

2011 GCEP Progress Report: Reactivity of CO₂ in the Subsurface

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1. ABSTRACT

We are investigating a range of homogeneous and heterogeneous reactions that occur as a result of the injection of CO₂ into several different subsurface environments relevant either to the extraction of energy (enhanced geothermal or oil recovery) or the disposal of energy waste products. The ability to predict and manipulate reservoir reactivity and reaction products during emplacement of CO₂ is the goal of our research tasks. Our initial focus has been on mineral carbon storage involving the reaction of CO₂ with silicates rich in Mg. Experimental studies have revealed that the optimum conversion of olivine (Mg₂SiO₄) to magnesite (MgCO₃) occurs at close to neutral pH and in the presence of certain organic acids that appear to accelerate the dissolution of olivine. Future work will focus on increasing the kinetics of these reactions, the role of organic acids as activators or inhibitors of dissolution reactions, and on preventing silica – a byproduct of the olivine-CO₂ reaction – from coating olivine grains, which would interfere with or stop the reaction. Field characterization of a natural analogue for mineral carbonation in Mg-silicate rocks (Red Mountain Magnesite District, CA) has revealed large monomineralic magnesite veins (up to 10 m in width) with late stage silica precipitation and zones of brecciation consistent with hydraulic fracturing of the low permeability ultramafic host rock. Theoretical calculations suggest that CO₂-rich fluids could have generated these fractures under certain pressure-temperature trajectories. Future work will focus on refinement of a model for the mechanical work created by the CO₂-rich fluids, development of field constraints on the pressure-temperature path of the fluids, and coupling field observations with reactive transport considerations. This work has implications for the behavior of CO₂-rich fluids in a range of engineered environments.

Initial studies are also underway to investigate the geochemical reactions that occur in deep saline aquifer formations as a result of the injection of CO₂. A new high-pressure experimental apparatus has been developed to allow for flow-through experiments on powdered material and we will use this apparatus to perform CO₂-H₂O-caprock experiments on well-characterized samples. The chemical and mineralogical compositions of two caprock units have also been determined in advance of these experiments, which will determine the key reactions that occur within the caprock units when exposed to CO₂-rich fluids. Future work will focus on experimental characterization and geochemical modeling of mineral transformations in caprock and reservoir materials and the impact of redox reactions involving organic compounds on the stability of silicates (primarily clay minerals, such as smectite and illite), Fe-oxy(hydrox)ides, carbonates, and serpentine minerals present in the caprock samples.

2. INTRODUCTION

Large volumes of carbon dioxide (CO₂) will likely be injected into the subsurface as: (1) a strategy for reducing the release of CO₂ to the atmosphere from fossil fuel burning, (2) a potential working fluid for enhanced geothermal systems, and (3) a continuing strategy for enhanced oil and gas recovery. This project will investigate the consequences of the reactivity of CO₂-bearing aqueous fluids in two key types of geologic reservoirs: crystalline ultramafic and mafic rocks associated with enhanced geothermal systems and sedimentary formations associated with hypersaline aquifers (Tester, 2006; Benson and Cole, 2008; Bickle, 2009). As the CO₂ and associated by-products interact with the subsurface minerals and dissolve into local fluids, the ensuing chemical reactions will transform the subsurface environment. Some of these transformations will occur under conditions where thermodynamic variables, such as ion activities and equations of state are incompletely defined (*e.g.*, in hypersaline solutions), necessitating the close coupling of experimental, theoretical, and observational approaches (Lu et al., 2009; Zhang et al., 2009).

To address these issues, we are combining batch and flow-through experimental studies with field studies of CO₂-fluid-solid interactions to quantify reaction kinetics and the spatial and temporal distribution of reaction products, and to identify potential processes that could be used to enhance key reactions. Our findings are interpreted using an integrated analysis that includes traditional thermodynamic and kinetic modeling of experimental results, mineralogical analysis and surface chemistry of experimental reaction products, isotopic tracer studies designed to provide estimates of reactive mineral surface areas, reactive transport modeling, and geological experience and observations.

3. BACKGROUND

A number of recently published studies have highlighted the potential influence of geochemical reactions on the long-term integrity of the caprock (Shao et al., 2010; Shukla et al., 2010; Wollenweber et al., 2010), convective mixing within the reservoir (Zhang et al., 2011b) and ultimately the long-term trapping of sequestered CO₂ (Liu et al., 2011). Collectively, these studies suggest that improved knowledge of chemical reactions that occur in systems composed of varying mixtures of CO₂, water, brine, and organic compounds is required before the evolution of subsurface environments exposed to CO₂ injection can be predicted. Other recent studies have also considered the co-injection of CO₂ and H₂S or SO₂, as well as the effect of CO₂ injection into reservoir brines already containing H₂S (Crandell et al., 2010; Ghaderi et al., 2011; Zhang et al., 2011a). The modeling studies of Zhang et al. (2011a) suggest that co-injection may lower the solubility and mineral trapping of CO₂ due to dissolution of H₂S into formation water and the precipitation of pyrite, while previous studies of H₂S and SO₂ co-injection suggest increased potential for siderite (FeCO₃) precipitation due to enhanced Fe reduction (Murphy et al., 2010; Palandri et al., 2005). Studies of the effect of co-injection (H₂S, SO_x, or NO_x) on redox process in saline aquifers are still relatively few, and to our knowledge no studies to date have addressed the role of organic acids on mineral transformations, although basinal brines can contain up to 5,000 to 10,000 ppm acetate and 100 to 2,500 ppm malonate, along with many other mono- and dicarboxylic acids at ppm levels (Kharaka and Hanor, 2003). Our initial experimental and modeling work (detailed in the following sections) suggests that organic acids can have a substantial and variable impact on the mechanisms and rates of mineral dissolution and precipitation. We have also identified redox transformations and the coupled chemical and hydrologic evolution of caprock and reservoir materials as important areas for future investigation.

