highlights the optimum positions for metal sorption. The (010) view of the sorption map indicates the lowest energy regions are associated with the deprotonated and negatively-charged aluminols. There is another favorable region for metal sorption that occurs in the interlayer near an isomorphic aluminum substitution in the lower layer. Sodium ions occupying the external basal surfaces of the cluster are characterized by the most positive energy values. The mid-cluster slice on the right side of Figure 9 compares the relative sorption energies for two different (010) cleavage positions. As before, the deprotonated aluminols and interlayer control the optimum binding sites. However, the rightmost energy surface exhibits an increase or destabilization of the energy related to the structural hydrogens and the greater distance to the octahedral vacancies. These results underscore the need to identify the most stable cleavage position within the structure for a particular surface, as in this example the sorption properties may vary considerably. Note that it is necessary to relate the sorption maps to the energy parameters of the sorbing metal. The minimum energy positions will shift depending on the size of the metal ion. The lowest energy contours for the sorption maps obtained for the three illite clusters are presented in Figure 10. Optimum sites for metal sorption occur mostly on the (010) surfaces. The intermediate pH results indicate a shift of this region to the rightmost (010) surface as the tetrahedral aluminols are deprotonated. The silanols are deprotonated at the highest pH and allow for the opposing aluminums in the tetrahedral sheets to control the optimum sorption site at the interlayer. The relative energy values decrease with increasing pH and the corresponding increase in negative surface charge.

Molecular Models for Metal Sorption

The specific interactions of a metal cation with a clay surface have recently been modeled using energy minimization and molecular dynamics methods (Cygan *et al.*, 1998). Cesium sorption onto the basal (001) and edge (010) surfaces of kaolinite at a pH value of 4 was simulated in order to identify the mechanisms of sorption relating to radioactive waste (^{135}Cs and ^{137}Cs) issues. Calculations were performed on molecular cluster models of kaolinite, a 570 atom three layer structure for the (010) surface and a 450 atom two layer structure for the basal surface (Figure 11). The heavy atom positions of the kaolinite were kept fixed for all simulations, while the structural and surface hydrogens were allowed to freely translate. The Discover energy code and the CVFF forcefield were used to perform the energy calculations. Energy parameters from Smith and Dang (1994) for the cesium-oxygen interactions supplemented the CVFF parameters. A pre-equilibrated cesium complex comprised of the metal ion with 26 water molecules (seven water molecules occur in the first hydration sphere) was allowed to energy minimize with each of the surface models. Molecular dynamics simulations were then performed at 300 K (NVT ensemble; constant number of atoms, volume, and temperature) using a one fsec time step for simulation times up to 50 psec. Typically, the cesium ion and water molecules equilibrated with the kaolinite substrate within 10 to 15 psec.

Figure 11 presents snapshots of the equilibrium configurations for each surface. The results indicate that cesium is preferentially sorbed at the aluminol edge sites of the (010) surface as an inner sphere complex. The cesium ion is coordinated by four aluminol oxygens with mean Cs-O

distances of 2.58 Å and 4.21 Å. In contrast, the simulation for the basal (001) aluminol surface of kaolinite indicates that cesium is less strongly bound and remains as an outer sphere complex. The charge distribution of the basal surface is significantly spread out in the octahedral sheet such that the cesium ion is unable to overcome the relatively stronger hydration bonds of the metal-water complex. Note that the simulations exhibit the equilibrated water molecules spread evenly (except where perturbed by the cesium ion) across each surface, and having the dipoles positioned with the hydrogens toward the surface. The simulation results are in agreement with the MEP and sorption map calculations and emphasize the contribution of the electrostatics term in controlling metal sorption. The molecular models are strongly supported by recent sorption isotherm experiments (Brady *et al.*, 1998) and are consistent with the results of surface charge and AFM observations for the significant role of edge sites for sorption (Brady *et al.*, 1996). Additionally, the simulation results are consistent with recent NMR spectroscopic analyses of Cs sorption (Kim *et al.*, 1996a, 1996b), and provide a mechanistic model for further NMR interpretations.

A refinement of the molecular cluster calculation for metal sorption is the use of periodic boundary conditions to better simulate the behavior of water on the clay surface. This approach removes the artifacts arising from high-energy edges and corners in cluster representations of surfaces. Of course, the influence of edge effects can be reduced by creating larger surface structures, but the computational cost becomes prohibitive. Alternatively, a smaller representation of a surface can be created by incorporating a void space within the bulk structure while using periodic boundary conditions. As long as the void space is reasonably thick (greater than approximately 10 Å), the opposing periodic surface will not influence the mechanism of metal sorption. This procedure was followed in the molecular dynamics analysis of sodium ion sorption on the (010) surface of kaolinite for a pH value of 4. A supercell of kaolinite with a 13 Å void space was created and then filled with bulk water molecules. The sodium ion was introduced and allowed to energy minimize with the bulk water and then minimized collectively with the kaolinite (010) surface; heavy atoms were kept fixed. This was followed by a molecular dynamics simulation at 298 K and 1 bar (periodic NVT ensemble) for a duration of 30 psec using 0.5 fsec time steps. The system equilibrated within 7 psec and is presented in Figure 12 along with the trajectory (blue line) of the sodium ion. The bulk water molecules equilibrated with their hydrogens pointing toward the appropriate surface; local perturbations of several far-field waters by the opposing surface (positive aluminum) also occur but are ignored. In comparison to the cesium simulations, the smaller sodium ion ultimately equilibrates at the interlayer edge site as an inner sphere complex and is coordinated by two aluminols and two silanols. However, there is a transient period of stabilization that occurs as the sodium is fully coordinated by six bulk waters as an outer sphere complex. Cesium sorption behavior on kaolinite as depicted in the cluster models of Figure 11 was likewise simulated using molecular dynamics calculations with periodic boundary conditions.

