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Final Report
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Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces

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Executive Summary

United States Department of Energy grant DE-FG02-10ER16128, "*Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces*" (Geoffrey M. Bowers, P.I.) focused on developing a molecular-scale understanding of processes that occur in fluids and at solid-fluid interfaces using the combination of spectroscopic, microscopic, and diffraction studies with molecular dynamics computer modeling. The work is intimately tied to the twin proposal at Michigan State University (DOE DE-FG02-08ER15929; same title: R. James Kirkpatrick, P.I. and A. Ozgur Yazaydin, co-P.I.).

During the recently concluded grant period, the spectroscopic contributions from our group have provided significant new insight into several areas of interest.

- **Water-Smectite Interfaces –** NMR results from our group show that the dynamics of H_2O confined in smectite interlayers and the activation energy for those dynamic behaviors depend on both the charge density and polarizability of the charge-balancing cation. We also find that H_2O mobility in the interlayer affects the NMR spectra of the charge-balancing cations differently depending on the charge density of the cation, with high charge densities and low polarizabilities (such as Ca^{2+}) leading to significant dynamic averaging at low temperatures due to reorientation of intact hydration shells. In contrast, ions with lower charge densities and high polarizabilities lead to "freezing out" of the H_2O impact on ion dynamics at higher temperatures. These results are important for understanding fluid behavior in both surface soils and subsurface clay-rich rocks, concepts ultimately crucial to conventional and unconventional fossil fuel extraction.
- **Cation-Natural Organic Matter Floccs –** Our data show that the Ca^{2+} dynamics in wet natural organic matter (NOM) depend on the presence or absence of excess Ca^{2+} in the system. When excess Ca^{2+} is present, dynamics are dominated by exchange between near-surface environments and those of bulk aqueous solution at warm temperatures. In contrast, when the temperature is low enough to form ice domains in the pores, the freezing H_2O forces all Ca^{2+} into near-surface environments and dynamics are dominated by exchange between different types of near surface sites. When functional groups are deprotonated and only enough Ca^{2+} is present for charge balance, dynamics at all temperatures are dominated by exchange between near surface sites with nearly no contribution from Ca^{2+} in the bulk fluid pore domains.
- **Smectite-NOM-H_2O Interfaces –** We have preliminary data currently being prepared for publication regarding how NOM coatings on smectite surfaces influence the binding and dynamics of cations and H_2O. We find that thin NOM coatings are produced at basic pH and that these coatings have little influence on the H_2O or cation binding or dynamics in these systems. Thicker NOM coatings always form for divalent cations and for all cations at more acidic pH. These thicker coatings influence H_2O and cation dynamics very little, though some of our data suggest that thick coatings stabilize the H_2O content of the system (slowing the kinetics of adsorption and desorption). The data suggest that reactive transport models that do not account for subsurface organic matter may provide reliable predictions of transport behavior even in clay-rich systems where organic matter is prevalent.
- **Smectite Interactions with Variably Wet Supercritical CO_2 –** Much of our effort in this grant period has focused on understanding the structure, dynamics, and thermodynamics of variably wet supercritical carbon dioxide ($scCO_2$) at smectite and smectite-NOM interfaces. We find that there is a critical basal spacing for CO_2 intercalation in the interlayer that is of the order of ~11.8-12.2 Å, a spacing similar to the monolayer hydrate interlayer state of smectites. For large ions with low H_2O affinity such as Cs^+, both H_2O and CO_2 exist in the smectite interlayer at essentially all $scCO_2$ relative humidities (RHs), including the anhydrous case. There is NMR evidence of direct CO_2-cation interactions for these systems. However, ions that have higher charge densities and greater affinities for H_2O such as Ca^{2+} tend to scavenge H_2O from the $scCO_2$. These materials do not

accept CO_2 in the interlayer until enough H_2O is present to reach the critical basal spacing. However, these water loving cations continue to adsorb H_2O from the $scCO_2$ phase with increasing RH, eventually forcing a substantial amount of CO_2 to exit the interlayer. We do not observe direct CO_2-cation interactions in these systems under any $scCO_2$ humidity. Our data allowed us to characterize the geometries and constrain the reorientation rates for CO_2 adsorbed in 1WL-type, 2WL-type (~15 Å basal spacing), and external surface sites. The occupancy ratios of each site vary with the supercritical fluid RH and properties of the charge-balancing cation. The presence of thin NOM coatings does not appear to influence the adsorption site geometry and dynamics of adsorbed CO_2, however, there is a small reduction in the fraction of CO_2 adsorbed when NOM is present. The results show that the humidity of the $scCO_2$ phase and the charge-balancing cation present in the clay phase are important in determining its adsorption and transport through smectite-rich materials, with potential implications for the integrity of clay-rich shale caprocks.

I. Introduction

This document serves as the final report for grant DOE DE-FG02-10ER16128, "*Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces*": Geoffrey M. Bowers, P.I. The research supported by this grant focused on developing a molecular-scale understanding of processes that occur in fluids, at solid-fluid interfaces, and in confined fluids using the combination of spectroscopic, microscopic, and diffraction studies and molecular dynamics computer modeling. The work is intimately tied to the twin proposal at Michigan State University of the same title (DOE DE-FG02-08ER15929: R. James Kirkpatrick, P.I. and A. Ozgur Yazaydin, co-P.I.). The Michigan State group provides all of the computational modeling while Bowers's group prepares and characterizes the physical samples. Personnel from both groups are involved in acquisition and interpretation of the spectroscopic, microscopic, and diffraction data.

We have $3,828 remaining in the budget at the conclusion of our no-cost extension on March 14, 2017. There are two main reasons for this balance. First, we were able to complete our work objectives without tapping into the budget line for elemental analysis/diffraction studies off-site, mainly a result of new collaborations with scientists at Pacific Northwest National Laboratory (PNNL). The second is that Bowers accepted a new position and relocated to St. Mary's College of Maryland in AY 2016/2017. Only travel in August to present research results obtained with funds from this grant was charged after Bowers's relocation.

The research collaboration supported by this grant was very productive during the current grant period (Table 1). Dr. Geoffrey Bowers is the primary author or co-author of several papers in print and several others still in the preparation stage as well as being a significant contributor to a number of publications in print and in preparation at Michigan State University. Bowers also delivered a number of invited talks at meetings and Universities (Table 2). Work during this grant period formed the basis of two undergraduate honors thesis in print. Bowers successfully authored several proposals that won instrumentation awards from PNNL. Our collaborations with PNNL have been quite successful during the current grant period, leading to our work being featured in several press releases and newsletters issued from the lab.

