

COMPUTATIONAL CLAY CHEMISTRY

Monday June 21, 2004

Computational Clay Chemistry I	
10:00 – 10:40a	<p>THEORETICAL APPROACH ON VIBRATIONAL AND CRYSTALLOGRAPHIC PROPERTIES OF DIOCTAHEDRAL 2:1 PHYLLOSILICATES. Claro Ignacio Sainz-Diaz^{*1}, Elizabeth Escamilla-Roa¹, Vicente Timón², T. Martin³, and Alfonso Hernández-Laguna¹</p> <p>¹Department of Earth Sciences and Environmental Chemistry. Estación Experimental del Zaidín (CSIC), C/ Profesor Albareda,1, 18008-Granada, Spain; ²Department of Physics, University of Durham, South Road, DH1 3LE Durham, U.K.; ³Department of Earth Sciences, University of Cambridge, CB2 3EQ Cambridge, U.K.</p>
10:40 – 11:00a	<p>INTERLAYER CATION ARRANGEMENT AND HYDRATION SHELLS IN SODIUM AND CALCIUM MONTMORILLONITE OBTAINED BY MONTE CARLO SIMULATIONS. Christian J. Müller^{*1}, Alfred Delville², Günter Kahr¹, and Michael Plötze¹</p> <p>¹Institute of Geotechnical Engineering, Swiss Federal Institute of Technology, ETH Hönggerberg, 8093 Zurich, Switzerland; ²CRMD, CNRS-Université d'Orléans, 1b rue de la Ferrolerie, 45071 Orléans Cedex 02, France</p>
11:00 – 11:20a	<p>MOLECULAR SIMULATIONS OF HYSTERESIS IN CLAY SWELLING. Tim J. Tambach[*], Peter G. Bolhuis, and Berend Smit</p> <p>Van't Hoff Institute of Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands: tambach@science.uva.nl</p>
11:20 – 11:40p	<p>UNDERSTANDING LAYER CHARGE DETERMINATION BY THE ALKYLAMMONIUM METHOD USING MOLECULAR SIMULATIONS. Tim J. Tambach^{*1}, Edo S. Boek², and Berend Smit¹</p> <p>¹Van't Hoff Institute of Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands: tambach@science.uva.nl; ²Schlumberger Cambridge Research, High Cross, Madingley Road, CB3 0EL Cambridge, England</p>
11:40 – 12:00p	<p>A COMPARISON OF THEORETICAL AND EXPERIMENTAL PROPERTIES OF THE ELECTRON DENSITY DISTRIBUTIONS FOR EARTH MATERIALS. G.V Gibbs^{*1}, D.F. Cox², and K.M. Rosso³</p> <p>¹Departments of Geosciences, Materials Science, and Engineering and Mathematics, Virginia Tech, Blacksburg, Virginia, USA; ²Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia, USA; ³Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington, USA</p>
Computational Clay Chemistry II	
1:20 – 1:40p	<p>CHARGE TRANSPORT IN MICAS: AN AB INITIO MODEL OF Fe^{II/III} ELECTRON HOPPING AND THE EFFECTS OF SUBSTITUTIONAL DEFECTS. Kevin M. Rosso[*] and Eugene S. Ilton</p> <p>Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington, USA</p>
1:40 – 2:00p	<p>SELF-CONSISTENT SELF-INTERACTION CORRECTED DFT STUDIES OF ANNITE. Eric J. Bylaska¹, Kiril Tsemekhman², Eugene Ilton¹, and Kevin Rosso¹</p> <p>¹Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA;</p>

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Computational Clay Chemistry Poster Session	
5:00p	FIRST-PRINCIPLE STUDY ON POLYTYPE STRUCTURES OF 1:1 DIOCTAHEDRAL PHYLLOSILICATES. Hisako Sato* ^{1,2} , Kanta Ono ^{2,3} , Cliff T. Johnston ⁴ , Jun Yoshida ¹ , and Akihiko Yamagishi ^{1,2} ¹ Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan; ² CREST, Japan Science and Technology Corporation; ³ Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801; ⁴ Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907-1150

MONDAY JUNE 21, 2004

COMPUTATIONAL CLAY CHEMISTRY I

MORNING SESSION

10:00AM

THEORETICAL APPROACH ON VIBRATIONAL AND CRYSTALLOGRAPHIC PROPERTIES OF DIOCTAHEDRAL 2:1 PHYLLOSILICATES

Claro Ignacio Sainz-Diaz^{*1}, Elizabeth Escamilla-Roa¹, Vicente Timón², T. Martin³, and Alfonso Hernández-Laguna¹