Conventional sorption theory assumes that the small sodium ion remains as an outer sphere complex due to the large hydration energies needed to be overcome by the clay surface. The above simulation shows this is a short-lived situation before the sodium ion converts to an inner sphere complex. In contrast, the larger cesium ion is characterized by a smaller hydration energy and will tend to form inner sphere complexes, as simulated for the (010) kaolinite surface.

Energy minimization calculations performed on the basal (001) surfaces of large cluster models of illite (Cygan, unpublished data) support the conventional model with sodium ion occurring as an outer sphere complex and cesium ion as an inner sphere sorption complex. However, calculations completed for sorption on the edge surfaces of illite suggest both ions occur as inner sphere complexes near the interlayer edge. The illite calculations were based on a pH value of 6 when the octahedral aluminol sites of the illite cluster are deprotonated.

Refinements in the molecular models of metal sorption on clays would necessarily include a better representation of the solution phase than that presented above. Counter ions have been excluded in these simulations and, if present, would modify the electrostatics of the near-field region of the clay-water interface. Similarly, the sorption calculations were performed for a single metal ion on a finite-sized substrate (cluster and periodic models), and one would expect competition for the lowest-energy sites by increasing the number of ions or adding different metal ions to the system. The incorporation of fully-relaxed surface structures (prior to and during the simulation) would also be a significant refinement. Finally, it is important that electronic polarization be properly incorporated into the sorption models, especially for the oxygens and large polarizable metal ions such as cesium. This can be accomplished through using either a point-polarizable ion or a core-shell representation of the ion. The latter method requires extremely short time steps or iterative energy minimizations for each time step for molecular dynamics, both prohibitively costly procedures.

SUMMARY

The fate of radionuclides and other hazardous metals in surface waters and groundwater environments largely depends on the ability of clay minerals to sorb and retard the contaminants. Although recent developments in X-ray absorption and NMR spectroscopies are providing sophisticated tools for determining the structure of clay-solution interfaces and the configuration of sorbed species, there are no direct means for evaluating the mechanisms and dynamics of the sorption process. Molecular modeling, however, provides a convenient theoretical tool that complements these experimental methods and allows for the detailed analysis of a large number of complex atomic interactions.

Due to their complex compositions and large unit cell size, most clay minerals are beyond the limits of calculation using quantum mechanical and molecular orbital methods. Empirical forcefield methods, however, provide a means of simulating large and compositionally-complex chemical systems. The accuracy of the forcefield method will rely on the quality of the experimental or molecular orbital data used to derive the energy parameters. Bonded and nonbonded forcefields are available for simulating the bulk structures of clay minerals, but may require further refinement for the analysis of metal and organic sorption processes. Metal sorption onto clay surfaces is dominated by the long-range electrostatic energy; the short-range repulsive and attractive van der Waals energies control the fine-scale structure at the sorption site. The inclusion of an electronic polarization term in the forcefield would be a significant improvement in the simulation. Energy minimization calculations of molecular clusters and periodic assemblies provide optimum configurations for the interacting atoms. Monte Carlo and molecular dynamics methods are useful in refining the configurations and exploring other favorable conformations. The molecular dynamics approach allows for the incorporation of thermal effects and the analysis of transient processes such as atomic diffusion.

Electrostatic potential maps of molecular clusters can be used to identify likely sorption sites on the external clay surfaces. Energy grids or sorption maps further refine this approach by including all nonbonded energy terms. The influence of the bulk crystal structure, cleavage position, surface protonation state, isomorphic substitutions, and vacancies on the mechanism of metal sorption can be assessed. The interaction of specific metal ions with different clay surfaces can be explicitly modeled using a combined energy minimization and molecular dynamics approach. The simulations provide a useful method of identifying surface sorption sites and discriminating between inner and outer sphere sorption complexes.

It is very important to emphasize that molecular modeling should not be treated as a "black box", nor as an isolated computational exercise. Numerous simulations must be run to test and sample all possible atomic arrangements. Sensitivity analysis of the various energy parameters will help to determine the appropriateness of a forcefield. Validation and verification of the atomistic models with accurate experimental data is critical and helps to set limits on the application of the simulations. The power of using these theoretical methods in clay mineralogy and geochemical research lies in their ability to evaluate the energies of atom-atom interactions, to provide a visual probe of atomic level processes, and to develop new insights on clay reactivity by performing "what if" theoretical experiments. Ultimately, the molecular models may be used to predict the

reactivity of candidate clay phases that may not be amenable to experimental techniques, or for that matter, clay phases that do not exist naturally and yet once synthesized may provide the solution to an important industrial or environmental problem.

