

# MOLECULAR DYNAMICS SIMULATION OF LAYERED DOUBLE HYDROXIDES

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## *Abstract*

The interlayer structure and the dynamics of  $\text{Cl}^-$  ions and  $\text{H}_2\text{O}$  molecules in the interlayer space of two typical LDH phases were investigated by molecular dynamics computer simulations. The simulations of hydrocalumite,  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ , reveal significant dynamic disorder in the orientation of interlayer water molecules. The hydration energy of hydrotalcite,  $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$ , is found to have a minimum at approximately  $n = 2$ , in good agreement with experiment. The calculated diffusion coefficient of  $\text{Cl}^-$  as an outer-sphere surface complex is almost three times that of inner-sphere  $\text{Cl}^-$ , but is still about an order of magnitude less than that of  $\text{Cl}^-$  in bulk solution. The simulations demonstrate the unique capabilities of combined NMR and MD studies to understand the structure and dynamics of surface and interlayer species in mineral/water systems.

## *Keywords*

Molecular dynamics, Layered double hydroxides, Interlayer structure, Hydrocalumite, Hydrotalcite.

## **Introduction**

Layered double hydroxides (LDHs), also called “anionic clays”, are among the few oxide-based materials with permanent anion exchange capacity. They occur in natural environments, are readily synthesized, and are receiving rapidly increasing attention from a wide variety of applications as materials for catalysis, environmental remediation, and medicine (Cavani et al., 1991; Ulibarri et al., 1995). LDHs have a layered structure based on that of  $\text{Mg}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$ . Isomorphous substitution of +3 cations (often Al) for +2 cations (often Mg or Ca) in the main hydroxide layer results in a permanent positive charge which is compensated by interlayer anions, often associated with water molecules.

For most LDHs, the arrangement of interlayer species is not understood well and is difficult to probe experimentally. Anions and water molecules strongly associate with particle surfaces, and some adsorbed  $\text{H}_2\text{O}$  is

indistinguishable from interlayer water in thermal analysis. Molecular dynamics (MD) computer simulations can give significant new insight into the local structure and dynamical behavior of this class of compounds. We performed MD simulations of two typical LDHs – hydrocalumite,  $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ , and hydrotalcite,  $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$ , with major emphasis on the interlayer structure and the dynamical behavior of the interlayer and surface species for the time scale from  $10^{-15}$  to  $10^{-10}$  sec. Hydrocalumite is well ordered and is the only LDH for which a single crystal structure refinement is available (Terzis, et al., 1987). Thus, it is currently the best model compound for understanding the structure and dynamical behavior of surface and interlayer species in LDHs. Such understanding is essential for full exploitation of the unique anion exchange capabilities of this important class of compounds.

## Molecular Dynamics Simulations

In many computer simulations of layered materials, the atoms of the main oxide layers are often treated as fixed in a rigid lattice, except for the degrees of freedom associated with swelling and lateral displacements of the lattice as a whole. This approach is computationally efficient at providing useful structural information, but it has inherent limitations for dynamic modeling of surface and interlayer species. Due to the immobility of the lattice atoms, there is no exchange of momentum and energy between the atoms of the main layers and the interlayer/surface species. Thus, in these models the imposed momentum and energy conservation laws *a priori* prevent accurate representation of the dynamics of such processes as hydrogen bonding, adsorption, and surface complexation. Surface diffusion rates can be overestimated, and the structure of the water layers at the interface can be distorted.

In our simulations (Kalinichev et al., 2000; Wang et al., 2000), all atoms were treated as completely movable. Except for the 3-dimensional periodic boundary conditions (e.g., Allen and Tildesley, 1987) imposed on the simulation supercell, there were no additional symmetry constraints. All structures were treated as triclinic, and all cell parameters,  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$  were considered independent variables during the isothermal-isobaric MD simulations.

The initial hydrocalumite structure was based on the single crystal refinement results (Terzis et al., 1987), and the simulation supercell contained  $2 \times 2 \times 1$  crystallographic unit cells in the  $a$ -,  $b$ - and  $c$ - directions, respectively. Simulations were performed for bulk crystals at temperatures between  $-100$  and  $500^\circ\text{C}$ , for dehydrated crystals at  $100^\circ\text{C}$ , and for the interface of hydrocalumite with bulk liquid water at  $25^\circ\text{C}$ . In the latter case the model crystal was initially cleaved in the interlayer along the (001) crystallographic plane; half of the  $\text{Cl}^-$  anions were left on each of the created surfaces, and the simulated periodic system consisted of 4 hydroxide layers (infinite in the  $a$  and  $b$  directions) interspersed in the  $c$  direction with a layer of water approximately  $20 \text{ \AA}$  thick (Fig.1).

