

# Geological Sequestration of CO<sub>2</sub>: Mechanisms and Kinetics of CO<sub>2</sub> Reactions in Mafic and Ultramafic Rock Formations

## Investigators:

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## Abstract

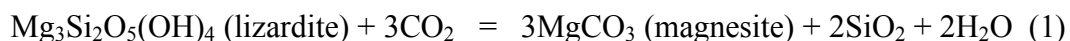
The main purpose of this exploratory project is to develop a more fundamental understanding of the long-term sequestration of CO<sub>2</sub> via mineral carbonation reactions involving the common Mg-silicates in serpentinite and basalt mineral assemblages. Past experimental studies have shown that these reactions are kinetically limited, so we are exploring ways to enhance their kinetics, including the use of activators such as organic acids and catalysts such as natural metalloenzymes that enhance the rate of conversion of hydrated CO<sub>2</sub> to bicarbonate ions. During the past year, we have combined surface science studies of (1) the interaction of CO<sub>2</sub> and H<sub>2</sub>O with Mg-oxides and Mg-silicates, (2) hydrothermal experimental studies of the rates of Mg-silicate carbonation reactions, (3) reactive transport modeling of these carbonation reactions in initially porous Mg-silicate rocks, and (4) field-based studies of natural analogs of serpentinite carbonation reactions. We have carried out first-of-their-kind *in situ* ambient pressure photoemission spectroscopy (APPEs) studies of the interaction of CO<sub>2</sub> and CO<sub>2</sub> + H<sub>2</sub>O with model Mg-oxide surfaces, initiated experimental hydrothermal studies of the rate of interaction of CO<sub>2</sub>-rich aqueous solutions with Mg-olivine and other Mg-silicates, completed preliminary simulations of these and other reactions of CO<sub>2</sub>-rich aqueous solutions with Mg-silicates using the reactive transport code *CrunchFlow*, and are beginning field studies of natural analogs with a focus on identifying all carbonate phases. Our *in situ* APPEs studies have shown that the interaction of 0.2 Torr of CO<sub>2</sub> with a model MgO (100) surface results in rapid formation of MgCO<sub>3</sub> and that subsequent exposure to 0.1 Torr of H<sub>2</sub>O enhances the reaction. In contrast, when water is reacted with MgO(100) first, followed by reaction with CO<sub>2</sub>, the carbonation reaction is inhibited. This observation may help explain enhanced carbonation of Mg-silicates upon preheating. Our numerical reactive transport simulations of the reaction of CO<sub>2</sub>-rich fluids with Mg-silicates have shown that under the conditions relevant for subsurface CO<sub>2</sub> injection, primary mineral dissolution, coupled with the spatial distribution of reaction fronts along the flow path, allow for efficient precipitation of Mg-carbonate without complete destruction of the initial porosity. This finding contrasts with previous closed-system batch reactor models that suggested the positive volume change during Mg-silicate carbonation would result in complete filling of the pore space. Over the range of initial

and boundary conditions considered, the rate of mineral carbonation was proportional to the flux of CO<sub>2</sub> into the system, with nearly complete removal of CO<sub>2</sub> by precipitation of Mg-carbonate. Our simulations also show that if silica concentrations are maintained below quartz saturation, the very large volume increase in the carbonation of Mg-olivine can be reduced substantially and passivation of the Mg-olivine surface by silica can potentially be reduced as well. We also conclude from our preliminary simulations that the effects of aqueous organic ligands on the dissolution rates, solubilities, and stabilities of Mg-silicates relative to carbonate minerals are likely to be of first-order importance in optimizing the industrial utility of geologic sequestration of CO<sub>2</sub> in ultramafic and mafic rock formations.