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The octahedral cation ordering of dioctahedral 2:1 phyllosilicates was studied taking into account two-species and three-species of cations (Al/Fe/Mg), which were relevant to clay compositions found in nature, that can represent different natural (smectites, illites, Fe-rich montmorillonites, nontronites, celadonites) and synthetic clay minerals, by means of Monte Carlo simulations based only on theoretical models. Most systems exhibit short-range order at low temperature. The ordering of the octahedral cations is highly dependent on the cation composition. In general, a segregation tendency of Fe and dispersion tendency of Mg is observed. In samples with a high Fe content and low Al content, the Fe cations form globular clusters, whereas they form linear clusters in samples with high Fe content and significant Al content. The low long-range ordering level in the Fe distribution in the octahedral sheet is similar in illites and smectites, but the relative population of unclustered Fe cations in smectites is higher than in illites according experiment. Quantum-mechanical calculations based on Density Functional Theory (DFT) approximation were performed on smectite and illite samples confirming these results.

This ordering is studied also within the *cis*-vacant/*trans*-vacant polymorphism of these minerals. These configurations can be distinguished from one another experimentally by X-ray diffraction and thermal analysis, but with great difficulty and only semi-quantitative accuracy. *Trans*-vacant and *cis*-vacant configurations were distinguished and studied for smectites and illites with different cation substitutions in octahedral and tetrahedral layers and in the interlayer space at the quantum-mechanical level. The energy differences between the *cis*-vacant and *trans*-vacant configurations for a certain composition are lower than the energy changes produced by the relative cation distributions and ordering process in the octahedral and tetrahedral sheets.

Spectroscopic methods are a very useful experimental tool for studying cation distributions in octahedral sheet of these minerals, especially the IR frequencies of OH groups. Vibrational frequencies of the OH groups, $\nu(\text{OH})$ and $\delta(\text{OH})$, were calculated at First Principles level reproducing the experimental values. The vibrations of the OH groups depend significantly on the nature of the cations which they coordinate, and also on the interactions of the H atom with the tetrahedral O atoms that surround the OH group. For a certain MOHM', different OH frequencies can exist depending on their structural environment. Therefore, a wider range of vibrations should be taken into account experimentally, especially in the assignment of frequencies and determination of relative intensities with the deconvolution analysis method. This theoretical approach can be a useful tool for a predictive application of crystallographic and vibrational properties that cannot be determined experimentally in these clay minerals.

INTERLAYER CATION ARRANGEMENT AND HYDRATION SHELLS IN SODIUM AND CALCIUM MONTMORILLONITE OBTAINED BY MONTE CARLO SIMULATIONS

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Today the interlayer structure of montmorillonite is simulated by computer experiments (e.g. Monte Carlo, MC). Early MC simulations focussed on the 1D-distribution of interlayer species perpendicular to the 2:1 layers and reproduced the well-established layer-wise arrangement of water molecules. Recently, more attention is drawn to the precise arrangement of interlayer species in 3D. However, no detailed picture of the interlayer structure has been proposed until now.

In the present study, we placed strong emphasis on position, orientation and geometry of cationic hydration shells, but also on structure of water layers and distribution of cations on the 2:1 layer surface. We performed MC simulations of a montmorillonite at two different layer spacings (sodium one- and two-layer hydrate and calcium two-layer hydrate). The relative arrangement of the 2:1 layers was equally chosen for all three, i.e. it was independent of the degree of expansion.

In the sodium one-layer hydrate, cations have a quadratic planar hydration shell. The diagonals of the square are rotated ($\sim 15^\circ$) with respect to the crystallographic a,b axes. This is deduced from paired hydrated cations. In the sodium two-layer hydrate, some cations stay coordinated to the 2:1 layer, their hydration shell is extended to a tetragonal pyramid. The rotation angle is preserved. Sodium ions detached from the 2:1 layer are octahedrally coordinated with six water molecules. The octahedron is lying parallel to the 2:1 layers with two of its triangular sides. All the extracted bond lengths compare well with literature data.

In the calcium two-layer hydrate, the cations are coordinated to the 2:1 layer and are found in/over the pseudo-hexagonal structural element of the 2:1 layer. In many examined cases, the first hydration shell is a pentagonal pyramid with its base parallel to the 2:1 layer. This geometry is in good agreement with recent simulation data on hydrated calcium in solution (pentagonal bipyramidal coordination).

All three simulations give clear indications of a superstructure caused by the ordered distribution of interlayer cations. This is evidenced from the cation-cation radial distribution functions.