In April of 2011, two members of our team (Maher and Brown) also visited Pacific Northwest National Laboratory (PNNL) to discuss potential collaboration on CO₂ sequestration research with members of the Energy and Environment Directorate and to learn about the new high-pressure experimental facilities within the Environmental Molecular Sciences Laboratory (EMSL, www.emsl.pnl.gov). These new facilities are designed to allow for *in situ* experiments at conditions relevant for CO₂ sequestration studies, and include a variety of observational/imaging approaches, such as a high-pressure atomic force microscopy (AFM) and microfluidic reactors, as well as X-ray diffraction (XRD) and nuclear magnetic resonance (NMR). We are in the process of designing several *in situ* XRD experiments that will take advantage of these unique facilities.

During our visit to PNNL we also learned about the planned injection of 1,000 tons of CO₂ into a flood basalt formation proximal to PNNL in June of 2011, as a pilot-scale demonstration of CO₂ mineralization in Ca-rich silicate rocks. A pilot scale injection of CO₂+water into basalt is also planned in Iceland (<http://www.or.is/English/Projects/CarbFix/>) as described in Gislason et al (2010). Recent experimental studies have explored carbonation potential of different basalts from around the world and have found vastly different rates and styles of mineral carbonation that cannot be explained purely by compositional differences (Schaefer et al., 2010), although the release of Fe appears to be an important factor. Despite a large number of studies addressing the injection of CO₂ into mafic and ultramafic rock formations and the resulting mineral fluid interactions (Andreani et al., 2009; Giammar et al., 2005; Hanchen et al., 2008; Hanchen et al., 2006; Hansen et al., 2005; Kelemen and Matter, 2008; Kelemen et al., 2011; Matter and Kelemen, 2009; Schaefer et al., 2010; Wogelius and Walther, 1991), none have employed an integrative approach that combines experimental studies of CO₂ (+H₂O) interaction with mineral surfaces, surface science characterization of reaction products and reaction intermediates, thermodynamic considerations, and field studies of natural analogs of mineral carbonation reactions. Our approach has yielded much needed information pertaining to the large-scale field-based constraints on mineral carbonation, baseline kinetic data on mineral carbonation, and the surface chemical changes of Mg-containing minerals upon reaction with CO₂ and water, including the important effect of surface passivation by organic ligands and silica.

4. RESULTS

Our research to date has focused on (1) experimental and field studies of the reaction of CO₂ with silicates rich in Mg and/or Ca, and (2) mineral-fluid reactions and reaction rates during and subsequent to the dissolution of CO₂ into hypersaline brines.

Reactions between CO₂-rich fluids and Mg-silicate rocks

Our work on the interaction of CO₂ with Mg-silicates has revealed a number of new findings with respect to the feasibility of mineral carbonation as a mechanism for permanently storing anthropogenic CO₂ as a stable carbonate phase. First, our experimental work has found that organic acids, such as those commonly found in natural waters and deep saline aquifers, are capable of both enhancing and potentially inhibiting dissolution and precipitation reactions. The olivine carbonation experiments suggest that while some organic acids enhance mineral-fluid reaction rates in the presence of CO₂, there is a threshold of organic acid concentrations (> ca. 0.1 g/L for salicylic acid) and/or pH (< ~ pH 5) where mineral dissolution rates may actually be suppressed due to interactions between the organics and the mineral surface. This finding is consistent with earlier ATR-FTIR spectroscopic studies of the interaction of carboxylic acids and natural organic matter (e.g., humic acid) with AlOOH mineral surfaces (e.g., Yoon et al., 2004a,b; Johnson et al., 2004a,b; Johnson et al., 2005a,b; Yoon et al., 2005), which found that organic acids, such as oxalic acid, that bond to mineral surfaces in an inner-sphere bidentate

fashion enhance dissolution, whereas those, such as maleate or humic acid, that form outer-sphere surface complexes inhibit dissolution.

The second important aspect of our field-based research has been the observations of substantial mineral carbonation accompanied by repeated brecciation events within the serpentinized ultramafic rocks of the Red Mountain Magnesite District. Our current model suggests mechanical energy generated by heating of CO₂-rich fluids at shallow crustal depths could generate mechanical work that exceeds the tensile strengths of the host rocks. As a result, repeated hydraulic brecciation and fracturing generate porosity and permeability allowing fluids to deposit substantial amounts of magnesite in veins of various sizes. Further characterization studies will be used to constrain a coupled thermodynamic, hydrologic, and mechanical model of the Red Mountain deposit in order to test our hypothesis for the apparent rapid and massive sequestration of CO₂ at this locality. If the processes we observe at Red Mountain can be engineered for CO₂ sequestration, we believe that ultramafic rock sequences provide an alternative strategy for long-term CO₂ sequestration in areas that lack access to deep saline aquifer storage capacity. The processes that occur at Red Mountain may also have implications for the use of CO₂ as a working fluid for enhanced geothermal systems.