## Introduction

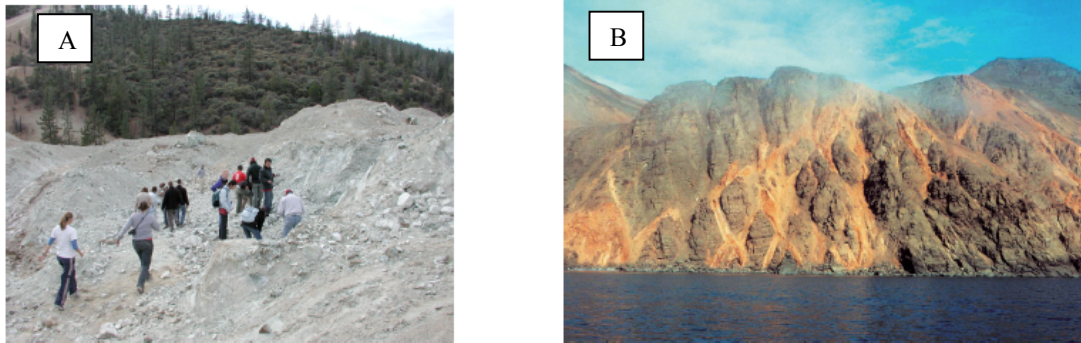
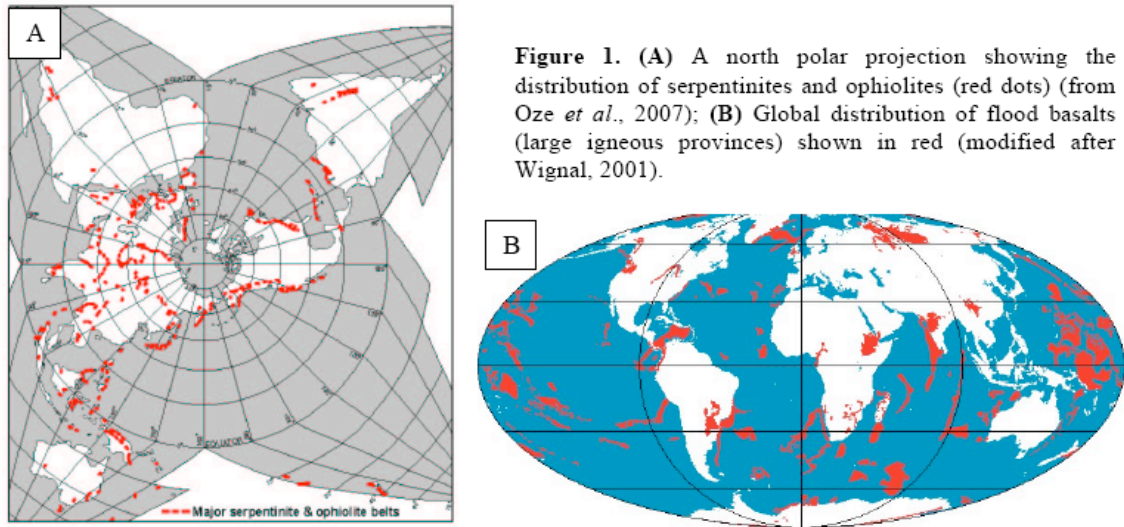
Recent estimates (*e.g.*, Deffeyes, 2005) suggest that world oil and natural gas reserves are sufficient to allow their continued use as major energy sources for the next 200 years. Coupled with the burning of coal for electric power generation, this usage will result in increasing levels of CO<sub>2</sub> in the atmosphere unless safe, efficient, and cost-effective means of CO<sub>2</sub> sequestration (capture and storage) are found. An attractive option for long-term storage of CO<sub>2</sub> is the use of deep sedimentary formations (*e.g.*, Gunter *et al.*, 2004; Hepple and Benson, 2005; Benson and Surlis, 2006; Marini, 2007), although there is some concern about potential migration and seepage of CO<sub>2</sub> from sedimentary formations, particularly if cement casings of old wells leak (*e.g.*, Kharaka *et al.*, 2006, 2007) or if the waste stream gas is not pure CO<sub>2</sub> (*e.g.*, Knauss *et al.*, 2005). Such formations typically consist of feldspathic sandstones (quartz, K-feldspar, plagioclase feldspar, calcite, kaolinite, chlorite, muscovite/illite, pyrite) and carbonates (calcite, dolomite, siderite, pyrite) that contain Na-Ca-Cl brine solutions in the pore spaces. The CO<sub>2</sub> injection causes the reservoir fluid to become acidic, resulting in the dissolution of silicate and carbonate minerals and subsequent growth of carbonate minerals that consume the liberated metal cations (Knauss *et al.*, 2005). Geochemical simulations by Knauss *et al.* (2005) suggest that the presence of SO<sub>2</sub> in the waste stream gas would result in a solution pH that remains too low for carbonate minerals to be stable in the short term (< 100 years); however, as the pH is neutralized over time due to increased silicate mineral dissolution, additional carbonate mineral formation should result in enhanced CO<sub>2</sub> sequestration.