The Bowers group made important contributions toward understanding ion and fluid behavior at pristine smectite-H_2O interfaces, at more authentic "dirty" organo-mineral interfaces with aqueous and non-aqueous fluids, and engaged in pioneering work regarding the structure and dynamics of smectite and smectite-organic interfaces with variably wet non-aqueous supercritical fluids during the current grant period. In paper 5 of Table 1, we showed ^{43}Ca NMR data that reveal Ca^{2+} remains fully hydrated with dynamics dominated by rapid reorientation of the intact hydration shell at temperatures as low as 173 K. Variable temperature ^{2}H NMR results were used to calculate activation energies for the hydration shell reorientation. In papers 10 and 22 (Table 1), we examined ion and H_2O dynamics in cation-natural organic matter (NOM) floccs and smectite-NOM composite materials as a function of pH and ionic strength. In the floccs, excess Ca^{2+} leads to dynamics dominated by rapid Ca^{2+} exchange between surface-associated and bulk aqueous states until the system temperature gets low enough to force all Ca^{2+} into a surface-associated state due to the exclusion of ions from ice domains that form in the pores. In contrast, when only an appropriate charge-balancing number of Ca^{2+} are present, cation dynamics in NOM floccs are dominated at all temperatures by slower hopping between various surface associated environments. The as yet unfinished paper 22 (Table 1) shows that the presence of NOM at different pH, ionic strength, and NOM oxygen-bearing functional group density do not substantially affect the binding or dynamics of the Ca^{2+} in hectorite-NOM composite materials, with the overall behavior mimicking that of the pristine Ca-hectorite at nearly all conditions. However, there are small variations in the observed ^{43}Ca chemical shift and line width at fixed relative humidity of the vapor phase that suggest small alterations in the local Ca^{2+} binding environment when NOM is present. Finally, pioneering work regarding the behavior of variably wet supercritical CO_2 was acquired and published in papers 6 and 16. The data show that supercritical CO_2 ($scCO_2$) can be adsorbed on external surfaces and in the confined interlayer spaces of hectorite at 50°C and 90 bar (conditions equivalent to a ~1 km storage depth), with the interlayer uptake of CO_2 favored at low H_2O content and when the basal spacing is similar to a monolayer hydrate of hectorite (1WL, ~12.5 Å). Charge balancing cations with small radii, large hydration energies, and low polarizabilities tend to scavenge H_2O from humid $scCO_2$ or retain the H_2O they held before $scCO_2$ exposure, swelling spontaneously to a bilayer hydrate (2WL) dominated state that largely prevents direct CO_2-ion interactions and influences the extent of CO_2 intercalation into the interlayer. In contrast, ions with large radii, low hydration energies, and large polarizabilities more readily form close associations with CO_2 with the energetics enabling coexistence of CO_2 and H_2O in the interlayer over a wide range of $scCO_2$ humidities. These results and those of related molecular dynamics simulations suggest that adsorbed CO_2 in 1WL-type interlayers is oriented with its long axis parallel to the clay sheets and reorients rapidly and anisotropically about the axis perpendicular to the CO_2 long axis at rates of at least ~10^5 Hz. If appreciable CO_2 is adsorbed in 2WL-type interlayers, it experiences a mean orientation and dynamic averaging affects that mimic the 1WL-type adsorption environment such that the NMR spectra are the same. External surface adsorbed CO_2 is dynamically similar to the 1WL case, but the CO_2 long axis samples a larger range of orientations with respect to the smectite surface and adopts a different mean angle between the long axis and the smectite surface. When fulvic acid is present, the CO_2-smectite interactions and dynamics are largely unaffected, as was the case for the H_2O-only smectite-NOM composites discussed earlier.

Table 1: Research papers published, under review and in preparation during the current grant period.

Published Papers

1. Morrow, C.P, Yazaydin, A.O., Krishnan, M., Bowers, G. M., Kalinichev, A.G., and Kirkpatrick, R.J., 2013, Structure, energetics, and dynamics of smectite clay interlayer hydration: Molecular dynamics and metadynamics investigation of Na-hectorite, J. Phys. Chem. C, 117, 5172-5187.

2. Saharay, M., Yazaydin, A.O., and Kirkpatrick, R.J., 2013, Dehydration-induced amorphous phases of calcium carbonate, J. Phys. Chem. B, 117, 3328-3336.

3. Krishnan, M., Saharay, M., and Kirkpatrick, R.J., 2013, Structure and dynamics of nano-confined CO_2 and poly(ethylene glycol) in montmorillonite composites, J. Phys. Chem. C., 117, 20592 - 20609.

4. Saharay, M., Yazaydin, A.O., and Kirkpatrick, R. J., 2014, Onset of orientational order in amorphous calcium carbonate (ACC) upon dehydration, Chem. Phys. Letters, 287-291.

5. Bowers, G.M., Singer, J.W., Bish, D.L., and Kirkpatrick, R.J., 2014, Structural and dynamical relationships of Ca^{2+} and H_2O in smectite/^2H_2O systems, Am. Min., 99, 318-331.

6. Bowers, G.M., Hoyt, D.W., Burton, S.D., Ferguson, B.O., Varga, T., and Kirkpatrick, R.J., 2014, In situ ^{13}C and ^{23}Na MAS NMR investigation of supercritical CO_2 incorporation in smectite-natural organic matter composites, J. Phys. Chem. C, 118, 3564-3573.

7. Saharay, M., and Kirkpatrick, R. J., 2014, *Ab initio* and metadynamics studies on the role of essential functional groups in biomineralization of calcium carbonate and environmental situations, Phys. Chem. Chem. Phys., 16, 26843-26854.

8. Kirkpatrick, R.J. Kalinichev, A.G., Bowers, G. M., Yazaydin, A.O., Krishnan, M., Saharay M., and Morrow, C.P., 2015, NMR and computational molecular modeling studies of mineral surfaces and interlayer galleries, Am. Min., 100, 1341-1354, Invited American Mineralogist Centennial Article.

9. Greathouse, J.A., Hart, D.B., Bowers, G.M., Kirkpatrick, R.J., and Cygan, R.T., 2015, Molecular simulation of structure and diffusion at smectite-water interfaces: using expanded clay interlayers as model nanopores, J. Phys. Chem. C, 119, 17126-17136.

10. Bowers, G.M., Argersinger, H.E., Reddy, U. V., Johnson, T.A, Arey, B., Bowden, M., and Kirkpatrick, R.J., 2015, Integrated molecular and microscopic scale insight into morphology and ion dynamics in Ca^{2+}-mediated natural organic matter floccs, J. Phys. Chem. C, 119, 17773-17783.

11. Yazaydin, A.O., Bowers, G.M., and Kirkpatrick, R.J., 2015, Molecular dynamics modeling of carbon dioxide, water and natural organic matter in Na-hectorite, Phys. Chem. Chem. Phys., 17, 23356-23367.

12. Sena, M.M., Morrow, C.P., Kirkpatrick, R.J., and Krishnan M., 2015, Structure, energetics, and dynamics of supercritical carbon dioxide at smectite mineral-water interfaces: molecular dynamics and adaptive biasing force investigation of CO_2/H_2O mixtures nanoconfined in Na-montmorillonite, Chem. Mater., 27, 6946-6959.

13. Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G., and Kirkpatrick, R. J., 2016, Structure, energetics, and dynamics of Cs^+ and H_2O in hectorite: molecular dynamics simulations with an unconstrained substrate surface, J. Phys. Chem., C, 10290-10310.

14. Reddy, U.V., Bowers, G.M., Loganathan, N., Bowden, M., Yazaydin, A.O., and Kirkpatrick, R.J., 2016, Water structure and dynamics in smectites: X-ray diffraction and ^2H NMR spectroscopy of Mg-, Ca-, Sr-, Na-, K-, Cs-, and Pb-hectorite, J. Phys. Chem. C, 120, 8863-8876.

15. Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G., and Kirkpatrick, R. J., 2016, Cation and water structure, dynamics and energetics in smectite clays: a molecular dynamics study of Ca-hectorite, J. Phys. Chem. C, 120, 12429-12439.

16. Bowers, G.M., Schaef, H.T., Loring J.S., Hoyt, D.W., Burton, S.D., Walter E,D., and Kirkpatrick, R.J., 2017, Role of cations in CO_2 adsorption, dynamics, and hydration in smectite clays under in situ supercritical CO_2 conditions, J. Phys. Chem. C, 121, 577-592.

Submitted Papers

17. Ferguson, B.O., Arey, B., Varga, T., Burton, S.D., Bowden, M., Argersinger, H.E., Kirkpatrick, R.J., and Bowers G.M., submitted, X-ray diffraction and helium ion microscopy of smectite-natural organic matter composites, Clays and Clay Minerals.

Papers in Preparation

18. Reddy, U.V., Nanda, R., Bowers, G.M., Loganathan, N., Yazaydin, A.O., and Kirkpatrick, R.J., in preparation, The structural and dynamical role of water in natural organic matter: a ^2H NMR study.

19. Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G, and Kirkpatrick, R.J., in preparation, Intercalation, structure and dynamics of CO_2 and H_2O into hectorite using GCMD simulations.

20. Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G, and Kirkpatrick, R.J., in preparation, Effect of size and ionic charge on the intercalation of CO_2 in hectorite using GCMD simulations.

21. Loganathan, N., Yazaydin, A.O., Bowers, G.M., Kalinichev, A.G, and Kirkpatrick, R.J., Adsorption of NOM at smectitic surfaces through classical molecular dynamics simulations.

22. Bowers, G.M., Loganathan, N., Yazaydin, A.O., Ferguson, B.O., Reddy, U.V., Argersinger, H.E., Aronson, T.A., Arey, B., Kirkpatrick, R.J., in preparation, Smectite-natural organic matter interactions in Ca^{2+} bearing systems on the molecular scale.

