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## **EFFECTS OF ORGANICS ON THE ADSORPTION AND MOBILITY OF METAL CATIONS IN CLAY SYSTEMS: COMPUTATIONAL MOLECULAR MODELING APPROACH**

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### **Abstract**

Understanding and prediction of many natural and anthropogenic environmental processes ultimately depend on a fundamental understanding of the chemistry occurring at the mineral-fluid interfaces. Clay-related minerals and natural organic matter (NOM) are ubiquitous in the environment, and metal-NOM complexation induces strong correlations between the NOM concentration in water and the capacity of clay particles to bind metals, thus affecting their speciation, solubility and toxicity in the environment. Despite significant geochemical, environmental and technological interest, the molecular-level mechanisms and dynamics of the physical and chemical processes involving NOM are not yet well understood.

In this presentation we compare three different molecular dynamics (MD) computer simulations of metal-NOM complexation in aqueous solutions. The simulation results indicate that despite some obvious quantitative variations in the computed values depending on the size of the simulated system and on the parameters of the force field models used, all three simulations are quite robust and consistent. In particular, approximately 35-50% of Ca<sup>2+</sup> ions in all simulations are associated with the carboxylic groups of NOM at near-neutral pH. The stability of bidentate-coordinated contact ion pair complexes is also always strongly preferred.

Easy association of metal cations with negatively charged NOM functional groups and negatively charged clay surfaces allows us to predict that cationic bridging could be the most probable mechanism of NOM association with clays in natural environments. New MD simulations are currently in progress to quantitatively assess these predictions on a molecular scale for nuclear waste disposal applications. New larger-scale clay models incorporate a more realistic representation of the structural and compositional disorder of natural illites and smectites and employ CLAYFF – a fully flexible general force field suitable for the molecular simulations of hydrated mineral systems in the presence of organics.

### **Background and Motivation**

Callovo-Oxfordian (COx) clay formations contain significant amounts (up to 1.5 mass %) of total organic carbon, and the soluble fraction of these natural organic substances is a potential vector in the transport of radionuclides (Andra, 2010). Recent measurements in batch and diffusion experiments with actual COx samples have demonstrated that organic

acids are noticeably mobile, despite the observed significant degree of irreversible adsorption, even leading to a complete saturation of clay adsorption sites (Durce, 2010). These processes can also be strongly affected by the presence of  $\text{Ca}^{2+}$  ions (Durce, 2010). The molecular mechanisms of the adsorption and transport phenomena in such complex systems are not well understood yet, but this knowledge is essential for a reliable predictive modeling of radionuclide behavior in natural and engineered barriers of nuclear waste repositories over the time periods spanning many orders of magnitude from picoseconds to a million of years.

Computational molecular modeling is one of the most powerful tools to develop quantitative atomistic understanding of such complex systems and phenomena and to unravel fundamental molecular-scale correlations between the structural, thermodynamic, spectroscopic, and transport properties of materials (e.g., Cygan et al., 2009). However, there are several sources of uncertainty which can potentially limit the applicability of these powerful computational molecular modeling techniques to the systems involving natural organic matter (NOM) and clays. First of all, NOM itself is structurally and compositionally heterogeneous, with reported apparent molecular weights ranging orders of magnitude from several hundred to several hundred thousand Daltons. Whether NOM represents a true macromolecular chemical entity or is only a supramolecular aggregate of much smaller molecules held together by relatively weak non-covalent interactions is still under discussion, although the most recent experimental evidence tends to support the latter view (Sutton and Sposito, 2005). These compositional and structural uncertainties have limited generally applicable quantitative characterization of metal-NOM complexation in molecular-scale detail.