Experimental investigations of the kinetics of mineral carbonation

We have carried out a series of batch experiments examining the carbonation kinetics of olivine (Mg₂SiO₄). The reactions occur inside a flexible gold cell that is attached to a valve, allowing for fluid sampling during the course of the experiment. The entire cell is placed inside a stainless steel vessel, which is filled with a pressure fluid (distilled water). The stainless steel vessel is then placed inside a rotating furnace. The experimental apparatus allows us to control both the temperature and pressure during the course of the experiment. An additional advantage of the experimental set-up is that we can sample fluid from the reactor without changing the pressure or temperature inside of the gold cell. All experiments have used olivine powder at a ratio of 1:20 by mass, and 3% NaCl solution. Temperature is 60°C and pressure is set by the addition of CO₂ to 100 bar resulting in 10-15 mL of supercritical CO₂ in the reaction vessel. Salicylic and acetic acids have been added to several experiments with the goal of improving the reaction rate. Results show that the dissolution rate of olivine is not constant with time, as measured by the change of magnesium concentration in solution (**Figure 1**). Within an hour of adding the CO₂ to the reaction mixture, the amount of magnesium in solution increases to several hundred ppm. The concentration of magnesium then stays constant for a period of time before increasing sharply up to a second apparent steady state. This second steady state is above thermodynamic saturation for magnesite (MgCO₃), and the only experiments that produce significant amounts of magnesite (10-30%) are the ones that reach the second plateau. This plateau may reflect the balance between olivine dissolution and magnesite precipitation.

Experimental data suggest that the pH of the reaction solution is one of the most important factors in controlling the rate of mineral carbonation (**Figure 2**). Over the course of reaction, the pH rises from a calculated value of 3.1 (the equilibrium pH of CO₂ and water at our reaction conditions) to as high as 6. The highest Mg release rates are observed at the higher (near-neutral) pH values. Our experimental findings are in contrast to previous olivine dissolution studies using pure water, which have found that dissolution rates decrease with increasing pH (Pokrovsky and Schott, 2000). The pH in the experiments is affected by several processes: (1) the olivine dissolution reaction which involves an exchange of protons for metal cations, (2) the dissolution of CO₂ into water to create carbonic acid, and (3) the addition of organic acids.

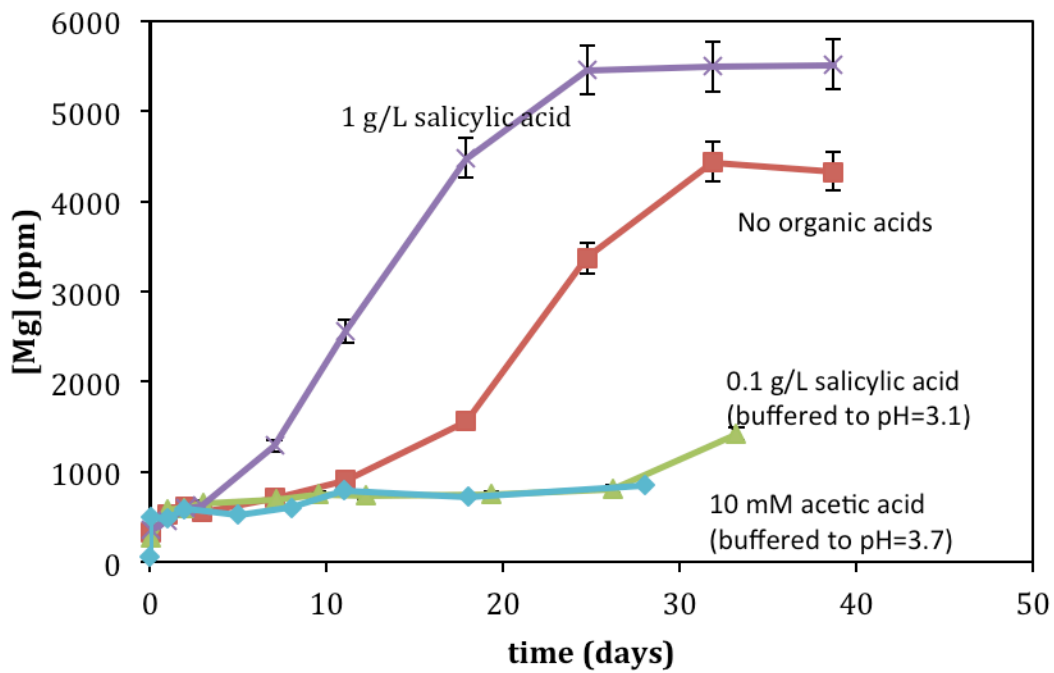


Figure 1: Magnesium concentration versus time for four different experiments. The rate of Mg change in solution is not constant. Also, while salicylic acid increases the rate of Mg release, buffered solutions of organic acids slow the rate below that of the control case (no added organics).