Table 2. Contributed and Invited Talks

Invited Talks

1. Geoffrey M. Bowers. *Bringing the Subsurface to Light (or Magnet): Role of Geochemistry in Energy and Climate*, St. Mary's College of Maryland Faculty Lecture Series, St. Mary's City, MD, March 2017.
2. Geoffrey M. Bowers. *Understanding Subsurface CO_2 Sequestration: Molecular-Scale Behavior at Smectite Interfaces,* Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science, Solomons, MD, September 2016.
3. Geoffrey M. Bowers, Narasimhan Loganathan, A. Ozgur Yazaydin, U. Venkataswara Reddy, R. James Kirkpatrick, David W. Hoyt, Sarah D. Burton. *Effect of Supercritical CO_2 on Cation Binding and Dynamics and H_2O in Smectites and Smectite-Natural Organic Matter Composites*, 252nd American Chemical Society National Meeting, Philadelphia, PA, August 2016.
4. Geoffrey M. Bowers. *Structure and Dynamics of Water, Ions, and Supercritical Fluids at Smectite and Smectite-Natural Organic Matter Interfaces*, State University of New York College of Environmental Science and Forestry, Syracuse, NY, April 2016.
5. Geoffrey M. Bowers. *Dirt, Energy, and PChem: Structure and Behavior of Natural Organic Matter Floccs, NOM-Clay Composites, and Their Solid-Fluid Interfaces Across Length and Time Scales*, Saint Mary's College of Maryland, Saint Mary's City, MD, December 2015.
6. Geoffrey M. Bowers. *Cation Dynamics in Clay-Natural Organic Matter Composites under Hydrated and Supercritical CO_2 Conditions*, Alfred State College, Alfred, NY, April 2015.
7. Geoffrey M. Bowers, Brennan O. Ferguson, Haley E. Argersinger, Timothy A. Johnson, U. Venkataswara Reddy, R. James Kirkpatrick, Bruce Arey. *Molecular-Scale Interactions of Ca^{2+}, NOM, H_2O, and Smectites in Ca-NOM-H_2O and Ca-smectite-NOM-H_2O Systems: Roles of pH History, NOM Activity, H_2O Activity, and Ionic Strength*, 249th American Chemical Society National Meeting, Denver, CO, March 2015.
8. R. James Kirkpatrick, Geoffrey M. Bowers, A. Ozgur Yazaydin, U. Venkataswara Reddy, Brennan O. Ferguson, David W. Hoyt, Sarah D. Burton, and Tamas Varga. *NMR and Computational Molecular Dynamics Investigation of Mineral-NOM Interactions at Atmospheric and Elevated Pressures*, 249th American Chemical Society National Meeting, Denver, CO, March 2015. – Modified and presented by G. Bowers.
9. Geoffrey M. Bowers. *Impact of Natural Organic Matter on Smectite-H_2O Interfacial Structure and Dynamics – Insights from NMR*, 50th Annual Meeting of the Clay Mineral Society, Champaign, IL, October 2013.

Contributed Talks and Posters

1. Geoffrey M. Bowers, Brennan O. Ferguson, Haley E. Argersinger, Narasimhan Loganathan, R. James Kirkpatrick, David W. Hoyt, Sarah D. Burton. *Molecular scale behavior at organo-mineral interfaces under supercritical CO_2 conditions,* 250th American Chemical Society National Meeting, Boston, MA, August 2015.
2. Haley E. Argersinger, Brennan O. Ferguson, R. James Kirkpatrick, Bruce Arey, and Geoffrey M. Bowers. *Role of pH and ionic strength in the structure and morphology of smectite-natural organic matter composite materials*, 250th American Chemical Society National Meeting, Boston, MA, August 2015.
3. Haley E. Argersinger, Geoffrey M. Bowers. *Influence of cation charge density, ionic strength, and pH on NOM particle size distributions in aqueous solution*, 249th American Chemical Society National Meeting, Denver, CO, March 2015.
4. Brennan O. Ferguson, Haley E. Argersinger, Timothy A. Johnson, R. James Kirkpatrick, Bruce Arey, Mark Bowden, Geoffrey M. Bowers. *Chemical controls of the micro-structure of NOM-smectite composite materials*, 249th American Chemical Society National Meeting, Denver, CO, March 2015.
5. Geoffrey M. Bowers, David W. Hoyt, Tamas Varga, Sarah Burton, Brennan O. Ferguson, R. James Kirkpatrick. *Influence of supercritical CO_2 on interfacial ion binding and dynamics in smectite-NOM composites*, 23rd Goldschmidt Conference, Sacramento, CA, June 2014.

6. Geoffrey M. Bowers, David W. Hoyt, Brennan O. Ferguson, Tamas Varga, Sarah Burton, R. James Kirkpatrick. *Influence of natural organic matter on CO_2 and Na^+ binding and dynamics under supercritical CO_2 storage reservoir conditions: An in situ MAS NMR study,* 247th American Chemical Society National Meeting, Dallas, TX, March 2013. **Presented by Session Chair due to Medical Emergency**
7. Geoffrey M. Bowers, Brennan O. Ferguson, Timothy A. Johnson, R. James Kirkpatrick. *Impact of natural organic matter on molecular-scale smectite-H_2O interfacial structure and dynamics,* 247th American Chemical Society National Meeting, Dallas, TX, March 2013. **Withdrawn for Medical Emergency**
8. Brennan O. Ferguson, Bruce Arey, Tamas Varga, Alice Dohnalkova, R. James Kirkpatrick, and Geoffrey M. Bowers. *X-ray diffraction, helium ion and electron microscopy of smectite-natural organic matter composites*, 50th Annual Meeting of the Clay Mineral Society, Champaign, IL, October 2013.

II. Research Completed During the Current Grant Period

Research during the current grant period has used NMR, XRD, IR, and computational methods to investigate the molecular scale structure, dynamics and energetics of a number of geochemically important topics, including the surfaces and interlayer galleries of clay minerals, NOM, NOM-clay composites including *in situ* high pressure and temperature NMR studies, and amorphous calcium carbonates. This work has been highly successful and has resulted in 16 peer reviewed papers published during the grant period, 1 paper submitted and in review, and 5 papers in preparation (Table 1). We have also been very active in publicizing our work at national and international meetings and seminars at US colleges and universities, with nine invited talks and eight contributed papers by Bowers and students alone during the four years DE-FG02-10ER16128 was active (Table 2). Important contributions were also made to many talks and seminars presented by our collaborators at Michigan State University. In addition, our work has been featured in several press releases and newsletters from PNNL's EMSL facility (October 2015 edition, "The Molecular Bond"; "Better Science" news brief, September 2015).

Clay Mineral Interlayers and Surfaces

The structure, dynamics and energetics of hydrous smectite interlayers and external surfaces is well suited for investigation using the combination of experimental NMR and computational molecular modeling, since both are sensitive to nearly every element in the periodic table, both provide information on molecular-scale structure, and together the two approaches allow us to access dynamic information over more than 10 orders of magnitude with respect to time. During the current grant period, we published a number of papers highlighting the complimentarity between NMR and MD. The American Mineralogist Centennial article (Kirkpatrick, et al., paper 8, Table 1) discusses the synergistic capabilities of the combined NMR and computational modeling approach and reviews the research on smectites and other layer structure materials up to late 2014. The paper by Morrow et al. (paper 1, Table 1) uses classical and enhanced (metadynamics) MD methods to investigate the changes in interlayer structure and energetics of Na-hectorite in the stable 1 and 2-layer hydrates. The results are in good agreement with our previous experimental NMR results (Bowers, et al., 2011) and provide a reference with which to compare the behavior and properties of smectites containing other cations. The experimental NMR paper investigating isotopically enriched ^{43}Ca-hectorite with ^2H_2O (Bowers et al., paper 5, Table 1) complements our previous work on ^{23}Na-,^{39}K-, and ^{133}Cs-hectorites (Bowers, et al., 2008, 2011; Weiss, et al., 1990) and extends the experimental basis for understanding the effects of cation hydration energy in smectite systems. The paper on modeling the external surfaces of Na-montmorillonite published jointly with our long-time collaborators at the Sandia National Laboratories (Greathouse et al., paper 9, Table 1) provides new results and a synthesis of the research on water-clay-cation interactions on the surfaces of nano-pores and is a reference for our ongoing research of the interaction of minerals, NOM, H_2O, and CO_2.