The structural models of Mg/Al hydrotalcite were based on a crystal structure obtained by a refinement of powder X-ray diffraction data using Rietveld methods (Bellotto, 1996). The simulation supercells contained  $6 \times 3 \times 1$  crystallographic unit cells in the  $a$ -,  $b$ -, and  $c$ - directions, respectively. To study the swelling behavior of hydrotalcite upon hydration, each supercell contained three interlayers, consisting of 6  $\text{Cl}^-$  ions and from 0 to 40 water molecules (Wang et al., 2000).

Each atom in the system had an assigned partial charge, and the total potential energy of the simulated system consisted of a Coulombic term representing the sum of all electrostatic interactions between partial atomic charges and a Lennard-Jones (12-6) term modeling the short-range van-der-Waals dispersive interactions. The force field used in the simulations was modified from the

augmented ionic consistent valence (CVFF\_aug) force field (Molecular Simulations Inc., 1999), and methods for choosing the potential energy expressions and their specific parameterization are described elsewhere in detail (Cygan et al., 2000; Kalinichev et al., 2000). For water, the flexible version of the simple point charge (SPC) interaction potential was used (Teleman et al., 1987).

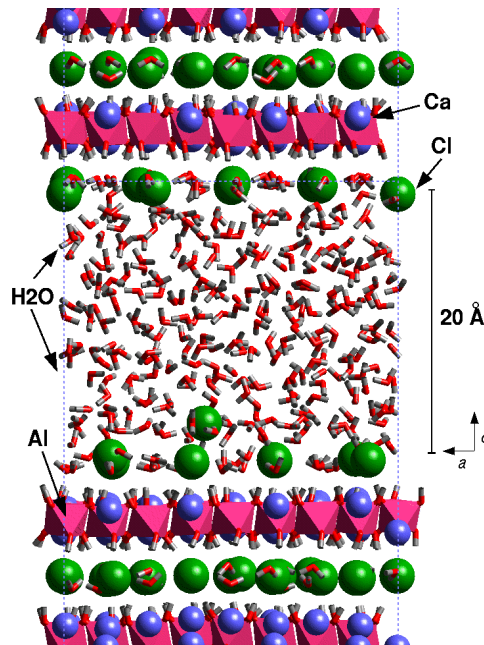


Figure 1. A snapshot of the simulation of hydrocalumite/water interface at  $25^\circ\text{C}$ .

## Results and Discussion

Although all atoms were treated as movable and the size and shape of the simulation cell were not constrained, the structural results demonstrate a remarkable ability of the modified force field to reproduce and preserve the structure and density of the simulated materials. For hydrocalumite, the monoclinic angle  $\beta$  and the density are about 2% smaller than in the X-ray results, but all other parameters at room temperature are well within 0.5% of their measured values (Terzis et al., 1987). Angles  $\alpha$  and  $\gamma$  remain within  $0.2^\circ$  of their nominal value of  $90^\circ$ .

For hydrotalcite,  $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot n\text{H}_2\text{O}$ , the computed crystallographic parameters and configurations of the hydroxide layers do not vary significantly with  $\text{H}_2\text{O}/\text{Cl}$  ratio,  $n$ , in the interlayer. The average  $a$ - and  $b$ -axis lengths remain around  $3.20 \pm 0.01 \text{ \AA}$ , the  $\gamma$  angle is  $120 \pm 0.5^\circ$ , and the  $\alpha$  and  $\beta$  angles fluctuate around  $90^\circ$ . Only the computed  $c$ -axis dimension increases with increasing  $n$  (see Fig. 3a below). The calculated crystallographic parameters compare well with the available experimental data:  $a=b=3.046 \text{ \AA}$ ,  $\alpha=\beta=90^\circ$ , and  $\gamma=120^\circ$  (Bellotto, 1996).

According to the X-ray data for hydrocalumite, the interlayer of composition  $[\text{Cl}\cdot 2\text{H}_2\text{O}]^-$  consists of a primitive hexagonal lattice, with  $\text{Cl}^-$  ions forming almost regular triangles of this lattice and water molecules located at the center of each triangle. The orientation of these water molecules is such that each  $\text{Cl}^-$  is coordinated by four H atoms forming ordered chains of hydrogen bonds along the  $a$  crystallographic direction. Each  $\text{Cl}^-$  anion is additionally coordinated by six OH groups (three from two adjacent hydroxide layers). In our simulations these hydrogen bonds prevent chloride diffusion even at temperatures as high as  $300^\circ\text{C}$ .