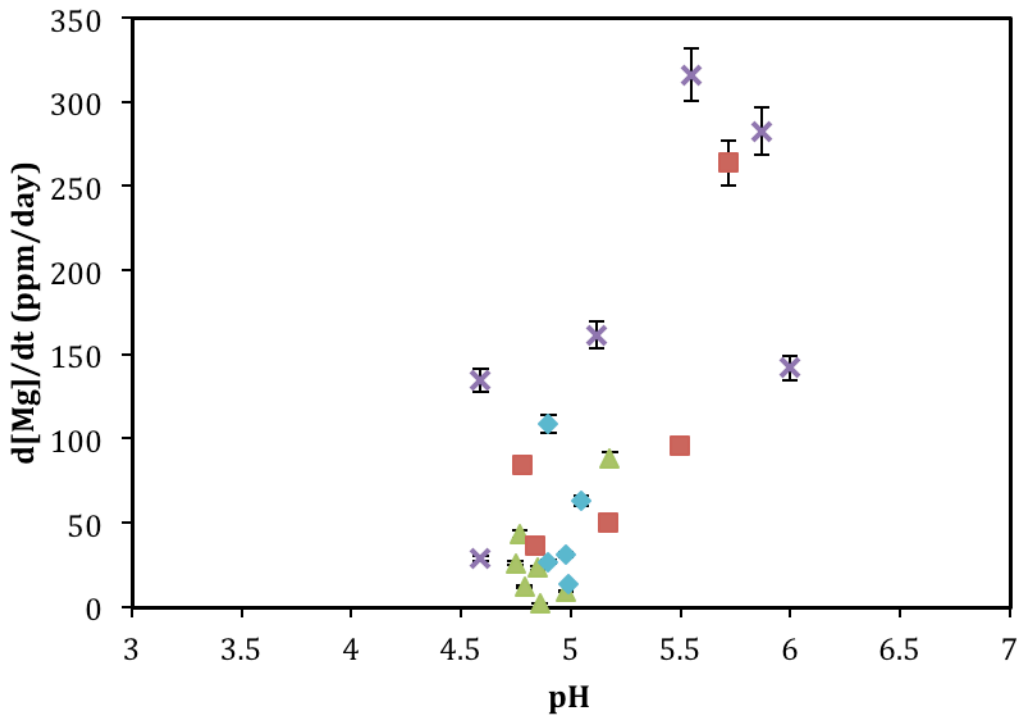


Figure 2: Change in Mg concentration with respect to time versus pH. The highest rates of Mg increase occur at $\text{pH} > 5.5$. The data plotted here are from 3 separate experiments with different fluid compositions: 1 g/L salicylic acid, no added organic material, and 0.1 g/L salicylic acid buffered to $\text{pH} = 3.1$. This plot does not include data from the first day of reaction or from the second plateau (where precipitation is assumed to occur and that rate of change of Mg is zero).

The exact mechanism for the increase in dissolution rate at higher pH has not been determined, but ligand adsorption at the olivine surface likely plays a role. At low pH, the organic acids are protonated and neutrally charged. Thus, there is a very weak electrostatic interaction between the organic molecules and the mineral surface. As the pH rises due to proton uptake during mineral dissolution, a higher percentage of the organic molecules become deprotonated and negatively charged. These negatively charged particles are more likely to interact electrostatically with the surface, particularly if the surface is positively charged. That interaction may lead to the weakening of near-surface bonds in the mineral structure and effectively accelerate dissolution. A similar argument could be made about dissolved CO₂ and bicarbonate. At low pH, dissolved CO₂ is a neutrally charged molecule (either hydrated CO₂ or carbonic acid). As the pH increases, carbonic acid is deprotonated to form bicarbonate (HCO₃⁻). The negatively charged bicarbonate ion may interact with the olivine surface in such a way as to accelerate dissolution.

Our current and near-future work seeks to understand the interface chemistry of olivine and other silicate minerals in the CO₂-H₂O-organic system. We have begun a series of short-term batch experiments using a variety of organic acids mixed with silicate minerals in the presence of water and 100 bars of CO₂. We are using x-ray photoelectron spectroscopy to study the surfaces of reacted silicates, specifically looking at the carbon 1s photopeak. All surfaces exposed to the atmosphere have adventitious carbon, but the carbon peak from adsorbed organic material is shifted several electron volts so it is distinguishable from adventitious carbon. XPS allows us to see the additional carbon on the surface and estimate the amount adsorbed. While significant previous work on organic molecule adsorption to oxide surfaces exists, very little has been done with silicate surfaces and none with silicates in the presence of water and CO₂.

Field investigation of a natural analogue for mineral carbonation

Subsurface concentrations of magnesite (MgCO₃) forming world-class economic deposits demonstrate Nature's efficiency in carbonating ultramafic rocks (Boschi et al., 2009). Characteristics of these deposits include cryptocrystalline magnesite in economic veins up to 45 m in thickness, structural lengths of 4 km, and mining depths of ~300 m. Such large concentrations of mineral carbonation illustrate a thermodynamically, kinetically, and structurally favored process, and their worldwide occurrence suggests that physical and chemical conditions for their formation are not unique to any one geologic locality.

We have focused our studies on the Red Mountain Magnesite Mining District, one of the world's largest magnesite deposits (Bodenlos, 1950) located ~100 km SE of San Francisco, California and a type locality for evaluating natural mineralogical CO₂ sequestration. The deposit is in variably serpentized ultramafic rocks of the Jurassic Coast Range ophiolite belt exposed at Del Puerto, CA (Bodenlos, 1950). Our objectives are to evaluate the physical and chemical processes responsible for this extraordinary CO₂ mineralization and to explore engineering approaches that replicate the natural phenomena of permeability and porosity generation and carbonate mineralization in these ultramafic rocks.