In a recent joint publication with our collaborators, Loganathan et al. (paper 15, Table 1) have used classical MD methods to extend the results of Morrow et al. discussed above to investigate the effects of cation hydration energy on the interlayer structure, energetics and dynamics of smectites (e.g., Figure 1). We find that Ca^{2+} has a relatively large hydration energy, and the results for Ca-hectorite (Loganathan et al. paper 15, Table 1) show the formation of a stable bilayer hydrate, consistent with XRD and NMR experiments (Bowers, paper 5, Table 1) from the current grant period. Ca^{2+} ions are adsorbed in outer sphere coordination both in the interlayer of the two-layer hydrate and on the external surfaces. Interlayer H_2O molecules in Ca-hectorite diffuse more slowly than in Na- and Cs-hectorite interlayers at all hydration states. The site residence times for H_2O molecules in nearest neighbor coordination to Ca^{2+} in hectorite interlayers are approximately eight times longer than in coordination to Cs^+ in Cs-hectorite and three times longer in H-bond coordination to the basal oxygens of the clay.

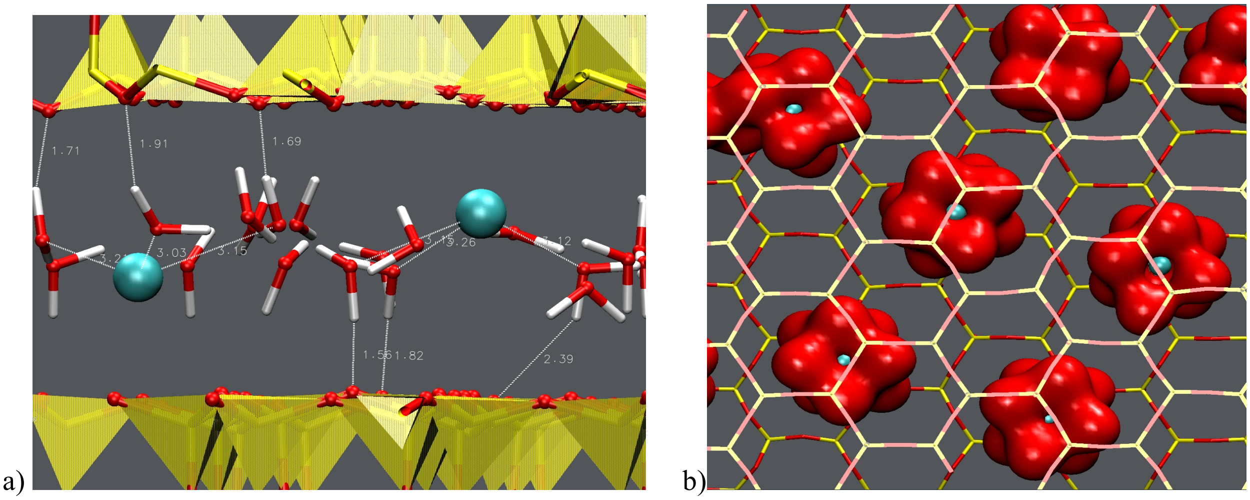

Figure 1: Schematic representations from MD simulations of H_2O molecules hydrating the basal surface and cations in a) the stable monolayer hydrate of Cs-hectorite viewed parallel to the clay surface showing the inner sphere Cs^+ coordination (Paper 13), and b) the stable bilayer hydrate of Ca-hectorite viewed along surface normal showing the outer sphere cubic antiprism Ca^{2+} coordination. For clarity only H_2O molecules coordinated to the metal ions are shown. Si tetrahedral, blue balls – Cs^+ / Ca^{2+} ions, red stick – O_{H2O}, white stick – $H_{H2O,}$ red surface in b) – O_{H2O} coordinated to Ca^{2+} ions.

In parallel, the joint comprehensive variable temperature and variable relative humidity ^2H NMR study of ^2H_2O dynamics in Cs-, Sr-, Ca-, Mg-, and Pb-hectorite (in conjunction with our previous ^2H_2O results for Na-, K-, and Ca-hectorite, Bowers et al., 2008, 2011; Bowers et al., paper 5, Table 1) shows that not just increasing hydration energy but also increasing cation polarizability cause decreasing rates of exchange of water molecules between sites coordinating the interlayer cation and only the basal surface (Reddy et al., paper 14, Table 1). This behavior is reflected in the increasing temperatures required for the transitions between rigidly held and anisotropically averaged water molecules and between anisotropically and isotropically averaged water molecules with increasing hydration energy and polarizability. For instance, for Mg-hectorite equilibrated at 43% R.H., at 298 and 313K the spectra contain one resonance representative of interlayer ^2H_2O undergoing anisotropic dynamics at frequencies $>10^5$ kHz (for a detailed description of the ^2H NMR spectra and shapes, see Bowers et al., 2011). The line shape and splitting of the two singularities is consistent with the combined H_2O rotation-hopping model of Bowers et al. (2011). At 233 and 253K, the narrow peak in the center represents water molecules not coordinated to Mg that are undergoing isotropic motion, and the two peaks on either side represent water molecules coordinated to Mg^{2+} and undergoing anisotropic rotational motion. The poorly resolved spectrum at 273K occurs because water molecules are exchanging between these two types of sites at frequencies of the order of 10^4 Hz. Mg^{2+} is the only cation for which this behavior is observed, because its high hydration energy (ΔH_{hydr}= 1907.5kJ/mol) results in relatively long residence times for ^2H_2O in nearest neighbor coordination to the cation. At 173K and 193K, the broad resonances with maxima near ±70 kHz represents rigidly held ^2H_2O molecules and the broad but symmetrical peak such molecules undergoing isotropic motion at frequencies of the order of 10^5 Hz. These are probably ^2H_2O molecules not coordinated to Mg^{2+}. The spectrum at 213K is transitional. The ^2H NMR quadrupolar coupling constant is proportional to the hydrogen bond strength (similar to the O-H stretching frequency observed by vibrational spectroscopy), and the results show that the H-bond strengths of rigidly held water molecules in hectorite interlayers (H-bond donation between H_2O molecules and from H_2O molecules to basal oxygens) are very similar to those in ice 1h. XRD shows that ice is not present for this sample at any temperature.

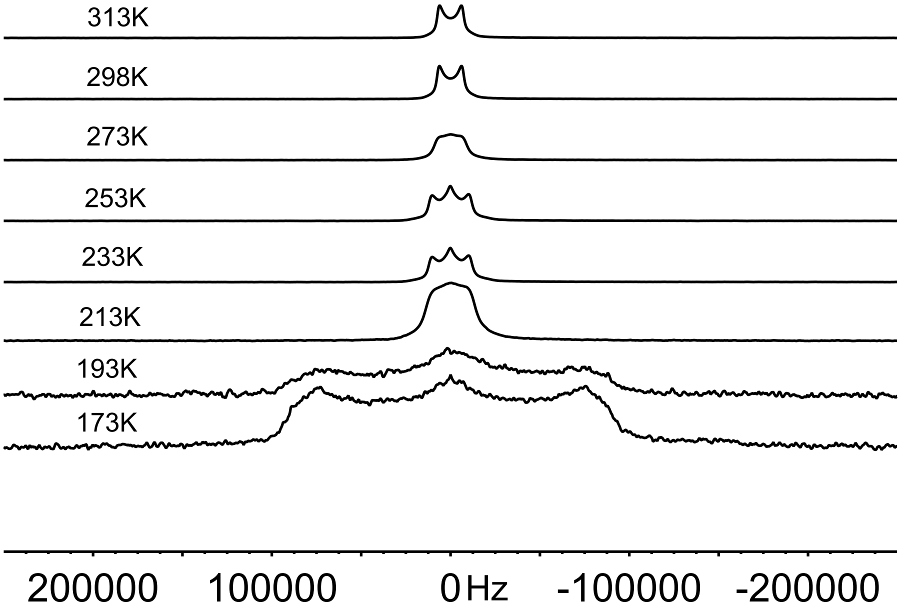

Figure 2. Static ^2H NMR spectra of Mg-hectorite equilibrated at 43%R.H. collected at the indicated temperatures.

