The Role of Interfacial Processes on Mineral Transformations in Wet Supercritical CO_2.

Andrew R. Felmy[1], David A. Dixon[2], Jianzhi Hu[1], Eugene Ilton[1], Kevin M. Rosso[1], James R. Rustad[3], and Zheming Wang[1].

1. The Pacific Northwest National Laboratory, 2. The University of Alabama, 3. The University of California, Davis.

Introduction: The capture and storage of carbon dioxide and other greenhouse gases in deep geologic formations represents one of the most promising options for mitigating the impacts of greenhouse gases on global warming owing to the potentially large capacity of these formations and their broad regional availability (Bachu 2002; Bachu and Adams 2003; Benson and Surles 2006; Bachu 2008). A critical issue is to demonstrate that CO_2 will remain stored over the long-term in the geological formation where it is injected. In this regard, mineral-fluid interactions are of prime importance since such reactions can result in the long term sequestration of CO_2 by trapping in mineral phases such as carbonates as well as influencing the subsurface migration of the disposed fluids via creation or plugging of pores or fractures in the host rock strata (Kaszuba, Janecky et al. 2003; Pruess, Xu et al. 2003; Kaszuba, Janecky et al. 2005; Xu, Apps et al. 2007).

Previous research on mineral-fluid interaction for subsurface CO_2 storage has focused almost entirely on the aqueous phase, i.e., reactivity with aqueous solutions or brines containing dissolved CO_2. However, interactions with neat to water-saturated non-aqueous fluids are of equal if not more importance over the long-term for the following reasons. First, the introduced supercritical CO_2 ($scCO_2$) is less dense than the aqueous phase (or oil if in an empty petroleum reservoir) over almost all conditions relevant to geologic sequestration. Consequently, a buoyant $scCO_2$ plume forms and ultimately dominates the contact area with the isolating caprock. Second, the injected $scCO_2$ is likely to contain water initially or soon after injection. The $scCO_2$ is both highly diffusive owing to its low viscosity and the presence of water alters the mineral wettability of the $scCO_2$ phase. Consequently, it is possible that wet $scCO_2$will permeate the overlying caprock pore network to a greater extent than previously considered. Third, mineral reactions in neat to water-saturated non-aqueous fluids fundamentally differ from those in aqueous solutions. Specifically, direct interaction of the $scCO_2$-dominated fluid with mineral surfaces results in localized mineral replacement or transformation reactions unlike dissolution/re-precipitation reactions involving solution phase ion transport. Furthermore, reactive layers that form in $scCO_2$-dominated fluids cannot back dissolve into a solution phase; such transformation reactions are more likely to result in pore or fracture plugging than the corresponding reactions in aqueous solution. Alternatively, low water $scCO_2$-dominated fluids are expected to drive some mineral transformations via dehydration/ hydration processes (such as interlayer water stripping from clays), which could lead to mineral volume decrease and enhanced permeability in caprocks. Collectively, therefore, mineral interactions with neat to water-saturated $scCO_2$-dominated fluids are pivotal and could result in either the stable sequestration of CO_2 by trapping in mineral phases such as metal carbonates, or degraded seals via creation of permeable zones in the caprock.

Approach: The primary objective of this project is to unravel the molecular mechanisms governing the reactivity of mineral phases important in the geologic sequestration of CO_2 with variably wet $scCO_2$ as a function of T, P, mineral structure/composition and solution phase composition. A key aspect of the research program is the integration of molecular level theory and experiment to provide unique insight into the molecular level phenomena that occur and establish a basis for how such molecular level processes can be represented at the macroscopic level.