Our characterization of the Red Mountain deposit to date has consisted of petrographic analysis, X-ray Diffraction (XRD), and stable and radiogenic isotopic analyses of the carbonate to understand the origin of the fluids, the CO₂ and the solutes. We will also investigate the use of the U/Pb radioactive dating system to determine the age of the carbonate veins and ideally the timescale over which they formed. This information will be used to constrain a model for the genesis of the deposit. The majority of the massive magnesite is cryptocrystalline, and XRD analyses showed that other mineral phases are absent or at levels less than that routinely detectable by powder XRD (~1% by weight). This pure cryptocrystalline magnesite coupled with the extensive re-brecciation of magnesite (e.g., **Figure 3**) suggests rapid precipitation and cyclic

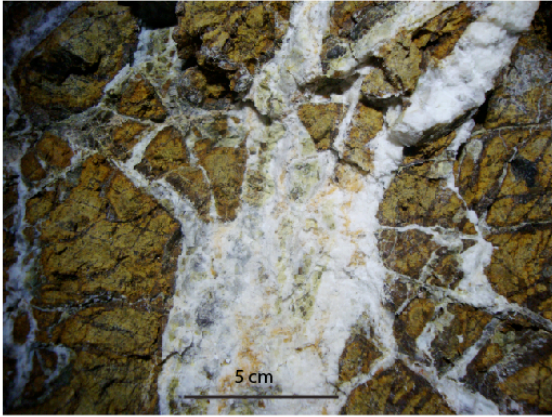


Figure 3: Example of “stockwork” magnesite vein feature in relatively unaltered ultramafic rock at Red Mountain, CA.

hydrofracturing of the veins. We hypothesize that mechanical energy generated by fluid-phase separation or volumetric changes during decompression of CO₂-rich fluids at shallow crustal depths provides the work to exceed tensile strengths of the host rocks, thus generating porosity and permeability through hydraulic brecciation and fracturing. By combining our observations and data from the experimental and natural system studies, our future work will focus on the development of a coupled thermodynamic, hydrologic and mechanical model of the Red Mountain deposit in order to test our above hypothesis for the apparent rapid and massive sequestration of CO₂ in ultramafic sequences. This approach will enable us to determine feasibility and approaches for injecting CO₂ into these types of deposits, which although

represent less storage volume than saline aquifers, present the opportunity to permanently remove CO₂ from circulating fluids.

Potential for mechanical work performed by CO₂-rich fluids

The conversion of ultramafic rocks to carbonate minerals is considered to be the most stable, long-term mechanism for storage of CO₂ (e.g. Oelkers et al. 2008). One of the barriers to large-scale carbonation of ultramafic rocks is the low porosity and permeability, which greatly reduces both the transport of fluids and the effective surface area. However, observations of natural analogues (e.g. Red Mountain, CA) and theoretical considerations suggest that fluids are capable of performing work on their lithologic environment when they undergo phase, pressure, and temperature changes, resulting in the generation of fracture porosity and permeability. These changes open new conduits for fluids and create fresh reactive mineral surfaces that greatly enhance the carbonation efficiency of ultramafic rocks.

To investigate the potential of CO₂-rich fluids to generate mechanical work on their environment, we have compared the isobaric expansivity (α ; °C⁻¹) and the isothermal compressibility (β ; bar⁻¹) of fluids under isochoric conditions (e.g. Knapp and Knight, 1977; Johnson and Norton, 1991) to average hydrostatic geothermal gradients. The ratio of expansivity to compressibility (α/β ; bar/°C) describes how the expansion of a fluid due to an increase in temperature has a reciprocal effect on the fluid because, as it expands, it also experiences an increased compressive force due to pressure increase. This can be written as $(\partial P/\partial T)_V = \alpha/\beta$, where V is volume, P is pressure, and T is temperature (Knapp and Knight, 1977). Mechanical work is generated when pore pressure increases proportionally to the α/β coefficient, that is, $\partial P = (\alpha/\beta) \times \partial T$, which implies that a change in temperature (°C) multiplied by the α/β coefficient (bar/°C) will result in a change in pressure (bar) under the constraint of constant volume. The α/β coefficient is uniquely defined by the equation of state for the fluid, and can be evaluated as a function of the independent variables temperature, pressure, and composition. Our preliminary investigation has focused on evaluating the fluid mixture of $xCO_2=0.1$ and $xH_2O=0.9$ as an illustrative example.

The mixture $xCO_2=0.1$ and $xH_2O=0.9$ shows a strong similarity to the H₂O-system (e.g. Knapp and Knight, 1977; Lachenbruch, 1980) except that addition of 10% of CO₂ increases isopleths of the α/β coefficient by ~20% with respect to pure water (**Figure 4**). The results depicted in **Figure**

4 reveal three regions of α/β where: (1) at temperatures $<50^\circ\text{C}$ for all pressures α/β reaches maximum values at 30°C and becomes more sensitive as pressure increases; (2) the system reaches a maxima (19-23 $\text{bar}/^\circ\text{C}$) between 80 to 160°C at all pressures; and (3) a systematic decrease in α/β as temperature increases at all pressures. Positive α/β values imply that isochoric fluid pressure increases will effectively occur if the fluid increases in temperature. For example, a minimum increase of 1.5°C under average hydrostatic geothermal gradients ($\alpha/\beta=20\text{-}21 \text{ bar}/^\circ\text{C}$) will generate ~ 30 bars of internal pressure, which is sufficient to overcome the tensile strength of shale (30 bar) (Bieniawski, 1984; Pollard and Fletcher, 2006) and possibly serpentinite. Several scenarios could lead to larger increases in temperature: (1) exothermic reactions (e.g. dissolution of serpentine) and changes in composition; (2) increases in heat flow (e.g. tectonic development of a regional slab window in the California Coast Ranges or local magmatic intrusions); (3) phase separation (e.g. molar heat capacity variations); (4) tectonic activity (e.g. frictional heating; Lachenbruch, 1980); and (5) increased lithostatic overburden. On average, >100 bars are needed to initiate a state of failure for an ultramafic rock (Bieniawski, 1984; Pollard and Fletcher, 2006), which can be reached by a thermal rise of approximately 5°C .