Interaction of Cations and Water with NOM

In order to investigate the interaction of organic species with mineral surfaces, it is essential to understand the molecular scale interactions of cations and water molecules with the organic species. In work from previous DOE BES supported grant periods, we used computational MD methods to show how the cation hydration energy affects the structural environments, dynamics and energetics of cation-NOM binding and the water dynamics in such systems, with the results broadly paralleling the behavior in smectite interlayers discussed above (e.g., Iskrenova-Tchoukova, et al., 2010). During the current grant period, we used experimental He ion microscopy (HeIM) and variable temperature ^{43}Ca NMR spectroscopy to probe similar questions for ^{43}Ca-exchanged Suwannee River NOM and its fulvic acid (FA) and humic acid (HA) fractions on molecular and micron length scales. HeIM provides significantly enhanced image resolution and depth-of-field compared to scanning electron microscopy due to the larger number of secondary backscatter electrons produced by the heavy helium ion and is a very effective tool for examining mineral-NOM systems (Figure 3). For these samples, HeIM shows a rich, scale dependent diversity of textures that are based on building blocks ~10 nm in diameter. This size is comparable to the radii of gyration of individual Suwannee River molecules in solution determined by small-angle X-ray scattering (Thurman, et al., 1982). The ^{43}Ca NMR results for samples equilibrated at 100% R.H. (equilibration over 99% isotopically enriched ^2H_2O) shows that both ionic strength and the protonation state of the reactive functional groups in NOM affects Ca^{2+} binding and dynamics (Bowers et al., paper 10, Table 1), as suggested by previous MD results (Sutton and Sposito, 2006; Iskrenova-Tchoukova, et al., 2010). The data show a wide range of disordered Ca^{2+} binding environments in floccs formed from Ca^{2+}/NOM solutions. There are two distinct populations of Ca^{2+} environments at low pHs, where all the amine, phenolic and carboxylic functional groups are protonated, and a continuous set of environments at high pH, where all the functional groups are deprotonated. When excess Ca^{2+} ions are present, the dynamic picture reflects a strong association of ions with the NOM surface at temperatures low enough to form ice in the pores but rapid dynamical exchange between excess pore Ca^{2+} and surface bound Ca^{2+} when the pores are filled with liquid water (Figure 4). When the critical NOM functional groups are deprotonated and no excess Ca^{2+} is present, dynamics representative of hopping between sites closely associated with the NOM surface occurs at all temperatures. This behavior is consistent with the MD results cited above that show strong associations of Ca^{2+} ions with deprotonated carboxylic acid groups.

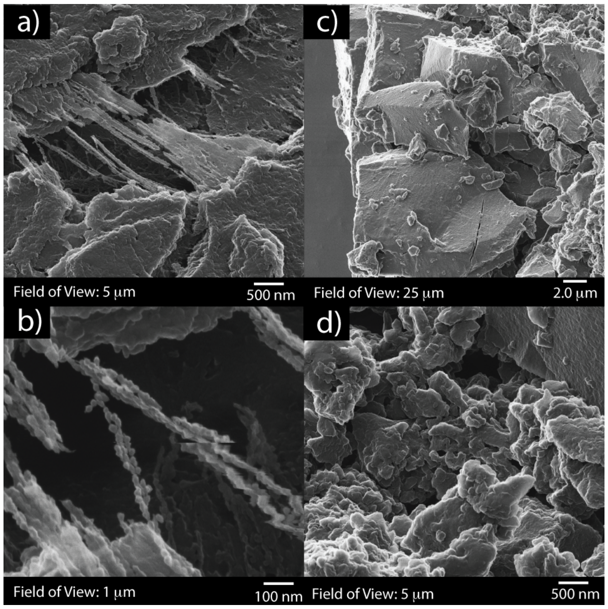

Figure 3. Helium-ion microscopy images of Ca-NOM-pH12 (a-d). Flocculated NOM is dominated by faceted pieces (c) and globular morphologies (d) that appear to be assemblages of ~10 nm spherical entities [see the "string of pearls" filaments between larger particles in (a-b)].

The variable temperature and variable relative humidity (0%, 43% and 100%) ^{2}H NMR results for Suwannee River NOM, HA, and FA as received and without exchangeable cations shows the presence of ^{2}H with a range of large quadrupole coupling constants (the broad features in Figure 5A) as well as ^2H_2O molecules that undergo isotropic dynamics (the narrower resonances in Figure 5A; Reddy et al., paper 18, Table 1). The intensity of the narrow peak decreases with decreasing temperature, probably due mostly to the frequencies of the rotational and translational motion of these molecules falling below ~10^4 Hz. The presence of the broad feature at even 313K is due to the exchange of deuterons onto the functional groups of the NOMs (probably dominated by exchange onto carboxylic groups), which prevents them from undergoing isotropic averaging. This interpretation is supported by the increase in the relative intensity of the broad feature from HA to the full NOM to FA for samples equilibrated at 43% R.H. (Figure 5B), since this change parallels the increase in the concentration of reactive oxygen-bearing functional groups in these three samples. SEM images show greater porosity for the FA than for the NOM and HA, as well. The lack of well-resolved singularities in the broad feature, which contrasts with the ^{2}H spectra of smectites at low temperatures (Figure 2), demonstrates a wide range of quadrupolar coupling constants representative of a distribution of H-bond (O─H-----O) distances generally less than the H-bond distances in ice 1h. For the 43% RH samples at room temperature 298K, the relative intensity of the broad quadrupolar pattern decreases in the order FA > NOM > HA (Figure 5B).

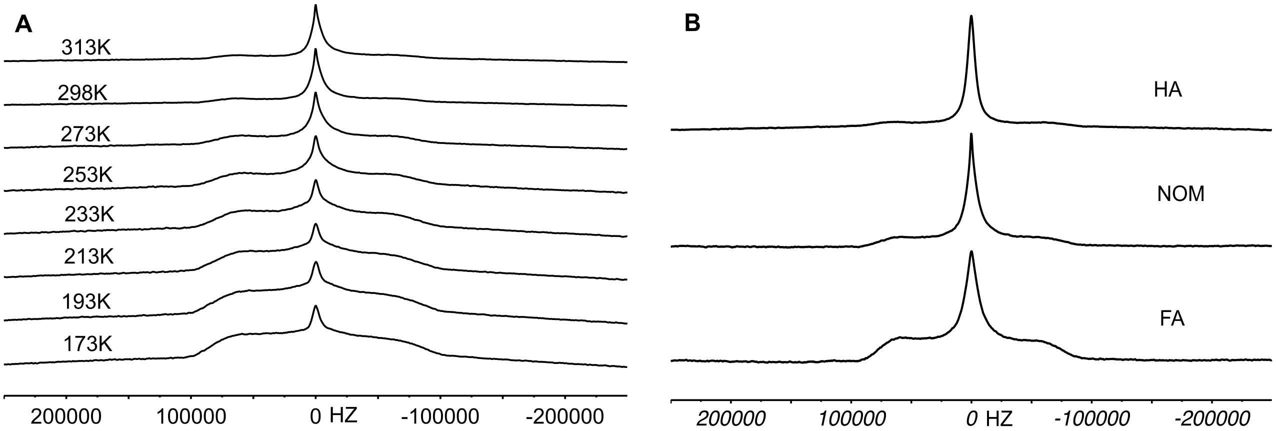

Figure 5. ^{2}H NMR spectra of A) NOM equilibrated at 43% R.H. and collected at the indicated temperature, and B) HA (top), NOM (middle), and FA (bottom) equilibrated at 43% R.H. and collected at 298K.

Hydrous Clay-NOM Composites

The molecular scale interactions that control the binding of organic species to mineral surfaces is thought to be dominated by hydrophobic interactions at low pHs (where the functional groups of the organic matter are protonated) supplemented by cation bridging and DLVO effects at neutral to high pHs (where some or all of the functional groups are deprotonated [e.g., Sutton and Sposito, 2006]). In many respects, several important aspects of these interactions, such as the effects of different cations; the role of water molecules and H-bond interactions; and detailed structure, dynamical behavior, and energetics remain poorly understood.