The 10-coordinate arrangement of H-bonds to  $\text{Cl}^-$  is well reproduced in our MD simulations. However, in contrast to the highly ordered orientations of the interlayer  $\text{H}_2\text{O}$  molecules interpreted from the X-ray diffraction measurements, the simulations reveal significant dynamic disorder in water orientations (Kalinichev et al., 2000). At all simulated temperatures, the interlayer water molecules undergo librations (hindered hopping rotations) around an axis essentially perpendicular to the layers. This results in breaking and reformation of hydrogen bonds with the neighboring  $\text{Cl}^-$  anions. At any instant each water molecule is hydrogen bonded to 2 chlorides, but because of the hopping among the three possible pairs of chlorides, it is, on average, hydrogen bonded to each one about  $2/3$  of the time. From the perspective of the  $\text{Cl}^-$  ion, this results in a time-averaged nearly uniaxial symmetry. Although at any instant there are four H-bonds to the neighboring water molecules, averaged over time there are six H-bonds with  $2/3$  occupancy.

The variable temperature  $^{35}\text{Cl}$  NMR experiments for hydrocalumite (Kirkpatrick et al., 1999) indicate the existence of a dynamical order-disorder phase transition near  $\sim 6^\circ\text{C}$ . Below the transition temperature, the  $\text{Cl}^-$  ion is rigidly held in a triaxial environment, whereas above this temperature, the  $\text{Cl}^-$  is in a dynamically averaged uniaxial environment. The frequency of the atomic motion causing the dynamical averaging which results in the phase transition, must be greater than  $\sim 10^5$  Hz. Thus, the librational frequencies for water of about  $10^{13}$  Hz determined from the present MD simulations are much more than sufficient to cause the dynamical averaging observed by NMR.

Power spectra of atomic motions in the translational, librational, and vibrational frequency ranges, calculated as Fourier transforms of the atomic velocity autocorrelation functions, allowed comprehensive and detailed analysis of the dynamics in this material. The spectral density of the low frequency vibrational motions of  $\text{Cl}^-$  ions in the interlayer consists of two distinct frequency bands centered at approximately  $50$  and  $150\text{ cm}^{-1}$  (Fig. 2). Decomposition of chloride velocities into components parallel and perpendicular to the interlayer plane indicates that the  $50\text{ cm}^{-1}$  band is associated with the “in-plane” motions of the anions, and the  $150\text{ cm}^{-1}$  band is associated with the

low frequency vibrations perpendicular to this plane. Because each chloride ion is H-bonded to neighboring  $\text{H}_2\text{O}$  molecules and OH-groups, these two  $\text{O}\cdots\text{Cl}\cdots\text{O}$  modes of molecular motions are clearly analogous to the intermolecular  $\text{O}\cdots\text{O}\cdots\text{O}$  bending and stretching motions of water molecules in the H-bonded network, respectively (e.g., Eisenberg and Kauzmann, 1969). Two weaker spectral peaks at  $\sim 110$  and  $\sim 190\text{ cm}^{-1}$  distinctly observable at lower temperatures (Fig. 2c) are merging with the  $150\text{ cm}^{-1}$  peak into one broad spectral band at higher temperatures (Fig. 2a-b). The intensity of the stretching peak is greatly reduced for  $\text{Cl}^-$  ions on the surface of hydrocalumite, where the shape of the  $\text{Cl}^-$  low frequency vibrational spectrum more closely resembles the spectrum in a bulk aqueous solution (Fig. 2b). In the collapsed, dehydrated hydrocalumite structure at high temperature, low frequency vibrations in the plane of the interlayer are the only possible chloride motions, as shown by the very intense peak at  $\sim 50\text{ cm}^{-1}$  in Fig. 2a.

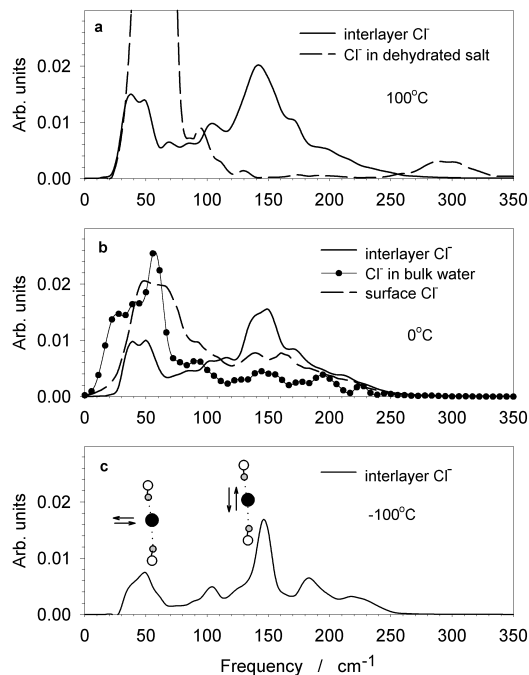


Figure 2. Spectral density of the interlayer  $\text{Cl}^-$  low frequency vibrational motions.