Two classes of mineral phases will be emphasized: orthosilicates (e.g., forsterite, Mg_2SiO_4) and hydrous phyllosilicates (e.g., montmorillonite, hydrated sodium calcium aluminium magnesium silicate hydroxide

$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$). Orthosilicates have been well studied with respect to their structure and aqueous dissolution behavior. This provides an information base to compare with their behavior in neat and hydrous $scCO_2$. Orthosilicates also represent important reactive phases with respect to carbonation in many reservoir environments (especially basalts), and our previous studies have shown the critical importance of small amounts of water in determining the reactivity of these phases in CO_2 dominated fluids. Phyllosilicates can be the majority phase in low permeability cap-rocks. Their reactivity towards CO_2, and wetting and hydration/dehydration behavior directly affect one of the most important issues in subsurface CO_2 sequestration, namely the long term sealing capability of shale dominated caprocks. By studying these two important mineral classes we will be able to develop important molecular level insight into the reactivity of water and CO_2 on mineral surfaces with different interface/interlayer water structures as well as provide insight into appropriate models for mineral reactivity and thermodynamics.

The orthosilicate and phyllosilicate phases will be initially examined for intrinsic water content and dehydroxylation temperatures will be determined by temperature programmed desorption. We will use *in situ* FTIR (Fourier Transform Infrared) to quantify the amount of adsorbed water and characterize its average molecular structure (i.e., disordered versus ice-like) as a function of the water content of $scCO_2$ and both mineral structure and composition. We will also seek relationships between the numbers of sorbed water layers, and hydroxyl group type (e.g., isolated, hydrogen-bonded, and bridging) and surface concentration. Deuteration of the water or surface hydroxyls will be used if necessary to avoid CO_2 rendering the hydroxyl spectral region opaque (Tripp and Combes, 1998). This approach, possibly in combination with oxygen isotopic labeling, should also allow us to determine water adsorption rates and water exchange kinetics at the surface/interlayer by recording isotopic scrambling. We will predict vibrational frequencies with electronic structure calculations on model systems for different structures and isotope combinations to help interpret the spectra. It is also feasible that, under certain conditions, surface/interlayer water and possibly hydroxyls will be largely stripped off by $scCO_2$ yielding an ostensibly CO_2 wetted interface. Studies of both the orthosilicate series and the phyllosilicates will enable correlations to be sought between water properties on the fluid side of the interface with dynamic properties of the mineral surface including ligand exchange rates.

The hydration/dehydration mechanisms of the mineral surfaces/interlayers in $scCO_2$ containing variable amount of H_2O will be also be probed *via* high pressure in situ ^2H and ^1H MAS NMR including high pressure static ^2H NMR spectroscopy using a high pressure *in situ* NMR probe in the EMSL. The dynamical studies of the clays will be coupled to *in situ* XRD measurements of the d_{001} spacing. For ^2H MAS NMR, H_2O will be replaced by D_2O to avoid the background proton interference from the clay materials, e.g., the surface Si-OH protons and other bulk and surface protons. Note that replacing H_2O with D_2O will not change the relevant chemistry. ^2H NMR is a well-established method[i] (Schmidt-Rohr and Speiss 1999) for probing the molecular dynamics and bonding environment of the deuteron. We propose to use a combination of our unique high pressure MAS probe and ^2H NMR (both MAS and static experiments) to study the bonding environment of water as a function of mineral composition/structure under $scCO_2$ conditions. We will obtain mechanistic details on the mobility of surface bonded D_2O, e.g., jump motion or rotation about certain symmetrical axis, using lineshape analysis coupled with various relaxation time, e.g., T_1 and T_2, measurements. The ratio of surface-bound D_2O to those dissolved in $scCO_2$ will be determined by quantitatively measuring their corresponding peak areas. The hydration/dehydration and dynamics/kinetics, and hence the activation energy, will be obtained by carrying out variable temperature ^2H NMR experiments. This will provide information about the chemical environment and the molecular dynamics of water in $scCO_2$. In parallel with the ^2H NMR study, ^1H MAS NMR will also be carried out to examine the mineral surface protons that are interacting with the D_2O. This information will complement the results from ^2H NMR study. NMR also represents an ideal method to probe the reactivity of the divalent orthosilicates since the reaction components including Si (via ^{29}Si), and carbonate (via ^{13}C) can be directly probed by NMR spectroscopy. By carefully