MOLECULAR SIMULATIONS OF HYSTERESIS IN CLAY SWELLING

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It is known for several decades that certain types of clay minerals (i.e. smectites) have the capability of swelling. Charge compensating counter ions in the interlayer space attract water molecules, forming up to four layers. Related to this layer formation, swelling occurs stepwise and depends on the type of clay mineral, counter ion, and thermodynamic variables. Interestingly, clay swelling shows hysteresis: the swelling pathway is different from the shrinking pathway. Experimentally, this hysteresis is observed as a function of the salt concentration, temperature, and relative humidity. There is little consensus about the explanation of clay swelling hysteresis^[1].

We used Molecular Dynamics simulations to study montmorillonite swelling hysteresis at constant volume, temperature, and water chemical potential. In particular, we focused on the swelling and shrinking of one- and two-layer hydrates, respectively. The atomic interactions between the clay mineral, cations, and water molecules (TIP4P model) are described with Lennard-Jones and Coulombic potentials. Insertions and deletions of water molecules are carried out with a Configurational Biased Monte Carlo scheme^[2]. We systematically varied the basal spacing, type of counter ion, water chemical potential (related to the relative humidity), temperature, and external pressure to simulate the effect on clay swelling hysteresis. By sampling the pressure normal to the clay layers during the simulation, we calculated the free energy as a function of the basal spacing.

The minima in our free energy profiles indicate stable layer spacings, which are in agreement with experimentally measured spacings of one- and two-layer hydrates. With increasing relative humidity, the free energy of the two-layer hydrate becomes lower than the free energy of the one-layer hydrate. However, a free energy barrier between the one- and two-layer hydrates blocks the swelling. According to our simulations, this free energy barrier explains clay swelling hysteresis and therefore does not support other hypothesized irreversible rearrangements in the clay mineral structure^[1]. Our simulations also predict a new form of hysteresis. At a given temperature and relative humidity, an increasing external pressure on the clay mineral induces shrinking. The original state is recovered at significantly lower external pressure^[3]. Swelling for different types of counter ion occurs in the following order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The relative humidity needed to induce swelling and shrinking is lower for small counter ions, because they are more easily hydrated.

[1] Laird, D.A., Shang, C., and Thompson, M. L. J. *Colloid Interface Sci.* 171(1995), 240.

[2] Hensen, E.J.M., Tambach, T.J., Blik, A., and Smit, B. *J. Chem. Phys.*, 115(2001), 3322.

[3] Tambach, T.J., Bolhuis, P.G., and Smit, B. *Ang. Chem.* Accepted for publication.

UNDERSTANDING LAYER CHARGE DETERMINATION BY THE ALKYLAMMONIUM METHOD USING MOLECULAR SIMULATIONS

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Layer charge is one of the most important properties of 2:1 clay minerals¹. Besides the fact that layer charge is a criterion for the classification of these minerals, it also determines the ion exchange properties and therefore the ability to adsorb all kinds of surfactants. The alkylammonium method can be used to measure the layer charge by measuring critical carbon chain lengths. Although this method has several advantages over other methods, its accuracy is questionable and the results are not completely understood^{1,2,3}.

We performed NP_zT molecular simulations of alkylammonium ions intercalated in three types of swelling clay minerals (Bentonite, Cheto montmorillonite, and Vermiculite) as a function of the carbon chain length in the range H_3NC_6 to H_3NC_{18} . We used Molecular Dynamics for moving the alkylammonium molecules and a Monte Carlo scheme to adjust the basal spacing, treating the clay layers as rigid bodies. For correct sampling of the phase space, a Configurational Biased Monte Carlo (CBMC) scheme was implemented to regrow⁴ the alkylammonium molecules during the simulation. We used the united atom OPLS force field with rigid bonds, flexible bending and torsion angles, and inter- and intra-molecular interactions. Throughout the simulations we quantified the configurations of the alkylammonium ions in the interlayer space by sampling the average positions of the atoms and the tilt-angle with respect to the normal of the clay surface.

Our simulated molecular configurations of layered alkylammonium ions in Bentonite and Cheto montmorillonite confirm theoretically suggested structures¹. On the other hand, several alkylammonium ions in Vermiculite adopt a tilted configuration. Our calculated basal spacings of all three types of clay are in agreement with experimentally measured basal spacings². For Bentonite and Cheto montmorillonite we calculated energetically favorable intermediate basal spacings between those of monolayers, bilayers, and pseudotrilayers, probably caused by a subtle balance between enthalpic and entropic effects. In combination with layer charge heterogeneity, these intermediate spacings make the layer transitions more gradual and might explain peak broadening in X-Ray Diffraction patterns³.