Another possible strategy for the geological sequestration of CO<sub>2</sub> involves the reaction of CO<sub>2</sub> with Mg silicates, which, in the form of serpentinites and picrites, are abundant and thermodynamically convenient rocks for the formation of Mg-carbonates (*e.g.*, Seifritz, 1990; Lackner *et al.*, 1995, 1997; Lackner, 2002; Schulze *et al.*, 2004; Zevenhoven *et al.*, 2006). For example, the carbonation reaction of lizardite, one of the common serpentine minerals in the rock serpentinite, may be written as



and is exothermic (-63.6 kJ/mol CO<sub>2</sub>), with a volume change ( $\Delta V/V$ ) of  $\sim +20\%$ . In addition, serpentinites are relatively abundant in Earth's crust and are widely distributed (**Figure 1**). Nature has performed relevant experiments in many of these serpentinite

localities, which show that this (or a similar) reaction is rather common and results in large quantities of magnesite and other Mg-, Ca- and Fe-carbonate minerals (**Figure 2**).



**Figure 2:** (A) Massive magnesite deposit formed by alteration of serpentinite by CO<sub>2</sub>-rich groundwater in the New Idria District, CA (Brown, pers. comm.; see Brown and Mattinson, 2007); (B) Photograph of picritic basalts cut by massive veins of magnesite (MgCO<sub>3</sub>) in Nuussuaq, West Greenland, that were formed by interactions of the picrite with CO<sub>2</sub>-rich fluids. (D. Bird, pers. comm.; see Rogers *et al.*, 2006).

Our exploratory study is focused on the mechanisms and kinetics of the interaction of CO<sub>2</sub> (and H<sub>2</sub>O) with both serpentinites and picrites, as well as with the individual serpentine minerals lizardite, antigorite, and chrysotile, and the individual minerals found in picritic basalts, including forsterite, Mg-pyroxene, and Ca-plagioclase. Our initial focus is on (1) changes in the surface chemistry of these minerals (both elemental and isotopic) following carbonation reactions, (2) molecular-level characterization of reaction products using synchrotron-based surface chemistry methods (from which information on reaction intermediates and products can be derived), (3) kinetic studies of these surface carbonation reactions using stable isotopes as tracers, and (4) development of a reactive transport framework for performing field-scale simulations of reactions between aqueous

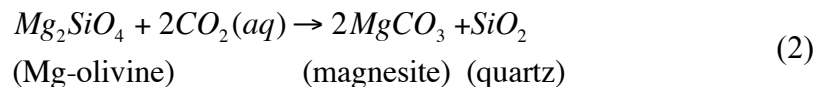
CO<sub>2</sub> and ultramafic rock formations. Assuming success during the initial year of our proposed investigation, our long-term goal is to discover ways to enhance reaction kinetics of CO<sub>2</sub> with these minerals such that costs associated with carbonation reaction of Mg-silicates can be reduced at the production/engineering scale.

## Background

Over the past year several papers have been published which discuss the advantages of CO<sub>2</sub> injection into ultramafic rock formations, including deep-sea basalts (Goldberg *et al.*, 2008; Oelkers *et al.*, 2008) and peridotites (Kelemen & Matter, 2008; Andreani *et al.*, 2009). The potential advantages are (1) rapid conversion of CO<sub>2</sub> to stable carbonate minerals thus reducing the risk of CO<sub>2</sub> release, (2) potential blockage of upward CO<sub>2</sub> migration due to impermeable (and previously undisturbed) sediment cover, (3) for sea-floor injections and the possibility of CO<sub>2</sub>-hydrate accumulation when escaped CO<sub>2</sub> contacts cool overlying formation water or seawater, and (4) substantial fracture networks due to the initial emplacement processes.

The first *in situ* CO<sub>2</sub> mineralization test project, CarbFix ([www.carbfix.com](http://www.carbfix.com)), also began this year in Hellisheidi, Iceland (Alfredsson *et al.*, 2008; Oelkers *et al.*, 2008). The injection site is located adjacent to a new geothermal power plant and will use CO<sub>2</sub> originating from operations at the plant. Approximately 30,000 tons/year of dissolved CO<sub>2</sub> will be injected into subsurface basalts at a temperature of approximately 30°C, a CO<sub>2</sub> partial pressure of 25 bars, and a depth of 500 to 700 meters (Oelkers *et al.*, 2008). The chemical evolution of the groundwater will be monitored at nearby wells to assess the effectiveness of the operation. This is the first field-scale CO<sub>2</sub> disposal into basaltic rocks and provides great promise for our understanding of the effectiveness of mineral carbonation as a permanent storage option for anthropogenic CO<sub>2</sub>.