analyzing the resulting NMR spectra using molecular simulation it will be possible to identify the specific coordination environments responsible for the observed NMR spectra. We have had a great deal of success in interpreting NMR spectroscopic measurements including identification of unknown enantomers of different silica clusters (Cho et al. 2006) by combining experimental and computational NMR approaches. In the case of ^{13}C NMR we will also take advantage of the significantly enhanced sensitivity using ^{13}C enriched CO_2 to better refine the species formed and the reaction dynamics.

Longer term macroscopic mineral reactivity and transformation mechanisms will also be studied using high pressure cells located outside of EMSL at PNNL. These cells are capable of measurement in both batch and flow-through mode and can be conducted at pressures ranging up to 200 bars and temperatures up to 475 K. *Ex situ* solid phase analysis both before and after reaction will be conducted in the EMSL using electron microscopy (FIB/SEM and TEM) scanning probe microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and time-of-flight SIMS chemical mapping analyses.

Our experimental effort will be closely integrated with a computational effort. Our overall computational approach will integrate molecular dynamics simulations with highly accurate electronic structure calculations and advanced chemimetric techniques which we have used previously to study the incorporation of carbonate anions into mineral structures (Rustad and Zarzycki 2008; Boily and Felmy 2008; Boily et al. 2006). A key initial effort in the computational approach will be the construction of a fully reactive parameterized interaction potential capable of describing all species in the CO_2-H_2O-MgO-SiO_2 system. We will begin with the FeO-SiO_2-H_2O potentials that we have built during the past 15 years (Halley et al.1993; Rustad and Hay, 1995; Rustad et al. 1995, 1998, 2003). Because of its ability to treat the dissociation of water into H^+ and OH^-, this has been a remarkably versatile functional form for potential development for modeling geochemical phenomena. This model will then be used to perform a series of molecular dynamics calculations of the Mg_2SiO_4-[CO_2-H_2O] interface for a range of CO_2-H_2O fluid compositions. The goal of this work is to obtain a qualitative understanding of the pathways for forsterite carbonation reactions.

Computationally intensive electronic structure calculations will also be performed of potential energy surfaces and spectroscopic properties for carbonation reaction pathways. We will perform quantum chemical calculations of critical regions of the potential energy surfaces (PESs) for the reactions of CO_2 and H_2O with different ions and cluster models of surfaces. We will model interactions of CO_2, HCO_3^- and OH^- with simple model complexes until we get the results of the MD simulations, for the M^{2+} ions which corresponds to a simple initial model for the edge and bridging sites present in silicates and M^{2+} substituted silicates. We will calculate the optimum geometries, vibrational spectra, and binding energies of CO_2, HCO_3^- CO_3^{2-}, and OH^- at these sites or by appropriate substitution. The effects of the solvent will be incorporated by using self-consistent reaction field (SCRF) approaches such as the polarizable continuum models PCM (Tomasi et. al., 2005), the COSMO approach (Klamt and Schüürmann, 1993), as in our recent study of the reaction of CO_2 with H_2O or the approaches originally developed by Chipman and co-workers (Chipman 1997, 1999, 2000; Zhan et al. 1998; Zhan and Chipman 1998) used in our previous studies (Zhan and Dixon, 2001, 2002, 2003, 2004; Gutowski and Dixon 2006). After, we understand the cluster results, we will embed the clusters into a host environment using a new approach developed in the EMSL at PNNL (Govind et al., 2009). In this approach the atoms closest to the embedded cluster being treated quantum chemically are treated by a shell model representation and the far-field is represented by an unpolarizable rigid atom model. Stationary points on the potential energy surfaces will be calculated at the coupled cluster CCSD(T) or MP2 levels as appropriate with up to the aug-cc-pVQZ basis set as the calculations of H_2O in clusters of CO_2 where the binding is moderately weak (Danten et. al., 2005) will require frequency calculations be done at the MP2 level most likely with the aug-cc-PVTZ basis set, which we have shown to be reliable at this level. Such calculations are very computationally intensive. NMR chemical shift calculations will also be done to compare with experiment with the ADF code using the BLYP functional and the Slater basis sets in ADF.

