

CLAY MINERAL SURFACE GEOCHEMISTRY: STRUCTURE OF WATER ADSORBED ON A MICA SURFACE

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RESEARCH OBJECTIVES

The objective of this project is to obtain the detailed structural properties of hydration water on a micaceous mineral surface.

APPROACH

Our approach uses Monte Carlo simulations as implemented in the program MONTE. The Muscovite model formula, $K_{16}Al_{23}(Al_{16}Si_{48})O_{160}(OH)_{32}$ was used with 256 water molecules in a simulation cell. This cell was then replicated infinitely in three dimensions to mimic a macroscopic mica-water interface system. The model potential functions used to represent water-water, counterion-water, counterion-counterion, counterion-mineral, and water-mineral interactions have been tested extensively and successfully for 2:1 clay-mineral hydrates. Our simulations were performed in a constant (NVT) ensemble, in which absolute temperature (T) and pressure applied normal to the mineral layers (s) are maintained at 300 K and 100 kPa, respectively.

ACCOMPLISHMENTS

We have ascertained the detailed molecular structure of the mica-water interface. Figure 1 compares the water O (oxygen) density profile we obtained by Monte Carlo simulation with that derived from x-ray reflectivity measurements (Cheng et al., 2001). The match between their profile and ours (within 4 Å from the surface O) is excellent, encouraging a direct interpretation of the two principal features in terms of adsorbed water species, as predicted by our simulation. The first peak in the O density profile describes the water molecules adsorbed near ditrigonal cavities, while the second peak corresponds to adsorbed water molecules distributed laterally at approximately 1.3 per surface cavity, as also reported by Cheng et al. (Figure 1). Visualization showed that most of these water molecules are oriented with one of their OH groups pointing toward the mineral-surface O, which is consistent with hydrogen bond formation.

SIGNIFICANCE OF FINDINGS

Our simulation results were consistent with liquid-like disorder for the hydrate as a whole (Cheng et al., 2001) on the basis of their water O density profile tending to approach the bulk liquid limit after only a few oscillations (Figure 1). Overall, the structure of water adsorbed by micaceous minerals appears to be significantly more disordered than that of ice Ih. Our Monte Carlo results may also help to clarify the molecular interpretation of recent surface-force balance experiments involving hydration water between mica surfaces (Reviv et al., 2001). These experiments indicate that K^+ counterions are displaced into the hydration layers, in agreement with our simulation results; that a single layer of strongly adsorbed

water may exist at the mica surface, in agreement with Figure 1; and that hydration water films thicker than about 4 Å are liquid-like.

RELATED PUBLICATIONS

- Cheng, L., P. Fenter, K.L. Nagy, M.L., Schlegel, and N.C. Sturchio, Molecular-scale density oscillations in water adjacent to a mica surface. *Phys. Rev. Lett.* 87, 156103, 2001.
- Reviv, U., P. Laurat, and J. Klein, Fluidity of water confined to subnanometre films. *Nature*, 413, 51, 2001.
- Park, S.-H. and G. Sposito, Do montmorillonite surfaces promote methane hydrate formation?: Monte Carlo and molecular dynamics simulations. *J. Phys. Chem. B.* 107, 2281, 2003.
- Park, S.-H. and G. Sposito, Structure of water adsorbed on a mica surface. *Phys. Rev. Lett.* 89, 85501, 2001. URL: http://esd.lbl.gov/GEO/aqueous_geochem/index.html.

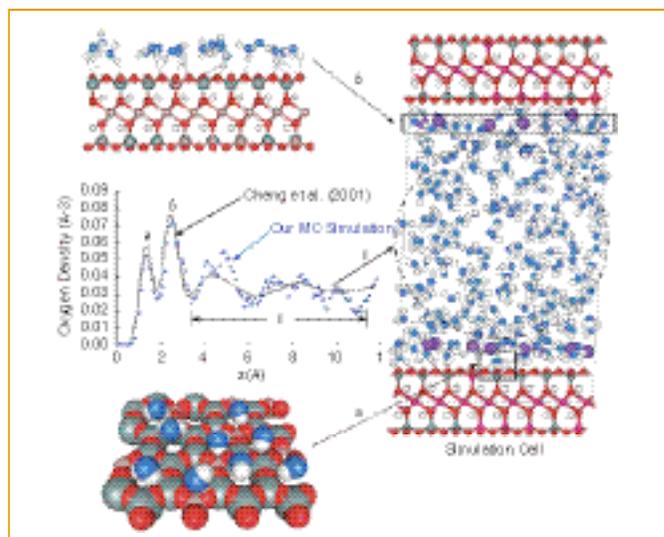


Figure 1. Simulation cell of the molecular structure of water adsorbed on muscovite (right); water O density distribution as a function of the distance z from the mean surface oxygen position (left, middle); water molecules adsorbed near ditrigonal cavities (left, bottom); adsorbed water molecules distributed laterally at ~ 1.3 Å and forming hydrogen bonds with mineral surface oxygens (left, top)

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. All calculations were performed at the National Energy Research Scientific Computing Center (NERSC).