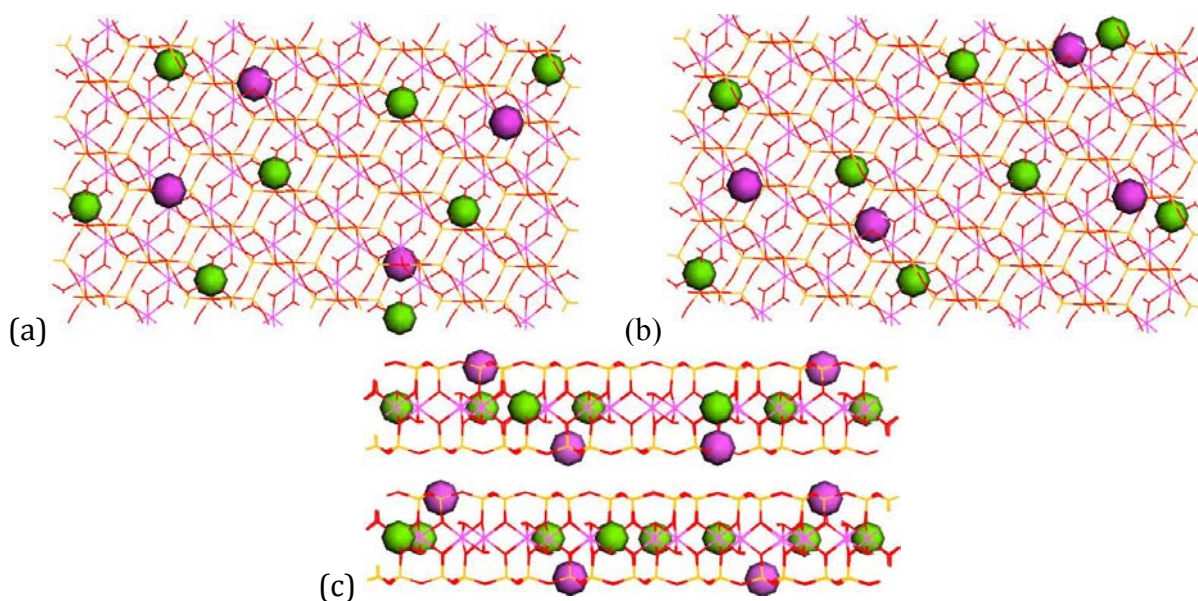
Compositional and structural heterogeneity of clays represent another source of uncertainties for molecular modeling (Cygan et al., 2004). Most common clay-related minerals are poorly crystalline and fine grained. In the absence of large single crystals suitable for X-ray refinement studies, detailed structural characterizations of these materials are usually lacking. Clay minerals typically possess low crystal symmetry and are characterized by a variety of multicomponent substitutions in the tetrahedral and octahedral sheets. These substitutions lead to a net negative charge on the clay structural layers that allows for the intercalation of solvated metal cations, and other charged complexes, within the interlayer region. However, the chemical diversity and structural disorder introduced by such site substitutions in clays makes their molecular modeling an especially challenging task.

Nevertheless, a significant progress has been achieved in recent years in the molecular modeling of cation-NOM interactions in aqueous solutions (Sutton et al., 2005; Xu et al., 2006; Kalinichev and Kirkpatrick, 2007; Iskrenova-Tchoukova et al., 2010; Kalinichev et al., 2011), as well as the molecular modeling of the structure and dynamics of ions and water molecules at clay surfaces and in its interlayers (Cygan et al., 2004; Marry et al., 2008; Rotenberg et al., 2010). However, the interaction of organic molecules with clay and other mineral surfaces has been studied only rarely (Shevchenko and Bailey, 1998; Perry et al., 2006; Sutton and Sposito, 2006; Kalinichev et al., 2010), and the focus is usually on the structure and properties of synthetic polymer-clay nanocomposites (e.g., Chen et al., 2008; Cygan et al., 2009; Fu and Heinz, 2010), rather than on natural clay-organic systems.

Therefore, we have recently launched a new research program of detailed quantitative studies of the energetic, structural, and dynamic aspects of different interaction mechanisms between metal cations (including radionuclides), organic molecules (including NOM), and clay particles (illite and smectite) using classical MD simulation methods. The free energies of adsorption and other thermodynamic and structural parameters obtained through these simulations will then be utilized to improve the predictive capabilities of the thermodynamic and geochemical models currently used for the performance assessment of nuclear waste repositories.