Relationship to EMSL Science Themes: This work falls within geochemistry/biogeochemistry and subsurface science area of EMSL. In particular it addresses the molecular geochemistry of important mineral phases.

Requested Resources:
This combined experimental and modeling proposal will require the use of both high precision surface microscopy/spectroscopy and high performance computation resources available in the EMSL. The proposal team has expertise to operate the instruments independently, except as noted below. Specifically, we request access to the following resources available in the EMSL.

NMR Spectrometer, Varian-CMX 300 MHz WB for solids (720 hours)
NMR Spectrometer, Varian 500 MHz WB for solids (1440 hours)
FTIR (600 hours)
Laser fluorescence (200 hours)
FIB/SEM (120 hours)—*Operator needed to help already trained student and provide analysis.*
XPS (80 hours) – *Operator needed to prep and run samples.*
DI Bioscope Geochemistry AFM (500 hours)
EMSL Spokane Cluster (10,000 node hours)
Chinook Supercomputer (100,000 node hours) – The proposed calculations will involve multiple CO2 molecules around a water molecule initially and we will also study water clusters embedded in CO2, for example, the energy of the reaction 2 H2O(CO2)4 _ (H2O)2(CO2)8. Such a calculation with the aug-ccpVTZ basis set would have just under 1300 basis functions so would be readily doable at the MP2 level with NWChem on Chinook. We have already shown that we can do MP2 frequency calculations with 1058 basis functions for B(OH)4-(H2O)8 to obtain isotopic fractionation factors. Such a calculation took 14.5 hr on 128 nodes with 8 processors per node for 1850 node-hours. We will have to do many such calculations and this was factored into our allocation request. The nmr calculations will be done with the ADF code for which we have a license.

EMSL Users:

Andrew R. Felmy (Chief Scientist, EMSL), will lead the scientific team and the mineral synthesis and characterization tasks. His research focuses on the structures and stabilities of species in aqueous solutions and in minerals, and thermodynamic modeling.

David A. Dixon (Robert Ramsay Chair Chemistry Department, The University of Alabama) will lead the electronic structure calculation effort. His has extensive experience with applications of the techniques of numerical simulation to chemical problems; electronic structure theory – molecular orbital theory and density functional theory; high performance computing; computational thermochemistry and kinetics; geochemistry and biogeochemistry; relativistic effects for environmental studies.

Dr. Jianzhi Hu (Senior Scientist, PNNL) – Dr. Hu will lead the NMR studies of surface water and CO2 reactivity. Dr. Hu has led the development of the high pressure *in situ* MAS probe at EMSL.

Dr. Eugene Ilton (Senior Scientist, PNNL) – Dr. Ilton is the scientific lead for the phyllosilicate studies. He will establish the scientific goals, determine the priority of the experiments and modeling efforts, coordinate the results from experiment and theoretical modeling, and lead the publication effort.

Dr. Kevin Rosso (Associate Director Geochemistry, PNNL) - Dr. Rosso will lead the orthosilicate experimental studies. Dr. Rosso's expertise is in experimental and computational mineral-water interface geochemistry.

James R. Rustad (Professor, Department of Geology, University of California, Davis) will lead the development of the molecular dynamics model. His research interests are in the areas of interfacial geochemistry, including mechanisms of acid base, ligand exchange, and electron transfer reactions and high-performance computing.

Dr. Zheming Wang (Senior Scientist, PNNL) – Dr. Wang will lead the FTIR/Raman spectroscopic studies of surface water and CO_2 reactivity. Dr. Wang has lead the development of the $scCO_2$-optical spectroscopy system at EMSL.

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