[1] CMS Workshop Lectures, Vol. 6 (1994), A.R. Mermut ed., p.134.

[2] Laird, D.A. Scott, A.D., and Fenton, T.E. *Clays Clay Miner.*, 37(1989), 41.

[3] Janek, M. and Smrčok, L'. *Clays Clay Miner.*, 47(1999), 113.

[4] Frenkel, D and Smit, B. *Understanding Molecular Simulation*, 2 ed., Academic Press 2002, p.638.

A COMPARISON OF THEORETICAL AND EXPERIMENTAL PROPERTIES OF THE ELECTRON DENSITY DISTRIBUTIONS FOR EARTH MATERIALS

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The electron density, ρ , is one of the most important properties of an earth material. It includes all of the information about the bonded interactions and structure together with important information about chemical reactivity¹⁻⁴. However, despite its high information content, the extraction of information from ρ is a very difficult and nontrivial task. But, if headway is to be made in acquiring this information, it is crucial that we explore the extent to which the properties of an experimental model distribution for an earth material agree with those of a theoretical model distribution generated with first principles quantum mechanics.

Electron density distributions have been calculated and bond critical point, bcp, properties have been generated for a large number of earth materials.⁵ As predicted by the theoretical calculations, the bcp properties observed for several materials correlate with the observed bond lengths. Those recently determined with essentially extinction and absorption free single crystal high energy synchrotron diffraction data agree with those calculated within 5%, on average, whereas those determined with lower energy single crystal diffraction data show substantial disagreements in several cases. The value of the electron density at the bcp is highly correlated with the strengths of the bonded interactions, providing a physical basis for Pauling's definition of bond strength.⁶

The Laplacian of an electron density distribution, $\nabla^2\rho$, is a powerful tool for locating regions of a material that are susceptible to electrophilic and nucleophilic attack. In the case of the silica polymorph coesite, theoretical and experimental $-\nabla^2\rho$ distributions show that the nucleophilic character of an O atom comprising a SiOSi bonded interaction increases in a regular way with decreasing angle. Further, the H positions in a H-bearing specimen were located on the basis of maxima in the distributions where the electron density is locally concentrated. The positions of the H atoms have been confirmed in a careful infrared spectroscopic study by Köch-Müller et al.⁷ The H atoms in H- and Al-bearing stishovite were also successfully located on the basis of the maxima in the $-\nabla^2\rho$ distribution.

¹Hohenberg and Kohn. 1964. Phys. Rev. B136:864.

²Riess and Münch. 1981. Theor. Chim. Acta 52:4133.

³Kraka and Cremer, 1990. *Theoretical models of chemical bonding*. Springer Verlag, 453 p.

⁴Bader. 1990. *Atoms in Molecules, A Quantum Theory*. Oxford Science Publ., 428 p.

⁵Gibbs et al. 2001. Rev. Mineral. Geochem. 42: 345.

⁶Pauling, L. 1929. J. Am. Chem. Soc. 51:1010.

⁷Köch-Müller et al. 2001. Phys. Chem. Miner. 28:693.

MONDAY JUNE 21, 2004

COMPUTATIONAL CLAY CHEMISTRY II

AFTERNOON SESSION

1:20PM

CHARGE TRANSPORT IN MICAS: AN AB INITIO MODEL OF Fe^{II/III} ELECTRON HOPPING AND THE EFFECTS OF SUBSTITUTIONAL DEFECTS

Kevin M. Rosso* and Eugene S. Ilton

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Phyllosilicate minerals, such as clays and micas, often comprise an important electron source in subsurface geochemical environments. The presence of oxygen limits the availability of reduced metals such as Fe^{II} in solution or sorbed on mineral surfaces. However, Fe^{II} can persist over long periods in these environments in the form of structural constituents in phyllosilicate minerals. Therefore, the rate oxidation of structural Fe^{II} to Fe^{III} in phyllosilicates can at times dictate the availability of electrons for redox reactions in the local environment. Phyllosilicate minerals, even those bearing a large fraction of structural Fe^{II}, are poor electrical conductors. However, charge transport, likely by electron hopping through valence alternation of Fe^{II/III} cations, has been demonstrated. Presumably, the process of oxidation of structural Fe^{II} would be progressive, involving rapid oxidation of outermost Fe^{II} sites with a relatively slow inward advance of an oxidation front. Central to this process is the effective accessibility of Fe^{II} electrons in the phyllosilicate mineral structure and, thus, the electron hopping mobility in the lattice.