## Force Field Models and Preliminary Results

To describe all the interatomic interactions of the clay layers, we are using the CLAYFF force field (Cygan et al., 2004) which has already proven to provide very reliable molecular description of various layered mineral structures (e.g., Cygan et al., 2009; Kalinichev et al., 2010). It is specifically designed to treat a great variety of isomorphic substitutions in the tetrahedral as well as in the octahedral layers. However, the actual ordering in the location of these substitutions is often exaggerated in MD simulations due to the application of periodic boundary conditions to the simulated structure and due to the relatively small size of the simulated systems. Therefore, as a first step in the construction of our larger-scale clay models, we are taking special care to represent the structural and compositional disorder of illites and smectites as realistically as possible. For this purpose, we have developed a set of new clay models with different degrees of ordering in the tetrahedral and/or octahedral layers up to a fully random distribution of the substitutions in both clay layers (Fig. 1). These models are currently being used in the preliminary MD simulations and will allow us also to evaluate the dependence of the simulation results on the degree of tetrahedral and/or octahedral ordering for the same clay composition.



**Figure 1:** Random distribution of isomorphic substitutions in a new montmorillonite model. (a) and (b) are top and bottom layers viewed from the top along the  $z$  direction; (c) is the side view along the  $x$  axis. Al/Si substitutions in the tetrahedral layers are shown as pink balls, Mg/Al substitutions in the octahedral sheets are shown as green balls.

The choice of the force field parameters to describe the interactions with the organic part of the system is not so obvious, because many different force field parameterizations for (bio-)organic molecules are available in the literature. In order to test the severity of potential force field dependence of our MD modeling results, we ran a series of simulations with three different force fields for the same molecular model of NOM interacting with  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Cs}^+$  in aqueous solutions (Kalinichev et al., 2011). The TNB model of an NOM molecular fragment (Sein et al., 1999) was used in all simulations. It has a molecular weight of 753 Da and contains three carboxylic groups, three carbonyl groups, two phenolic groups, two amine

groups, and four other R-OH alcohol groups. In terms of the molecular weight, atomic composition, degree of aromaticity and total charge density the TNB model fragment is in good agreement with available experimental characterizations and theoretical considerations (e.g., Sutton and Sposito, 2005). The composition of the TNB model is also quite close to the composition of Suwannee River NOM (SRNOM), which is often used in experiments as a typical representative of natural organic matter (e.g., Xu et al., 2006; Ahn et al., 2008).

To quantitatively assess the structural and dynamic effects of metal-NOM complexation, we calculated the radial distribution functions (RDFs) and running coordination numbers using standard procedures (e.g., Allen and Tildesley, 1987). The running coordination numbers of species  $j$  around species  $i$  in the solution,  $n_{ij}(r)$ , are calculated from the RDFs as

$$n_{ij}(r) = 4\pi\rho_j \int_0^r g_{ij}(r) r^2 dr \quad (1)$$

where  $\rho_j$  is the number density of species  $j$  in the system,  $g_{ij}(r)$  are the atom-atom RDFs.

Potentials of mean force (PMFs) for the interaction between the  $\text{Ca}^{2+}$  cations and the carboxylic groups of the NOM fragments were also calculated. The PMF characterizes the change in the free energy of the system due to the changes in its configuration (e.g., Kollman, 1993). If the free energy of a system in thermodynamic equilibrium in the  $NVT$  statistical ensemble is

$$F = -k_B T \ln Z \quad (2)$$

where  $Z$  is the canonical partition function and  $k_B$  is the Boltzmann constant, then the potential of mean force,  $W(r)$ , for two interacting species is defined as the potential that would generate the mean force between the two species, averaged over all orientations, for each separation distance  $r$ . Thus, the PMF represents the free energy profile of the system as a function of  $r$ , and it can be shown that