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TABLE 1
Functional forms for several interatomic potentials

Bonded Terms

Bond stretch (simple harmonic) $E = k_2(r - r_o)^2$

Bond stretch (quartic) $E = k_2(r - r_o)^2 + k_3(r - r_o)^3 + k_4(r - r_o)^4$

Bond stretch (Morse) $E = D\{[1 - \exp(-\alpha(r - r_o)^2)]^2 - 1\}$

Angle bend (three body) $E = k_2(\theta - \theta_o)^2$

Torsion (four body) $E = k(1 + \cos(n\phi - \phi_o))$

Out-of-plane stretch (four body) $E = k(1 + \cos(n\chi - \chi_o))$

Nonbonded Terms

Electrostatic $E = q_i q_j / r$

Lennard-Jones $E = Ar^{-m} - Br^{-n}$

Born-Mayer $E = A\exp(-r/\rho)$

Buckingham $E = A\exp(-r/\rho) - Cr^{-6}$

FIGURE CAPTIONS

Figure 1. Graphic representation of the atomic interactions associated with a bonded energy forcefield. The nonbonded contribution includes electrostatic and short-range interactions.

Figure 2. Schematic representation of a rigid ion or point charge model (top) and a polarizable ion model (bottom). E_{polar} is the polarization energy where k is a spring constant and x is the displacement of the shell from the core.

Figure 3. Schematic plot of the repulsive short range and attractive van der Waals energy contributions, and the total energy contributions for a two atom system based on a nonbonded model. The equilibrium bond distance is determined by the minimum in the total energy function.

Figure 4. Comparison of the experimentally observed structure for kaolinite (top) with an ionic shell model (middle) and a bonded model (bottom).

Figure 5. Fully-optimized constant pressure structure for hectorite based on a nonbonded model. A supercell comprised of eight formula units of $Na_x(Mg_{0.88}Li_{0.12})_3Si_4O_{10}(OH)_2 \cdot nH_2O$ was allowed to energy minimize with three interlayer sodium ions and eighteen water molecules.

Figure 6. Kaolinite structure based on the refinement of Bish (1993) modified to include the surface protonation of a (010) cleavage surface expected at pH 4. The nomenclature used to identify the various hydrogens is noted. The kaolinite unit cell is indicated by the gray outline.

Figure 7. Molecular electrostatic potential surface (right) and corresponding molecular cluster (left) for a hydrated kaolinite at pH 4 based on ten unit cells as modified from Brady *et al.* (1996). Oblique view is approximately normal to the (010) surface. The kaolinite (001) basal surface with the gibbsite sheet is on top and the silica sheet on the bottom.

Figure 8. Sorption map for a kaolinite molecular cluster indicating the most-negative energy contour surfaces for metal sorption. The kaolinite structure for each pH is determined by the protonation scheme for the exposed aluminols and silanols followed by an energy minimization of the hydrogens. The outline for each cluster represents the limit of the grid used in the calculation.

Figure 9. Sorption map for an illite cluster (twelve unit cells) at pH 6 as represented by a surface plane located at 1.2 Å above the silanol hydrogens of the (010) surface (left), and at a mid-structure cross-section sub-parallel to the (100) surface (right). The sorption maps are transparent to provide a partial view of the hidden illite structure where the aluminum atoms substituting for tetrahedral silicon are highlighted by a sphere. The yellow outlines represent the limit of the grid used in the calculation; the grid outline is viewed at an oblique angle in the image on the right.

Figure 10. Sorption map for an illite molecular cluster (twelve unit cells) indicating the most-negative energy contour surfaces for metal sorption. The illite structure for each pH is determined by the protonation scheme for the exposed aluminols and silanols followed by an energy minimization of the hydrogens. Aluminum atoms substituting for tetrahedral silicon are denoted by a sphere. The outline for each cluster represents the limit of the docking grid used in the calculation.

Figure 11. Snapshots from molecular dynamics simulations of the sorption of cesium ion onto the (010) surface (left) and (001) surface (right) of kaolinite molecular clusters for pH 4 as modified from Cygan *et al.* (1998). The images represent the equilibrated configurations based on a fixed kaolinite substrate where only the hydrogen positions are allowed to freely translate.

Figure 12. Snapshot from a molecular dynamics simulation of the sorption of sodium ion onto the protonated (010) surface of kaolinite under periodic boundary conditions (NVT ensemble) for pH 4. The irregular line represents the partial trajectory of the sodium ion starting from its initial position in the fluid to the sorbed position denoted by the cross at the interlayer after 10 psec of simulation. Note the temporary stabilization of the sodium ion as an outer sphere complex halfway through the trajectory.