The two principal Fe^{II/III} electron exchange reactions underlying charge transport in the octahedral sheet of ideal end-member annite were modeled using a combination of ab initio calculations and Marcus electron transfer theory. A small polaron model was applied which yielded electron hopping activation energies that agree well with the limited available experimental data. A small ab initio cluster model successfully reproduced several important structural, energetic, and magnetic characteristics of the M1 and M2 Fe sites in the annite octahedral sheet. The cluster enabled calculation of the internal reorganization energy and electronic coupling matrix elements for the M2–M2 and M1–M2 electron transfer reactions. The M2–M2 electron transfer is symmetric with a predicted forward/reverse electron hopping rate of 10⁶ s⁻¹. The M1–M2 electron transfers are asymmetric due to the higher ionization potential by 0.46 eV of Fe^{II} in the M1 site. The electronic coupling matrix elements for these reactions are predicted to be small and of similar magnitude, suggesting the possibility that the coupling is essentially direction independent among hopping directions in the octahedral sheet. M1 Fe sites are predicted to be efficient electron traps and charge transport should occur by nearest-neighbor electron hops along the M2 Fe sublattice.

SELF-CONSISTENT SELF-INTERACTION CORRECTED DFT STUDIES OF ANNITE

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We have recently developed a framework for the self-consistent calculation of self-interaction corrections (SIC) to pseudopotential plane-wave density functional theory (PSPW). The technique implements the original method due to Perdew and Zunger and combines two procedures: construction of maximally localized Wannier functions (MLWF, procedure due to Marzari and Vanderbilt and to Silvestrelli) and direct minimization of the DFT+SIC total energy functional. The technique developed can be employed in PSPW-DFT methods without adding significant expense. Furthermore, atomic forces and stresses are straightforward to implement, making it applicable to both confined and extended systems, as well as to Car-Parrinello ab initio molecular dynamic simulations. This method has been applied to several systems for which standard DFT methods do not work well.

We present here results from a recent study of the oxidation of annite in air. Some evidence exists that oxidation of annite will result in a charge states inside the single-particle band gap, associated with localized Fe^{3+} ion state. Such a state is typically the result of local distortion of the lattice leading to localization of the electronic wave function. So far, only small cluster models within Hartree-Fock approximation have yielded such a localized Fe^{3+} state. However, it is well known that the Hartree-Fock approximation unnecessarily favors localized states. In contrast, large-scale periodic DFT calculations using standard DFT functionals do not localize these types of states. It has been suggested that standard DFT functionals which are not self-interaction free tend to favor delocalized electronic states since self-interaction creates a Coulomb barrier to charge localization. Using or newly developed self-interaction corrected DFT method we have been able to obtain a significant degree of charge localization. Various aspects of this application and implications will be discussed.

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POSTER SESSION

5:00PM

FIRST-PRINCIPLE STUDY ON POLYTYPE STRUCTURES OF 1:1 DIOCTAHEDRAL PHYLLOSILICATES

Hisako Sato*^{1,2}, Kanta Ono^{2,3}, Cliff T. Johnston⁴, Jun Yoshida¹, and Akihiko Yamagishi^{1,2}

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Kaolinite ($\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$) is a 1:1 dioctahedral phyllosilicate (layered aluminosilicate) with little, if any, isomorphous substitution. The polytype structures of the three 1:1 dioctahedral phyllosilicates found in nature, kaolinite, dickite and nacrite, have been investigated. The calculations were performed using the plane-wave pseudo-potential software CASTEP. The calculated structural parameters, including the orientation of the OH groups, for the three polytypes are in good agreement with experimental data as shown Table 1. In particular, for kaolinite and dickite, the three-inner surface OH groups were predicted to be oriented nearly perpendicular to the (001) plane. In contrast, one of the inner surface OH groups of nacrite was predicted to be nearly parallel with respect to the (001) plane.

Table 1. Orientation of OH groups with respect to the (001) plane

Angle(degree)	Kaolinite C site	Kaolinite (ref a)	Dickite	Dickite (ref b)	Nacrite	Nacrite (ref c)
O-H	70.8	73.2	74.0	75.5	54.3	50.3
O-H	67.8	60.2	54.5	51.9	62.5	65.9
O-H	52.2	68.2	61.5	74.1	58.7	56.8
O-H(inner)	-8.9	0.4	-8.6	-1.3	-23.7	-18.6

(ref a) Bish, D.L.(1993). Clays and Clay Minerals, 41, 738-744.

(ref b) Bish, D. L. and Johnston, C. T. (1993). Clays and Clay Minerals, 41, 297-304

(ref c) Zheng, H. and Bailey, S.W. (1994) Clays and Clay Minerals, 42, 46-52.