During the current grant period we prepared composites of hectorite and Suwannee River NOM and its FA and HA components at acidic and basic pHs and characterized them using X-ray diffraction, SEM/energy dispersive X-ray composition analysis, and HeIM (Ferguson, et al., submitted; paper 17, Table 1). To our knowledge, this paper will be the first published HeIM study of clays and clay-NOM composites. The results show that NOM is not incorporated into the smectite interlayers. Rather, at basic pHs, it forms relatively thin (< 1 µm) and hummocky coatings. The structure of these coatings is probably influenced by cation bridging and DLVO stabilization of NOM in solution at these pHs. In contrast, at acidic pHs, the coatings are relatively thick (> 3 µm) and have a complex morphology with many different types and size-scales of bumps, ridges, and faceted surfaces (Figure 6). Behavior in these systems is probably dominated by hydrophobic interactions and rapid precipitation of NOM from solution with decreasing pH. In general, the properties of the cation appear to have little influence on the morphology and micron-scale structure of NOM-smectite composites, although the Ca^{2+} system is the only one that forms NOM floccs at acidic pH that then agglomerate onto the clay surface, suggesting that ionic strength or cation valence may be important in the NOM-smectite association process. XRD results show that none of these NOM coatings prevent interlayer hydration and that expansion of the composites is generally consistent with the behavior of base clays with Cs^+, K^+, Na^+, or Ca^{2+} as the charge-balancing cation. The thicker coatings do appear to decrease the rate of hydration and dehydration, at least in the case of the Ca^{2+} bearing system. The NOM coatings stabilize interlayer H_2O, with “dry” clay-NOM composites generally exhibiting larger basal spacings than their corresponding base clay when the charge balancing cation has a relatively high affinity for H_2O. These observations are consistent with the known ability of NOM to sorb and retain water in surface soils.

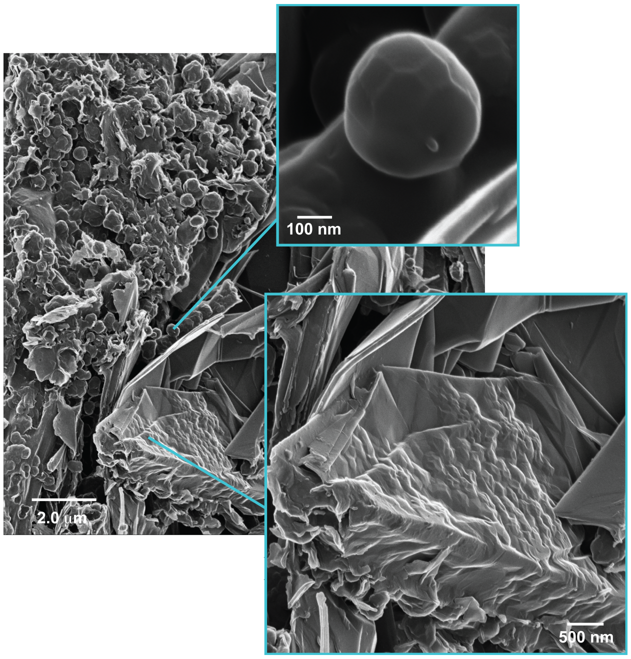

Figure 6. Image of Ca-hectorite-NOM composite prepared at pH 2. One can see flat sheets corresponding to the original smectite layers, plus several different textures and coatings of nearly pure NOM.

Variable temperature ^{43}Ca NMR spectroscopy of Ca-hectorite-NOM composites shows that the NOM fraction (HA, FA, or NOM), preparation pH, and ionic strength have little influence on the binding and dynamics of Ca^{2+} in the composites (Bowers et al., in preparation, paper 22 in Table 1). The ^{43}Ca NMR results suggest that a majority of the Ca^{2+} is associated with environments nearly identical to those of base Ca-hectorite; most likely fully hydrated Ca^{2+} ions located within the interlayers or ~5Å of the clay external surfaces (Figure 7). This is in full agreement with the HeIM observations discussed above and SEM/EDS results that suggest little Ca^{2+} incorporation in NOM floccs. However, the composites all exhibit consistent shifts to more positive NMR resonance frequencies and slightly greater linewidths with respect to base Ca-hectorite. The magnitude of the shift and linewidth increase are independent of pH, NOM fraction, or ionic strength. These observations suggest that the presence of NOM does exert some influence on the mean Ca^{2+} coordination environment, either reflecting a small amount of cation bridging predicted by the molecular modeling of Sutton and Sposito (2006) or a slight increase in the overall disorder in the system (perhaps more turbostratic disorder, for example). Similar small variations in the ^{43}Ca chemical shift have been observed for another inorganic/organic hybrid in a study funded previously by this grant (Ca-oxalate based renal stones; Bowers and Kirkpatrick 2011). Together, the two studies suggest that these small shifts compared to purely inorganic systems may be diagnostic of Ca^{2+} bridging between the inorganic surface and organic molecules in inorganic/organic hybrid materials.

Computationally, MD modeling of the exterior surfaces of a Na-hectorite-H_2O system containing molecules of the standard TNB model for NOM shows that at near-neutral pH conditions (carboxylic groups deprotonated, phenolic and amine groups protonated) Na^+ does not bridge the NOM to the clay surface and the NOM molecules along with their charge balancing Na^+ ions drift into the aqueous fluid (Yazaydin, paper 11, Table 1). In terms of energetics, hydration of the net-charge neutral Na-NOM molecule outweighs the sum of its Coulombic and dispersive interactions with the net-charge neutral Na clay particle and the interactions of the water molecules with the hydrophobic structural elements of the NOM. The aggregation of NOM molecules in solution appears to be driven not by Na^+ bridging between the molecules but by hydrophobic interactions between them.

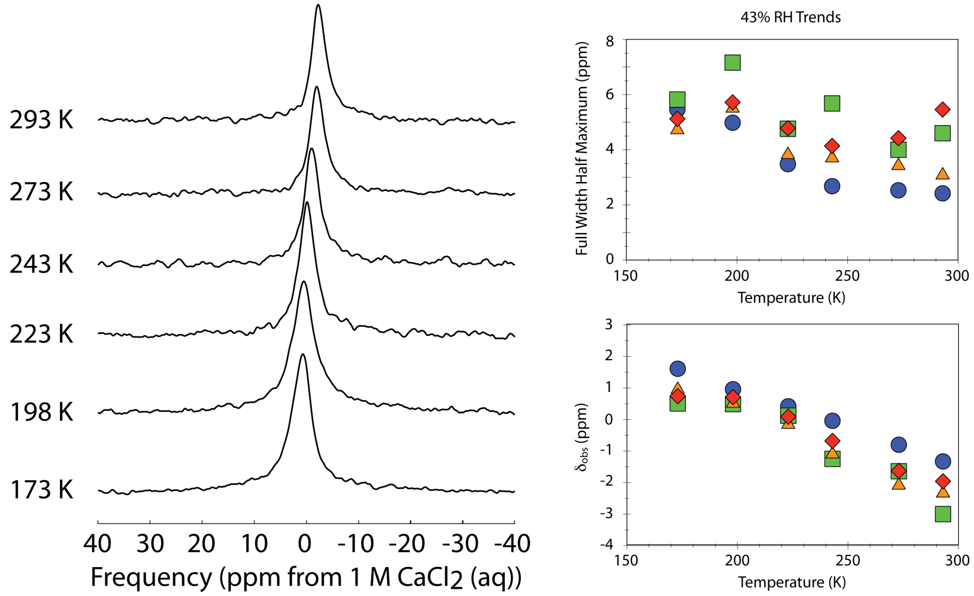

Figure 7. ^{43}Ca variable temperature NMR spectra of a Ca-hectorite-NOM composite (left), showing line shapes and temperature variations quite similar to base Ca-hectorite published in Bowers et al. 2014. However, when comparing the trends in chemical shift and line width with temperature (right), one can see that composites (red, green, orange) all exhibit slightly more negative chemical shifts and slightly greater line widths compared to the base Ca-hectorite (blue dots). These small changes are independent of the NOM fraction, preparation pH, and solution ionic strength.