Despite the increased interest in CO<sub>2</sub> mineralization there are still fundamental gaps in our knowledge of mineral reactions in the presence of CO<sub>2</sub>, particularly for mafic and ultramafic mineral assemblages. A major challenge is the substantial volume change that occurs during the transformation from Mg- and Ca-silicate minerals to carbonates (and the associated by-products of the carbonation reactions). For example, the reaction of olivine (Mg<sub>2</sub>SiO<sub>4</sub>) with aqueous CO<sub>2</sub> to yield the final products magnesite (MgCO<sub>3</sub>) and quartz (SiO<sub>2</sub>)



results in a volume increase of solid phases ( $\Delta V/V$ ) of 79%. There is little doubt that such high volume changes will result in sealing of the natural rock porosity and a dramatic reduction in the efficiency of carbonation reactions. Thus, volumetric changes accompanying carbonation reactions must be considered as a first order problem in evaluating the potential of geologic sequestration of CO<sub>2</sub>. We note, for example, that if silica concentrations are maintained below quartz saturation, then the solid volume change for the stoichiometric replacement of Mg-olivine by magnesite (reaction 1) is -23%.

However, very few detailed experiments and/or modeling simulations have been presented regarding the chemical and physical processes associated with CO<sub>2</sub> injection into serpentinites, basalts, and peridotites. The majority of studies have consisted of closed-system, batch reactor experiments or theoretical simulations. However, a recent study by Andreani *et al.* (2009) considered the injection of CO<sub>2</sub>-rich brine into peridotite (97% olivine, 2% diopside) using an experimental percolation bench. Their experimental apparatus enabled them to perform flow-through simulations at CO<sub>2</sub> partial pressures of 11 MPa, total pressures of 12 MPa, and flow rates of 0.3 m<sup>3</sup>/yr. By monitoring the pressure drop between the inlet and the outlet points, the evolution of the permeability throughout the experiment could be monitored, in addition to the net mineral transformations based on the changes in solute chemistry. There are several key features of the experimental flow-through study, the first of which is that the porosity decreased and permeability increased over the duration of the experiment as a result of the development of preferential flow paths. However, the system did not experience the “clogging” that batch reactor simulations had predicted. Secondly, mineral transformation processes were found to depend strongly on the local flow regime with carbonate precipitation occurring in domains of reduced flow, while high flow zones were characterized by Si-rich passivating layers on the olivine surfaces. The development of preferential flow paths and high flow zones also resulted in the spreading of CO<sub>2</sub> rich fluids and other reaction products, while much slower flow in the matrix created conditions favorable for the carbonation reactions (Andreani *et al.*, 2009).

The work by Andreani *et al.* (2009) is the first to consider the mineral carbonation process under flow conditions. Their work demonstrates that carbonation efficiency is likely to be high under certain optimal flow conditions. A critical finding of this study is that the reduction in permeability and porosity is confined to reduced flow or diffusion-limited zones, while high-flow rates result in apparent armoring of mineral surfaces following initial dissolution, suggesting that optimal flow rates should exist that will result in high CO<sub>2</sub> removal efficiencies. In these highly reactive fluid-rock systems, the differing transport and geochemical regimes resulting from heterogeneity and dual-porosity conditions may be serendipitous. Unfortunately, Andreani *et al.* (2009) did not perform any detailed modeling of their experimental results, which limits their utility for upscaling to field-systems. Our current work builds on the experimental results of Andreani *et al.* (2009) and others in two ways: (1) experimental studies of olivine dissolution and carbonation are still needed to calibrate the thermodynamic and pore-scale reactive transport processes occurring during the dissolution of olivine and the formation of magnesite (and other product phases) and (2) development of a reactive transport framework for predicting flow and boundary conditions that are optimal for CO<sub>2</sub> injection into basalt and serpentine rock formations

## Results

Although there have been a number of studies addressing the injection of CO<sub>2</sub> into mafic and ultramafic rock formations and the resulting mineral fluid interactions (Wogelius & Walther, 1991; Giammar *et al.*, 2005; Hansen *et al.*, 2005; Bearat *et al.*, 2006; Hanchen *et al.*, 2006; Alexander *et al.*, 2007; Matter *et al.*, 2007; Goldberg *et al.*, 2008; Kelemen & Matter, 2008; Oelkers *et al.*, 2008; Andreani *et al.*, 2009; Flaathen *et al.*, 2009), none have employed an integrative approach that combines experimental