$$W(r) = -k_B T \ln g(r) \quad (3)$$

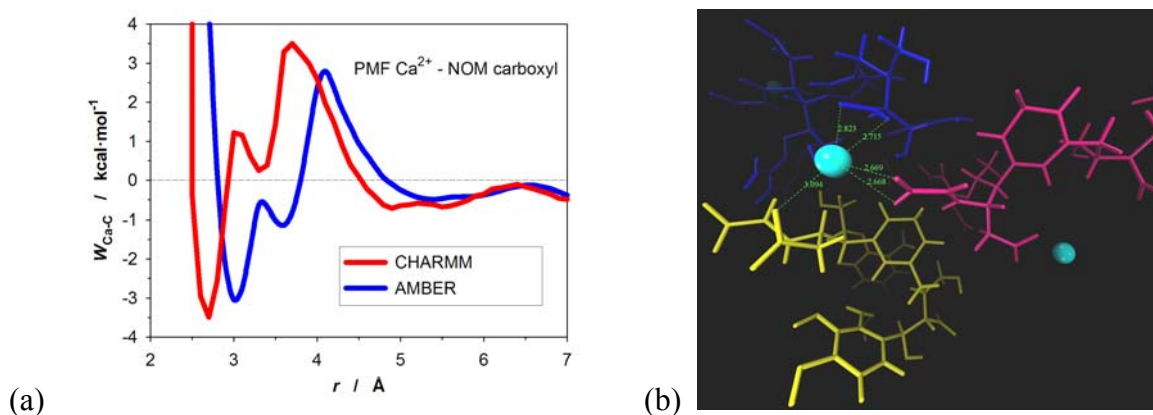
where  $g(r)$  is the corresponding radial distribution function for this pair of species with the standard normalization for large separations,  $g(r) \rightarrow 1$  at  $r \rightarrow \infty$ . Thus,  $W(r)$  asymptotically approaches zero with large separation distance. A detailed analysis of the PMF calculations for the metal cation complexation with the carboxylic groups of NOM molecules and the resulting estimates for the metal-NOM association constants have been recently published elsewhere (Iskrenova-Tchoukova et al., 2010).

For the neutral pH conditions modeled in our simulations, the three carboxylic groups of the NOM fragments can be assumed to be completely deprotonated ( $\text{pK}_a$  values between 4 and 5), whereas the hydroxyl groups are protonated ( $\text{pK}_a$  values of  $\sim 9$ ). The deprotonated carboxylic groups of NOM are known to be the principal source of the NOM negative charge development at the near-neutral pH range. These negatively charged carboxylic groups are the most important binding sites for metals, and  $\text{Ca}^{2+}$  appears to be among the most strongly NOM-associating ions (e.g., Leenheer et al., 1998; Wall and Choppin, 2003).

Metal cations can associate with these carboxylic groups via several typical and relatively stable coordination geometries (Iskrenova-Tchoukova et al., 2010; Kalinichev et al., 2011). In a *bidentate* contact ion pair (CIP) configuration, the cation is coordinated simultaneously with the two oxygen atoms of the carboxylic group and stays approximately

equidistant from both of them predominately near the bisector plane orthogonal to the plane of the carboxylic group. In a *monodentate* CIP configuration, the cation is coordinated with only one of the carboxylate oxygen atoms. Thus, in both bidentate and monodentate cases, the H<sub>2</sub>O molecules in the first coordination shell of cations are partially replaced by the carboxylate oxygens. In contrast, in an outer-sphere coordination, the cation is separated from the NOM carboxylate oxygens by a mono-molecular layer of H<sub>2</sub>O, and one can consider this coordination as a fully hydrated metal ion weakly associated with the carboxylic group forming a solvent separated ion pair (SSIP).

A comparison of potentials of mean force for Ca<sup>2+</sup> interaction with the carboxylic groups of NOM obtained in MD simulations with two different force fields (AMBER and CHARMM) is presented in Figure 2(a). Both simulations consistently result in a potential well of about -3.0 kcal/mol characterizing the bidentate cation-carboxyl coordination at interatomic separations of about 3.0 Å and in a shallower and broader potential well of -0.7 kcal/mol at about 5.5 Å corresponding to a solvent-separated ion pair coordination. However, the potential barrier between the CIP and SSIP coordinations is higher by almost 1 kcal/mol for the CHARMM force field, indicating a stronger preference for inner-sphere vs. outer-sphere coordination for the latter model. This model dependence is also visible in the energy of monodentate-coordinated CIPs between the two force fields. For the CHARMM force field, the corresponding potential well (red line in Figure 2(a) at about 3.5 Å) is located in the region of positive energies, indicating that such metal-NOM coordinations, although relatively stable, are generally unfavorable.