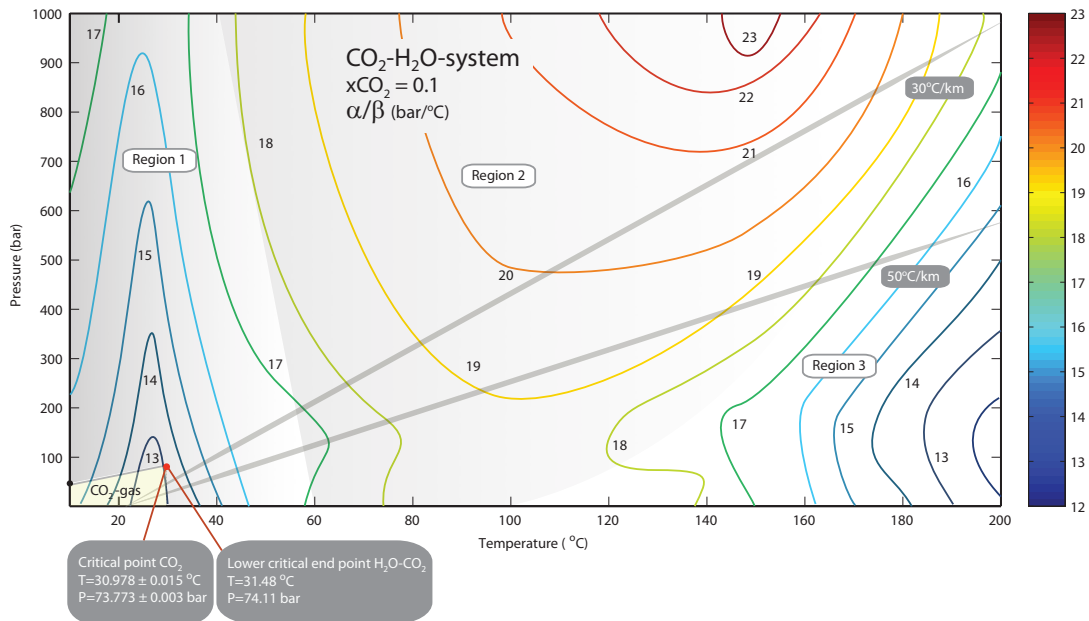


Figure 4: α/β isopleths for the $\text{CO}_2\text{-H}_2\text{O}$ -system. Refer to text for discussion on Regions 1-3. The expansivity (α) and compressibility (β) of the mixture $x\text{CO}_2=0.1$ and $x\text{H}_2\text{O}=0.9$ were evaluated from 10 to 200°C and 1 to 1000 bar using the equation of state of $\text{CO}_2\text{-H}_2\text{O}$ -mixtures of Duan and Sun (2003) and Duan and Zhang (2006). Although the equation of state presents experimental, mathematical, and theoretical limitations, it is valid for the pressure-temperature regimes where carbon sequestration will occur (e.g. Marini, 2007) as well as for the natural analogue of carbon sequestration that pertains to this study (Red Mountain). Red dot represents the critical point of CO_2 and the lower critical end point of the $\text{CO}_2\text{-H}_2\text{O}$ -system (Span and Wagner, 1996). Gray lines represent conditions for two geothermal gradients (30 and $50^\circ\text{C}/\text{km}$) at hydrostatic pressure with constant unit specific gravity.

Our initial analysis of the α/β coefficients of the system $x\text{CO}_2=0.1$ and $x\text{H}_2\text{O}=0.9$ indicate that CO_2 -rich fluids are capable of generating porosity, permeability, and fractures due to temperature and pressure changes (Figure 4). This mechanism may explain the large-scale magnesite vein deposits at Red Mountain, where CO_2 -rich solutions saturated with magnesium might have experienced a particular thermal perturbation that allowed the fluids to overcome the tensile strength of the ultramafic host rocks (>100 bar) to precipitate magnesite. In this case, the fluids create the conditions necessary for enhanced carbonation of ultramafic rocks. Further, the α/β coefficient may permit the assessment of rock stability at injection points, fluid response to

thermal perturbations in porous media (e.g. saline aquifers), and susceptibility of caprock formations to underlying thermally pressurized fluids. The significant mechanical work that CO₂-fluids are able to perform on their lithologic environment can be used in the engineering and implementation of large-scale carbon capture and storage projects, and will thus be the subject of future research.

Reactions between CO₂-rich fluids, shale caprock and reservoir sandstone

Injection of CO₂ into deep sedimentary basins containing oil-field type brines will generate the potential for a wide variety of homogeneous and heterogeneous irreversible reactions affecting the brine and its interaction with sedimentary rocks. Oil field brines contain organic acid concentrations up to 10,000 mg/L (Kharaka and Hanor, 2003). Carboxylic acids are reactive aqueous components that also increase the apparent mineral solubility by forming metal-organic complexes with the common mineral-forming elements Si, Na, K, Fe(II), Mg, Ca, and Al (Shock and Koretsky, 1995). Our initial investigations are thus focused on understanding the effect of CO₂ injection on the distribution of organic acids, the redox state of the system, and reactions between aqueous solutions, CO₂ and sedimentary minerals, and in particular the smectite-to-illite transformation, an important diagenetic reaction that liberates water and may be moderated by Fe(III)-reducing bacteria (Kim et al., 2004). The smectite-illite reaction may also be promoted by the co-injection of H₂S or the presence of supercritical CO₂. In order to conduct the relevant experiments, we have constructed a new flow through apparatus that will enable us to use well-characterized disaggregated minerals. In addition we are designing experiments that can utilize the new high-pressure high-temperature experimental facilities at the Environmental Molecular Science Laboratory (EMSL) at Pacific Northwest National Laboratory.