studies of CO<sub>2</sub> (+H<sub>2</sub>O) interaction with mineral surfaces, surface science characterization of reaction products and reaction intermediates, thermodynamic considerations with reactive transport and mass transfer limitations, and field studies of natural analogs of mineral carbonation reactions. Our experimental approach will yield much needed information on surface chemical changes of Mg-containing minerals upon reaction with CO<sub>2</sub> and water, including the important effect of surface passivation. Our recently initiated experimental studies of the interaction of CO<sub>2</sub>-rich fluids with olivine will yield baseline kinetic data on mineral carbonation that will be compared with planned studies of the effects of organic acids and natural enzymes on reaction kinetics. Thermodynamic considerations are critical because the reaction kinetics and mechanisms are currently defined only to a limited extent under standard temperatures and pressures, yet must be eventually applied with confidence over a range of temperatures, pressures, and chemical conditions (pH, ionic strength, etc.). The reactive transport approach is critical because porosity and permeability changes are distributed along a flow path as different reaction fronts move through the system. The different reaction fronts are, in turn, controlled both by the thermodynamic properties of the mineral (solubility, kinetics, etc) and the fluid conditions experienced by each phase. Field systems, where CO<sub>2</sub>-rich fluids have interacted with rock formations under pressure and temperature conditions similar to those proposed for many CO<sub>2</sub> injection sites, provide critical constraints regarding both the likely phase assemblages and reaction zones and the physical processes that occurred during over-pressurization of the surrounding rocks.

Below we summarize initial results from this combination of tasks. The experimental portion of our project has only recently begun with the recruitment of a new graduate student (Natalie Johnson) from the Department of Chemical Engineering at Stanford University in February 2009 and the initiation of a new collaborative research program with Robert Rosenbauer of the U.S. Geological Survey (Menlo Park, CA), who has provided us access to his experimental hydrothermal laboratory where we have initiated a study of the interaction of CO<sub>2</sub> and water with Mg-rich olivine.

### **CO<sub>2</sub> sequestration by carbonation of alkaline metal silicates and hydroxides**

One of the goals of this project is to determine reaction products and reaction intermediates when CO<sub>2</sub>, CO<sub>2</sub> + H<sub>2</sub>O, or CO<sub>2</sub> + concentrated aqueous solutions (brines) are reacted with the surfaces of alkaline earth metal oxides, hydroxides, and silicates commonly associated with serpentinites and basalts, which are among the most common types of Mg-silicate rocks exposed at Earth's surface. Emphasis is being placed on reactions of CO<sub>2</sub> and CO<sub>2</sub> + aqueous solutions with brucite (Mg(OH)<sub>2</sub>), portlandite (Ca(OH)<sub>2</sub>), and, in particular, with key Mg-silicate minerals including olivine (forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)) and the serpentine polymorphs (chrysotile, lizardardite, and antigorite - Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>). As model Ca-silicates we have chosen wollastonite (CaSiO<sub>3</sub>), diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). We are initially studying these reactions using oriented single crystal substrates of the minerals, which will serve a simplified models of the more common polycrystalline minerals. Following these studies, we will continue with fine-grained powders of the aforementioned minerals as well as with samples that have been heat-treated to potentially activate their reaction with CO<sub>2</sub> (see, *e.g.*, Gerdemann *et al.*, 2007). The key objective is to develop a fundamental understanding of intermediates and products of the CO<sub>2</sub> reaction with Mg- and Ca-silicate mineral

surfaces and, in particular, to find conditions under which carbonation kinetics are optimized. Important components of our study are to identify appropriate activators or catalysts that enhance reaction kinetics and to find conditions under which reactions are not limited by surface passivation caused by silica or carbonate coatings.

We are utilizing a relatively new synchrotron branch line (BL 11.0.2.1) at the Advanced Light Source at Lawrence Berkeley National Lab (Bluhm *et al.*, 2005) to conduct ambient pressure photoelectron spectroscopy (APPES) on mineral carbonation reactions. This recently developed high-pressure photoemission facility – one of only two in the world (the other being at BESSY in Berlin, Germany) – allows one to study equilibrium reactions of CO<sub>2</sub> and CO<sub>2</sub> in conjunction with water or aqueous solutions at environmentally important pressures and thus extends the analytical power of photoelectron spectroscopy to environmentally and technologically important pressures. Specifically, in the system developed on the BL 11.0.2.1, data can be acquired up to pressures of a few Torr, which allows one to follow carbonation reactions to pressures well above the current partial pressures of atmospheric CO<sub>2</sub> (0.288 Torr). In addition, since the triple point of water is at 4.6 Torr pressure, reactions of CO<sub>2</sub> under wet conditions can be followed up to 100% relative humidity.

MgO (periclase) and Mg(OH)<sub>2</sub> (brucite) are the model surfaces being used in our initial studies. Although these minerals are less abundant in nature than Mg-silicates, they are highly relevant for understanding carbonation reactions of Mg-silicates. In fact, in many sequestration scenarios, silicates are transformed to brucite or porous periclase for which carbonation reactions are more efficient (Huijgen & Comans, 2005). It has also been established, that the interplay between hydration and dehydration plays an important role in effective carbonation. We are in unique position to follow these processes on the atomic level.