In the simulations of Mg/Al hydrocalumite, the computed  $c$ -axis dimension increases with increasing  $n$  (Fig. 3a), but there are three important ranges where it is almost independent of the degree of hydration. For  $n < 1$ , the  $c$ -axis lengths are about  $21.7\text{ \AA}$ . Near  $n = 2$  the  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  form a complete single layer in each interlayer region (similar to the interlayer of Ca/Al hydrocalumite, but significantly more disordered) and the computed  $c$ -axis dimension is  $23.9\text{ \AA}$ . This is in excellent agreement with the value of  $23.6\text{ \AA}$  obtained from X-ray diffraction for hydrated Mg/Al  $\text{Cl}^-$ -hydrocalumite under ambient conditions

(Boclair et al., 1999). Near  $n = 5$  a second layer of water molecules is formed in each interlayer space, and the simulations give a  $c$ -axis dimension of 31.8 Å. In reality, however, Mg/Al  $\text{Cl}^-$ -hydrotalcite does not expand beyond 23.9 Å at any relative humidity and atmospheric pressure, and this hydration state is not observed experimentally.

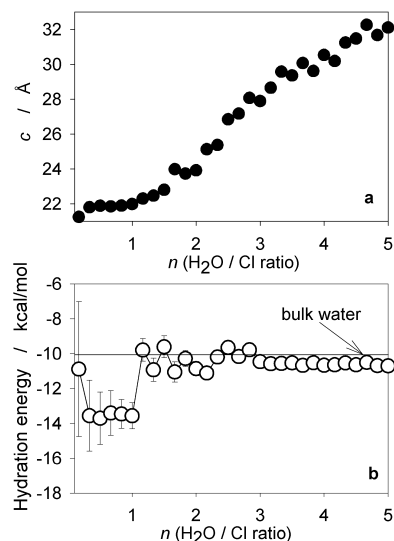


Figure 3. Hydrotalcite  $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$  swelling upon hydration. (a)  $c$ -axis dimension of hydrotalcite. (b) Hydration energy.

The energy of hydrotalcite hydration (Fig. 3b) was calculated as the average potential energy of the system per mole of water with dry hydrotalcite taken as a reference state. For  $n < 1$ , the hydration energy is quite negative, indicating a strong tendency for water molecules to enter the dry structure. At  $n \approx 2$ , there is a clear minimum of the hydration energy that corresponds to the region of  $n$ -independent  $c$ -axis dimensions (Fig. 3a). The computed hydration energies suggest that almost dry Mg/Al hydrotalcite with just a few interlayer water molecules and hydrotalcite with two water molecules per formula unit should be stable, and indeed the second composition,  $\text{Mg}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ , is readily observed in experiments (Boclair et al., 1999). Large negative values of the hydration energy at low  $n$  suggest a strong tendency of dry hydrotalcite to sorb water even at low relative humidities.

Diffusion coefficients of interlayer and surface species were calculated for hydrocalumite. On the space and time scale of the present simulations no statistically appreciable  $\text{Cl}^-$  diffusion is observed in the interlayer, which is experimentally known to be about  $10^{-8} \text{ cm}^2/\text{s}$  (Buenfeld and Zhang, 1998). However, the simulations show two distinct types of surface  $\text{Cl}^-$  with diffusion rates differing by a factor of  $\sim 3$ . The inner-sphere complex ( $D_{\text{is}} = 8.1 \times 10^{-7} \text{ cm}^2/\text{s}$ ) is strongly bonded directly to the OH groups of the hydroxide layer and is most common. The other type ( $D_{\text{os}} = 2.6 \times 10^{-7} \text{ cm}^2/\text{s}$ ) has one molecular layer of water

between the anion and surface hydroxides (outer-sphere surface complexing), making them much more mobile (see Fig. 1). These results are in good qualitative agreement with the  $^{35}\text{Cl}^-$  NMR data for hydrocalumite under controlled relative humidity conditions (Kirkpatrick et al., 1999). However, even the diffusion rates of the outer-sphere  $\text{Cl}^-$  are almost an order of magnitude smaller than those of  $\text{Cl}^-$  in bulk aqueous solution. The exchange of  $\text{Cl}^-$  between inner-sphere and outer-sphere environments is clearly observable on the 100 ps time scale of our simulations.

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