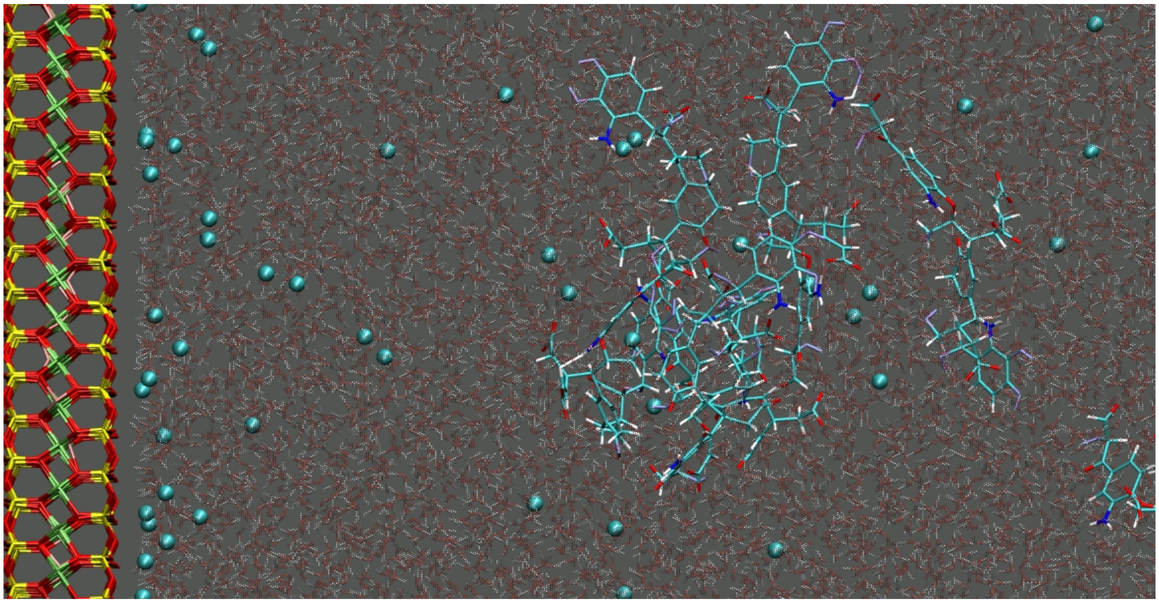

Figure 8. Snapshot from an MD simulation of the H_2O-NOM-Cs-hectorite system showing the aggregation of NOM (molecules with blue spokes) at distances far from the hectorite (001) surface (structure with red, green and yellow spokes). Blue atoms are Cs^+.

Similar calculations with Ca^{2+} and Cs^+ replacing the Na^+ are being completed as part of the no-cost extension of the sister grant at Michigan State University. Preliminary analysis of the trajectories for the system with Cs^+ and only H_2O shows that NOM remains in the aqueous phase forming aggregates (Figure

8). As for Na-hectorite, hydrophobic interactions between NOM molecules are responsible for the formation of the aggregates in Cs-hectorites. In contrast, in the Ca^{2+} system with only H_2O, some of the NOM molecules are located close to the hectorite surface, apparently bridged through outer sphere adsorbed Ca^{2+}. Ca^{2+} also aides the aggregation of the NOM molecules in solution.

Clay-H_2O-CO_2-NOM Systems

For the laboratory experiments, we established a new collaboration with scientists at PNNL leading to publication of the first *in situ* NMR experiments with clay-NOM composites at temperatures and CO_2 pressures in the supercritical CO_2 ($scCO_2$) field (Na-hectorite-Suwannee River HA at T = 50°C, P_{CO2} = atmospheric and 90 bar; Bowers et al., paper 6 in Table 1) and the first systematic study of how the properties of the charge-balancing cation impact the adsorption/intercalation and dynamics of CO_2 in smectite interlayers exposed to $scCO_2$ (Paper 16, Table 1).

Our first study focused on using *in situ* $scCO_2$ NMR to understand how a NOM coating affects the intercalation and dynamics of the ions, H_2O, and adsorbed CO_2 at 90 bar CO_2 and 50°C. The samples were initially equilibrated at 43% RH at atmospheric pressure, leading to a supercritical fluid humidity in the NMR rotors of between 0 % and 43% RH, conditions that likely produce a well-hydrated Na-hectorite interlayer. The ^{13}C NMR spectra contain signal for only ^{13}C-enriched CO_2 rapidly tumbling in the supercritical fluid phase, but do show small line-width increases reflecting increased association of CO_2 with the base clay and composite surfaces. The ^{13}C and ^{23}Na T_1 relaxation rates and the ^{23}Na lineshapes show that CO_2 influences the Na^+ coordination environment and dynamics, leading to more symmetric Na^+ coordination and generally more rapid Na^+ relaxation with $scCO_2$ present. This could be a result of altered H_2O dynamics in the presence of the hydrophobic fluid, an alteration in the stacking of the layers in the presence of $scCO_2$, or more likely a change in interlayer hydration state due to the presence of $scCO_2$. The presence of Suwannee River HA has little effect on the ^{23}Na or ^{13}C NMR spectra but did lead to slower T_1 relaxation rates for a portion of the ^{23}Na population with and without $scCO_2$ present.

More recently, we obtained ^{43}Ca, ^{133}Cs, and ^{13}C NMR data for hydrated Cs- and Ca-hectorite (Bowers et al., paper 16, Table 1) exposed to CO_2 at 90 bar and 50°C and integrated that with in situ $scCO_2$ IR spectroscopy and XRD to describe the role of cations on CO_2 adsorption and dynamics. We find that CO_2 can enter hectorite interlayers, but only when the basal spacing is approximately that of a one water layer (1WL) hydrate and that its total uptake and binding environments are strongly influenced by the properties of the charge-balancing cation (CBC). For example, charge-balancing cations with low charge density and large radii can incorporate CO_2 into the interlayer in a dry state and tend to continue retaining much of this CO_2 even at 100% RH of the $scCO_2$ phase. There is evidence that at least a fraction of this interlayer CO_2 is part of the coordination shell of the CBCs in this case. However, when ions with high charge densities and small radii are present, interlayer adsorption of CO_2 requires that enough H_2O is present to produce a 1WL-type basal spacing (~11.8-12.2 Å). Here, the cations scavenge H_2O available in the supercritical fluid and tend to remain fully hydrated in the interlayer space, with adsorbed CO_2 not participating in ion coordination shells. Likewise, the fraction of interlayer adsorbed CO_2 drops more significantly with increasing RH for these types of systems, though some CO_2 remains adsorbed in the interlayer at all $scCO_2$ RH values. The ^{13}C MAS NMR showed a spinning sideband pattern indicative of anisotropically reorienting CO_2 in all samples at low H_2O content (Figure 9). The data show significant interlayer incorporation of Cs-hectorite at low RH (the broad sidebands), but that interlayer CO_2 is not significant for Na-hectorite or Ca-hectorite until they are equilibrated at a humidity producing a 1WL-type basal spacing. For Na-hectorite and Ca-hectorite, as the humidity increases beyond the 1WL-type state, the ratio of surface-adsorbed to interlayer adsorbed CO_2 increases, while the Cs-hectorite appears to increase its interlayer adsorbed CO_2. These data are consisten with previous publications by Loring et al. (2012, 2013, 2014) and Schaef et al. (2012, 2015). By comparing the breadth and sideband intensity patterns to theoretical spectra in Ratcliffe and Ripmeister (1986), we showed that CO_2 adsorbed in 1WL-type interlayers reorients rapidly (> 10^5 Hz) about an axis perpendicular to the clay basal surface, with the long axis of the CO_2 molecule parallel to the clay basal surfaces. For 2WL-type interlayers (~15 Å basal spacing), the signal for adsorbed CO_2 is either not visible or experiences reorientational dynamics that make its ^{13}C NMR signature match that of the 1WL-type case. External surface adsorbed CO_2 largely has similar dynamics, but is able to sample a greater number of angular orientations with respect to the clay basal surface, leading to narrower resonances and spinning sideband patterns for external surface adsorbed CO_2. The ^{13}C NMR peak areas and masses of clay/CO_2 in the rotors allowed us to constrain the fraction of $scCO_2$ adsorbed in each environment.