To avoid surface charging in the photoemission and electron yield adsorption measurements, we grew a several monolayer thick epitaxial layer of MgO on a silver (100) surface (Newberg *et al.*, 2009). Several prior studies have verified that these layers have all the characteristics of bulk MgO (*e.g.*, Wollschläger *et al.*, 1999; Rodriguez *et al.*, 2000; Grönbeck, 2006), making them reliable surrogates for bulk single crystal MgO. The uniformity of our layers can be checked directly by measuring attenuation of the silver substrate signal. The high quality of the surface was ascertained by low energy electron diffraction. In addition, the near-perfect epitaxial match between the same crystallographic surfaces of MgO and silver allows one to choose the termination of the MgO layer. The two most common terminations – (100) and (111) – were grown on Ag(100) and Ag(111) substrates, respectively. Although, most of our initial data are for the (100) surface, the (111) surface is also highly relevant due to the topotactic relationship between the (111) surface of MgO and the (0001) surface of Mg(OH)<sub>2</sub>. In fact, we predict that the (111) surface of periclase will undergo an instantaneous transformation to brucite even at modest relative humidities. This transformation would facilitate the study of the effect hydration and dehydration of brucite on the efficiency of carbonation. From prior studies of the brucite-periclase transformation, it is known that dehydration of brucite leads to a porous form of periclase, which, due to bond

unsaturation effects, should be particularly prone to the carbonation reaction. It is important to confirm these predictions experimentally. Because of the near ambient conditions offered by our experimental set-up, we are in a unique position to study these effects as they occur under equilibrium conditions. Under ultra high vacuum (UHV) conditions, these processes cannot be followed because the topmost brucite layer is instantaneously dehydrated. As an indication of the relevance of these model systems to carbonation reactions on Mg-silicates, we note that the fibrous serpentine mineral chrysotile, which is a key silicate in our studies of carbonation of Mg-silicates, is terminated with brucite-like layers.

In our pilot experiments the (100) surface of MgO was reacted with dry CO<sub>2</sub> and a combination of CO<sub>2</sub> and H<sub>2</sub>O at ambient temperature. We have utilized Ambient Pressure Photoemission Spectroscopy (APPEs) and near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy to follow these reactions as they occur on the MgO (100) surface in equilibrium with water and/or CO<sub>2</sub> gas. In **Figure 3** we present APPEs O1s, C1s, and Mg2p data taken at energies required to excite the respective core level electrons such that the photoelectrons have the same kinetic energy of 150 eV. This choice guarantees the same probing depth and allows quantification of the reacted species (scattering from gas in the chamber is also energy dependent).