Mineral transformations in caprock and reservoir rocks: results of characterization and preliminary modeling studies

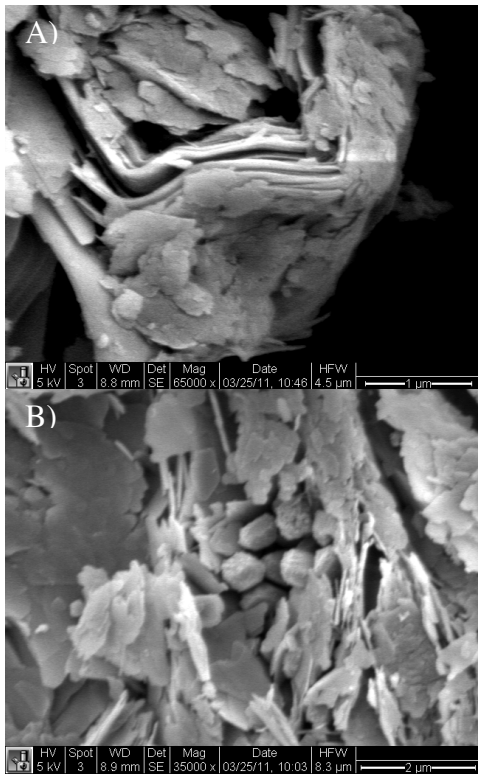


Figure 5. SEM images of (a) the Eau Claire caprock shale and (b) the marine Tuscaloosa shale.

The injection of CO₂ into saline aquifers may alter the stress state of the shale caprock, potentially opening new fractures and/or connecting pre-existing fractures (Smith et al., 2011). Percolation of CO₂ or CO₂+brine through the fracture network may result in alteration of the caprock and either sealing of the fractures or enhancement of the fracture network. To assess the geochemical factors that impact the chemical and mechanical evolution of shale caprock and as a guide for future experiments, a series of reactive transport simulations are currently underway. These simulations suggest that the type of cement (carbonate or clay) and the porosity distribution will be first-order controls on the chemical evolution. To refine these simulations and to provide well-characterized experimental media, two representative shale caprocks — one from the Eau Claire formation, Macon, IL and one from the marine Tuscaloosa formation in Mississippi — have been characterized using XRD, SEM, XRF and XPS in order to determine the morphology of the grains and their elemental and mineralogical compositions. Reactions between the caprocks and

both supercritical and dissolved CO₂ (± organic acids) will be studied using a new high-pressure flow through apparatus constructed in collaboration with Sally Benson's group at Stanford. The SEM images of the Eau Claire shale sample show typical platy micaceous habits of phyllosilicate minerals, and the presence of muscovite and glauconite were confirmed by XRD analyses (**Figure 5**). The Tuscaloosa shale also shows platy micaceous habit, although the mineral components are slightly different than those in the Eu Claire shale. XRD analysis revealed the presence of chlorite, antigorite, and vermiculite. The presence of antigorite ($Mg_3Si_2O_5(OH)_4$) has been observed by other studies of shale caprock and is likely to be highly reactive to CO₂. Experiments on the natural caprock and pure mineral separates, including antigorite and smectite/illite, will be conducted in the presence of CO₂, brine, and organic acids.

Preliminary reactive transport analysis of the performance of mineral dissolution rate laws under CO₂ sequestration conditions

Over the last three decades it has been increasingly recognized that the rates of fluid-mineral reactions measured in natural systems are generally several orders of magnitude (10^2 to 10^5) slower than those determined experimentally (Maher, 2010; White and Brantley, 2003). The extreme variability in natural reaction rates has posed a long-standing problem in aqueous geochemistry as it creates substantial uncertainty in the kinetic parameters incorporated into interpretive and predictive reactive transport models, such as those used to assess the consequences of CO₂ injection in the subsurface (Liu et al., 2011; Maher et al., 2010). Growing evidence suggests that a chemical explanation of the apparent rate discrepancy may be the non-linear behavior of mineral dissolution rates near equilibrium, combined with pervasive transport-control of reaction rates (Maher et al., 2009). However, factors that affect thermodynamic departure from equilibrium of the dissolving phase(s), such as the rates of secondary mineral precipitation, the effect of secondary mineral coatings on dissolution of primary minerals, and the evolution of pH, flow rate, reactive surface area, and porosity/permeability are poorly understood. This understanding is required if we hope to accurately model the evolution of a reservoir during and after injection of CO₂.

A preliminary reactive transport analysis of the reaction between aqueous fluids equilibrated with supercritical CO₂ and both arkosic sandstone suggests that the outcome of reactive transport model predictions will be highly dependent on the assumptions made about the form of the kinetic rate law describing mineral dissolution and the rate of precipitation of secondary phases as they strongly control the departure from equilibrium. Flow-through experiments using a combination of microfluidic approaches and mesoscale column experiments will be conducted to develop approaches for modeling the nucleation and precipitation of secondary phases (SiO₂(am) and metastable aluminosilicates).