**Figure 2:** (a) Potentials of mean force for interactions of Ca<sup>2+</sup> ions with carboxylic group of NOM from the results of two different MD simulations. (b) A snapshot from MD simulations illustrating the NOM complexation and aggregation in the presence of Ca<sup>2+</sup> ions. H<sub>2</sub>O molecules and other ions are removed for clarity.

The analysis of larger-scale MD simulations reveals that when Ca<sup>2+</sup> ions are present in the system, not only a stronger degree of metal-NOM complexation is observed, but also a significant degree of supramolecular NOM aggregation (Iskrenova-Tchoukova et al., 2010; Kalinichev et al., 2011). A snapshot from such simulation is presented in Figure 2(b), where three aggregating NOM fragments are shown in different colors, Ca<sup>2+</sup> ions are shown as the light blue balls, and all H<sub>2</sub>O molecules are removed for clarity. One Ca<sup>2+</sup> ion is seen here in a strong bidentate CIP coordination with the carboxylic groups of two different NOM molecules (red and dark blue in Figure 2(b) and, simultaneously, in a weaker monodentate CIP coordination to a third NOM molecule (yellow in Figure 2(b)). Such simultaneous coordination of Ca<sup>2+</sup> ions by two carboxylic groups of the same NOM molecule was also observed in our simulations. This picture is in good agreement with an earlier hypothesis that

Ca<sup>2+</sup> ions are capable of accepting up to four NOM carboxylic groups in their inner-sphere coordination shell (Leenheer et al., 1998). This observation also suggests that the complexation with Ca<sup>2+</sup> ions may affect the supramolecular NOM aggregation in two different ways. Ca<sup>2+</sup> ions can directly affect aggregation by bridging carboxylic groups of different NOM molecules, effectively bringing and holding them together. In addition, simultaneous Ca<sup>2+</sup> coordination with two carboxylic groups of the same NOM molecule can produce a metal-NOM complex with reduced net negative charge, thus allowing such complexes to approach each other more readily and to coordinate with each other via weaker hydrogen bonding interactions.

## Conclusions

Clays and NOM are two good examples of complex natural materials which, for natural reasons, cannot be completely characterized in full atomistic compositional and structural detail. This makes it particularly hard to approach a quantitative investigation of their behavior with traditional computational molecular modeling techniques. We have analyzed and quantitatively assessed the degree of possible model-dependence in the results of such molecular computer simulations taking the complexation of Ca<sup>2+</sup> with a realistic and well defined TNB model of NOM as an important example (Kalinichev et al., 2011). Some degree of dependence of the simulated results on the size of the simulated system and on the parameters of the force field models is, indeed, observed. However, we find it quite encouraging, that the main results are very robust and quite consistent with available experimental data and other results of molecular modeling. Independent on the force field used, all MD simulations indicate that about 35-50% of the NOM carboxylic groups are associated with Ca<sup>2+</sup> cations and provide other valuable molecular scale information concerning the structure, energetics, and dynamics of the metal-NOM association. This includes bidentate vs. monodentate configuration of the complexes, inner-sphere (CIP) vs. outer-sphere (SSIP) coordination of the ion pairs and their relative stability (Iskrenova-Tchoukova et al., 2010). The degree of supramolecular aggregation of NOM in aqueous solutions can also be addressed in such simulations, at least semi-quantitatively. However, much larger scale simulations (both in terms of the sizes of the modeled systems and the duration of the simulations) would have to be performed for Ca<sup>2+</sup>-containing systems with different and more structurally diverse NOM models to further explore and quantify the phenomenon of aggregation, the relative importance of different aggregation mechanisms and the thermodynamic stability and transport properties of such aggregates.

The same conclusions should generally hold for the association of metals with clay surfaces. In view of the well-known strong association of metal cations with negatively charged clay surfaces and negatively charged NOM functional groups, it is natural to expect that cationic bridging could be the most probable mechanism of NOM association with clays in natural environments. New MD simulations are currently in progress to quantitatively assess these predictions on a molecular scale for the clay compositions, organic molecules, and metal cations most relevant for nuclear waste disposal applications.

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