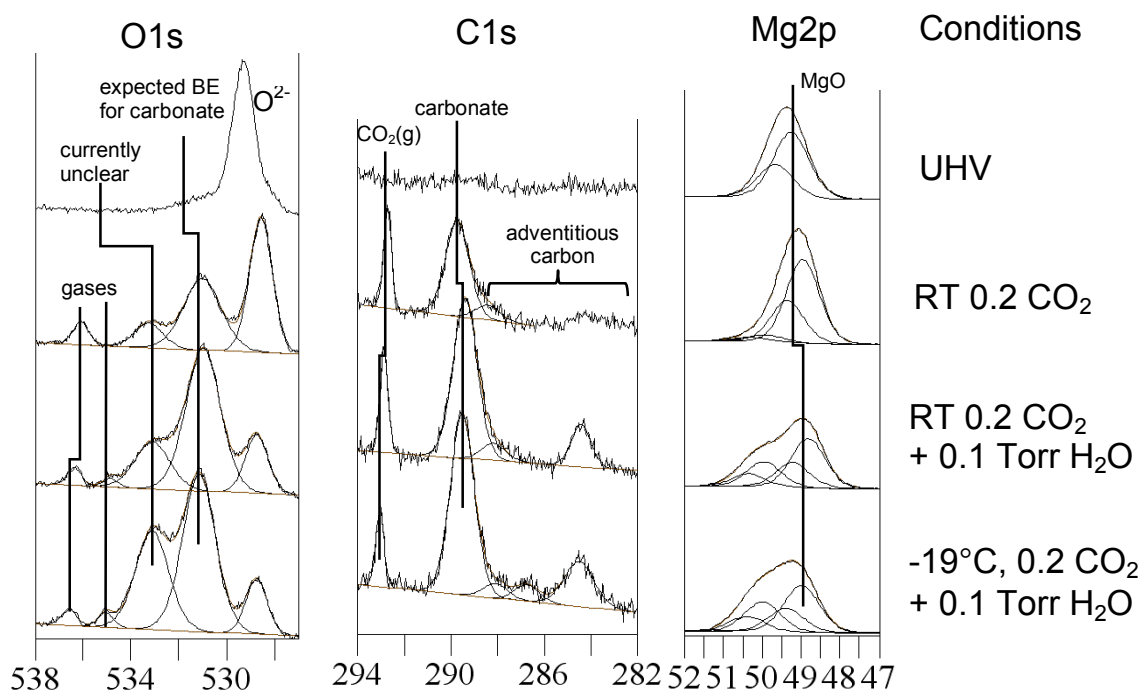
The top-most spectra in **Figure 3** represent data for the as-grown layer of MgO(100) without CO<sub>2</sub> or H<sub>2</sub>O. The second row of spectra represent the results of dry carbonation (*i.e.* without H<sub>2</sub>O) at 0.2 Torr of CO<sub>2</sub> at room temperature. The MgO surface exposed to this pressure of CO<sub>2</sub> clearly reacts to form a carbonate. The nature of the reacted species is verified through the binding energy and by a “carbonate spike” in the NEXAFS spectrum, which is shown in **Figure 4**. The third row of spectra from the top of **Figure 3** represents an additional exposure of the MgO (100) surface to 0.1 Torr of water (sample now at 0.2 Torr of CO<sub>2</sub> and 0.1 Torr of H<sub>2</sub>O); carbonation is seen to increase. Interestingly when the reaction is conducted in the reverse order (*i.e.* exposing the surface to H<sub>2</sub>O first, then to CO<sub>2</sub>), the yield of Mg carbonate is reduced. Apparently water blocks the adsorption sites. This observation helps explain the enhanced carbonation of preheated Mg-silicate minerals presumably due to the dehydration of their surfaces. Our planned APPEs studies of the carbonation of hydrated Mg-silicate surfaces will determine if there is a similar inhibition of the carbonation reaction. The lowest row of spectra in **Figure 3** represents the reaction of MgO(100) at the same partial pressure of CO<sub>2</sub> and H<sub>2</sub>O, but with temperature reduced to attain high relative humidity. The reaction is again enhanced. We observe that Mg2p shows very little reactivity towards CO<sub>2</sub> and yet carbonate is clearly formed. This finding indicates that CO<sub>2</sub> is preferentially bound to the surface O to form carbonate species.

In **Figure 4** we present C K-edge NEXAFS spectra taken in Auger electron yield to maximize the surface sensitivity of our NEXAFS spectra. The samples correspond to those used in the APPEs measurements discussed above (**Figure 3**). The data are normalized both to the energy dependence of the photon flux and to the gas-phase spectrum taken in the absence of the MgO(100) sample. The data were taken at different relative polarizations of the E-vector of the incident X-ray beam with respect to the



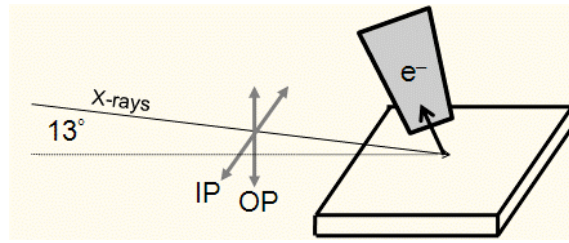
substrate surface in order to determine the spatial orientation of  $\text{CO}_3^{2-}$  groups relative to the substrate surface. The sharp feature just above 290 eV in the NEXAFS spectra provides an unambiguous fingerprint of the formation of carbonate on the surfaces. The same characteristic spectrum is observed for all carbonates, and its energy is independent of the metal. The increase in intensity of this feature illustrates the increase in carbonate coverage for the series of exposures. Polarization dependence indicates that carbonate species are preferentially oriented away from the surface.