5. PROGRESS

We have chosen to work on the two primary subsurface reservoir types proposed for the injection of CO₂ (deep saline aquifers and ultramafic/mafic rocks) because many of the processes such as mineral dissolution and precipitation in these major reservoirs are similar. Highly reactive ultramafic rocks may reveal important mechanisms regarding the permanent mineralization of CO₂, and the evolution of physical properties such as porosity, permeability, and fracturing due to the array reactions with net positive volume changes. In particular, one component common to both systems, SiO₂, is the chemical constituent most likely to result in rapid alteration of the porosity of reservoir rocks, providing a critical opportunity for geoengineering porous media. In addition, the organic acids present in saline aquifers and potentially in ultramafic/mafic systems, have a substantial but poorly understood impact on the reactivity of different solid phases and aqueous components, and potentially on the bulk redox state of the system when CO₂ is injected. Previous studies of CO₂ sequestration have not explicitly considered the effects of organic acids,

redox reactions, and porosity evolution in detail, although they constitute critical controls on geochemical evolution and provide numerous engineering opportunities and the potential for geoengineering at significant scales.

6. FUTURE PLANS

Mineral Carbonation: Experimental studies on olivine carbonation will focus on addressing the role of organic acids on mineral dissolution. These batch experiments will be supported by analysis of $\delta^{26}\text{Mg}$ isotopes on minerals and aqueous Mg in order to assess the role of passivating layer formation as a barrier to Mg release and the isotopic fractionation during magnesite precipitation. Research at Red Mountain, CA will focus on quantifying the mechanical work generated by the CO_2 -bearing fluids responsible for the mineralization, development of geochronologic and physical constraints (age dating and fracture mapping) and modeling of observed mineralogic relationships. We plan to submit 2 to 3 papers from this research in the coming year (2011).

CO₂ Storage in Sedimentary Basins: Flow-through experiments will be conducted using the core flooding system (Perrin and Benson, 2010) and the newly constructed flow-through cell for powdered samples. Our experiments will focus on the reactions between shale caprock and reservoir material, and representative mineral separates such as serpentine, smectite and smectite illite. Saline brines pre-equilibrated with CO_2 at pressures of approximately 80 to 100 bars will be used in the experiments. *In situ* experiments are being designed for the new facilities at EMSL and using the hydrothermal facilities at the USGS currently in use for the olivine carbonation studies. Currently, we are considering making *in-situ* observations of the smectite-illite transformation in the presence of CO_2 (\pm H_2O , brine, and organics) using the high pressure XRD apparatus and the ability to conduct mineral precipitation experiments in the microfluidic reactor system using a realistic pore geometry to understand mechanisms for mineral precipitation and how to describe them numerically. For mineral precipitation experiments the brines will be mixed with supersaturated solutions at the injection port in order to assess mineral precipitation rates. Post-reaction core flooding with CO_2 will be used to assess the physical changes in the core. A range of approaches, including XPS, STXM, μXRF , and computed X-ray tomography, similar to the approaches discussed in the results, will be used to specifically link the mineralogical changes to the physical changes at minimum spatial scales of several microns. The solute fluxes, calculated *in-situ* pHs, isotopic composition of fluids, mineral saturation state, and mass loss/depletion (or τ values) will be used to constrain a continuum multi-component reactive transport model of the experimental system. This combination of experimental work with reactive transport modeling approaches is an important step in scaling from laboratory work to field-scale systems. Geochemical and reactive transport modeling will be used to calculate reaction rates and kinetic rate laws, and to assess the feedback between chemical reactions and transport parameters. With respect to CO_2 sequestration, very few studies have closely coupled reactive transport modeling with appropriate data constraints from both experimental and field-systems.

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Abstracts and Publications:

- Johnson, N. C., Thomas B. Maher, K., Bird, D. K., Rosenbauer, R. Brown, G. E. Jr. (2011) Adsorption of organic ligands on silicate mineral surfaces in the presence of CO₂ and water: Insight into olivine dissolution rates. Goldschmidt Conference, Prague, Czech Republic.
- Johnson N. C., Thomas B., Maher K., Bird D. K., Rosenbauer R. J., Brown G. E. Jr. (2011) Kinetics of olivine carbonation for carbon sequestration. Carbon Capture and Storage Oman, Muscat, Sultanate of Oman, 8-10 Jan.
- García Del Real, P., Maher, K., Bird, D.K., and Brown, G.E. Jr.(2011), CO₂ Sequestration in Ultramafic Rocks: Insights from the Red Mountain Magnesite District, California, Geological Carbon Capture and Storage, Muscat, Sultanate of Oman, 8-10 Jan.
- García Del Real, P. Maher, K., Bird, D. K., Brown, G.E. Jr. (2010) CO₂ Sequestration in ultramafic rocks: insights from the Red Mountain Magnesite District, California. Abstract EP41C-0719 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13–17 Dec.
- (Invited) Maher, K., García del Real, P., Bird, D. K., Brown, G. E. Jr., Johnson, N., Kharaka, Y. K., Rosenbauer, R. J. (2010) Discrepancies between laboratory and field-based mineral-fluid reaction rates: implications for CO₂ sequestration based on reactive transport studies of natural systems. Geological Society of America Fall Meeting, Denver, CO. GSA Abstracts with Programs Vol. 42, No. 5.
- Johnson, N. C, B. Thomas, K. Maher, T. Kendelewicz, D. K. Bird, R. B. Rosenbauer, and G. E. Brown, Jr. (2010) Kinetics of Mg-silicate carbonation for the geologic storage of carbon dioxide. Abstr. ACS Ann. Mtg., San Francisco, CA.
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