Similar experiments with Cs-hectorite-NOM composites at several pHs and Ca-hectorite-NOM pH 12 show that the fraction of adsorbed CO_2 decreases when NOM is present, consistent with the idea that NOM has little interactions with $scCO_2$. Likewise, the ^{133}Cs chemical shift shows strong evidence of dehydration in the Cs-hectorite-NOM samples when $scCO_2$ is introduced (large negative chemical shift), just as for the base Cs-hectorite. This observation is consistent with the weak hydration of Cs^+ in hectorite interlayers shown by the MD simulations of publication 13 (Table 1) and incorporation of some CO_2 molecules directly in the Cs^+ coordination shell. The effects of NOM and $scCO_2$ on the ^{43}Ca NMR

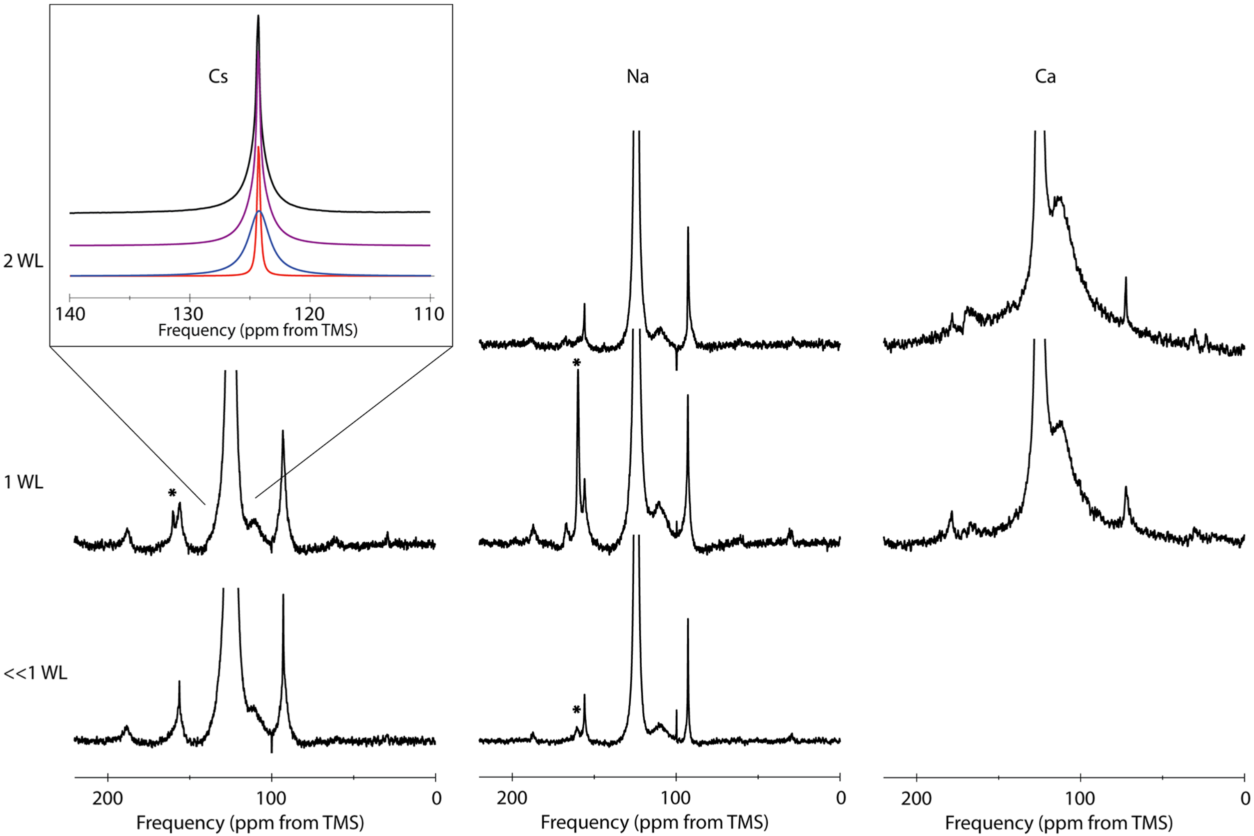

Figure 9. ^{13}C MAS NMR spectra of Cs-hectorite, Na-hectorite, and Ca-hectorite equilibrated at initial humidities designed to produce basal spacings of the type shown on the far left of each row. Narrow sidebands in the narrow sideband manifold are external surface-adsorbed CO_2 with more dynamic degrees of freedom with respect to the angle with the basal surface. Broader sidebands in the broader manifold represent CO_2 adsorbed in 1WL-type (~12.2 Å basal spacing) clay interlayers. Low charge density and large radius of the ion favors interlayer CO_2 adsorption; high charge density ions favor hydration and interlayer exclusion/external surface adsorption of CO_2.

behavior is quite similar to those observed for ^{23}Na-hectorite described earlier; namely a small increase in the site symmetry that does not impact the main Ca^{2+} coordination environment (in this case, a full hydration shell). The final interpretation of the composite samples in contact with $scCO_2$ is nearly identical to that of the base clays discussed in the previous paragraph.

MD modeling of Na-hectorite-CO_2 and Na-hectorite-CO_2-H_2O systems show that with only CO_2 as the fluid phase the NOM molecules are pushed tightly to the clay surface with Na^+ ions bridging the carboxylic groups on the NOM to the clay surface and the dominantly hydrophobic side of the molecule with aromatic and aliphatic groups facing the CO_2 (Yazaydin et al., paper 11, Table 1). With both H_2O and CO_2 present, the H_2O forms a film on the clay surface that contains only a few CO_2 molecules, and the CO_2 with only a few H_2O molecules forms a separate phase in the center of the modeled nano-pore. This mutual insolubility of the H_2O and CO_2 is in full agreement with the known low mutual solubility of these species at the P and T conditions modeled (e.g., Takenouchi and Kennedy, 1964). With both H_2O and CO_2 present, the NOM molecules move to the H_2O and CO_2 interface, with their dominantly hydrophilic side and associated Na^+ ions on the H_2O side and their dominantly hydrophobic side on the CO_2 side of the interface.

With respect to the effects of CO_2 on the dynamics in smectite interlayers, we have undertaken classical MD and adaptive biasing force modeling of Na-montmorillonite with a mixed mono-layer of 4 H_2O/Na^+ and 1.33 CO_2/Na^+ (0.75 Na^+/20 oxygen formula unit) at supercritical CO_2 conditions (T=323K and P=89 bars). The results show that H_2O and CO_2 form a single layer in the middle of the interlayer and that the H_2O clusters around the Na^+ with few CO_2 in nearest coordination to the Na^+ (Sena et al., Paper 12, Table 1). This configuration provides dynamic percolation pathways that allow single-file diffusion of the CO_2 molecules parallel to the clay layers and allows for Na^+ diffusion between the basal surfaces on the opposite sides of the interlayer.

Similar classical MD modeling of Na-montmorillonite interlayers containing CO_2, poly(ethylene glycol) (PEG), and both CO_2 and PEG provide a detailed structural model for the arrangement of this important model polymer in smectite interlayers and show that the arrangement of the CO_2 molecules is similar to that in supercritical CO_2 (Krishnan et al., paper 3, Table 1). One of the important insights from this study is that the dry ice structure is a good reference model for CO_2 in systems containing O-atoms in the same way that the ice 1h structure is a reference model for the structure of liquid water. The results show that relative to the base clay, the cooperative motion of the Na^+ and CO_2 increases the Na^+ diffusion rate and demonstrate the importance of the –C-O-C- ether oxygens in coordinating to CO_2 molecules.

Amorphous Calcium Carbonate

The Bowers group concluded its experimental studies in the prior three year grant period and did not contribute new data to this work during the recently concluded grant period.

III. References

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IV. Budget Explanation

We have \$3,828 remaining in the budget. The reasons for this are discussed in the introduction, but namely we were able to complete our work objectives without tapping into the budget line for elemental analysis/diffraction studies and because Bowers relocated to St. Mary's College of Maryland in AY 2016/2017.

V. Estimate of Unobligated Balance

See above.