### In Situ XPS (150 eV KE)



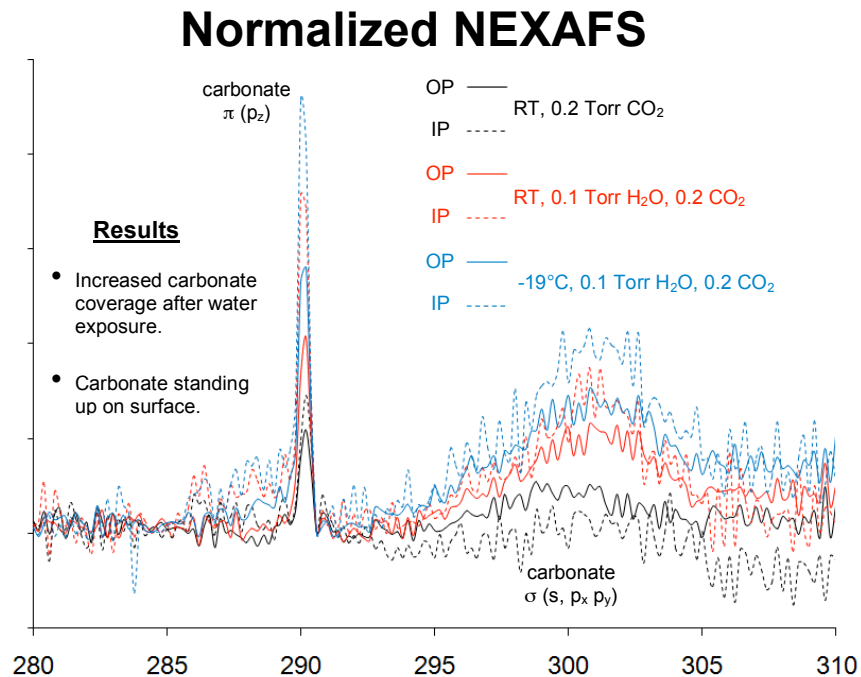
**Figure 3.** Ambient pressure X-ray photoelectron spectra of the O1s, C1s, and Mg2p on MgO(100) before and during reaction with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Newberg *et al.*, 2009).

This model system APPES study of the interaction of  $\text{CO}_2$  and water with MgO(100) shows the potential of this approach in determining the initial reaction products and potentially reaction intermediates in carbonation reactions of Mg-silicates. It also helps explain the enhancement of carbonation reactions by preheating Mg-silicates. This approach will also be useful in evaluating the effects of activators such as organic acids and catalysts such as carbonic anhydrase on these reactions.



## C K-Edge In Situ NEXAFS

Auger yield, 150 eV KE



**Figure 4.** *In situ* Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra of MgO(100) under reactive conditions in which  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are exposed to the surface. (Newberg *et al.*, 2009).

### Olivine dissolution and carbonation kinetics under conditions relevant for $\text{CO}_2$ sequestration

The recent literature contains studies reflecting many aspects of the serpentine  $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ -carbon dioxide-water reaction system with a focus on mineral carbonation as a means of sequestering carbon dioxide for long time periods. The reaction can be divided into three main steps: magnesium dissolution from the mineral, conversion of hydrated carbon dioxide into bicarbonate, and magnesite ( $\text{MgCO}_3$ )

formation. The mineral dissolution reaction has been well studied for many years, and existing data suggest that high temperatures, acidity, and small particle size generate the optimal environment for mineral dissolution (*e.g.*, Gerdemann *et al.*, 2007). However, recent studies have sought to achieve reasonable extents of dissolution under milder conditions, such as by using sodium chloride, which reduces the activity of other charged ions in solution (Chen *et al.*, 2006), or organic acids instead of harsher inorganic acids to control the pH of the solution (Park *et al.*, 2003). The use of inorganic acids also appears to prevent the formation of a silica-rich passivating layer observed by Bearat *et al.* (2006). This layer is hypothesized to come from either silica precipitating from solution or incongruent dissolution due to preferential release of magnesium relative to silica in the mineral substrate (Luce *et al.*, 1972).

Conversion of hydrated CO<sub>2</sub> into bicarbonate is also known to increase with increasing pressure and decrease with increasing temperature. The dissolution rate is also increased by carbonic anhydrase, a natural zinc-metalloenzyme that greatly increases the rate of formation of the bicarbonate ion and protons (Badger & Price, 1994). Several studies have examined carbonic anhydrase for this application, and found that its activity is not affected by pH (Mirjafari *et al.*, 2007) or by the presence of other chemical species that may be present in CO<sub>2</sub> input streams (Bond *et al.*, 2001).

Finally, magnesite formation appears to occur to a greater extent at higher pH, suggesting that a one-reactor batch process may not be optimized by the initial addition of acid because this will limit the product precipitation (Chen *et al.*, 2006). If acid is used to facilitate olivine dissolution, the pH must later be increased to precipitate magnesite. Also, while magnesite is the most stable magnesium carbonate, it is not formed at ambient temperature and pressure. Instead, its direct formation is favored at high temperature and high carbon dioxide pressure (T>150°C and P>150 bar), and indirect formation via hydromagnesite occurs at more moderate temperatures and pressures (T>60°C) (Hanchen *et al.*, 2008).

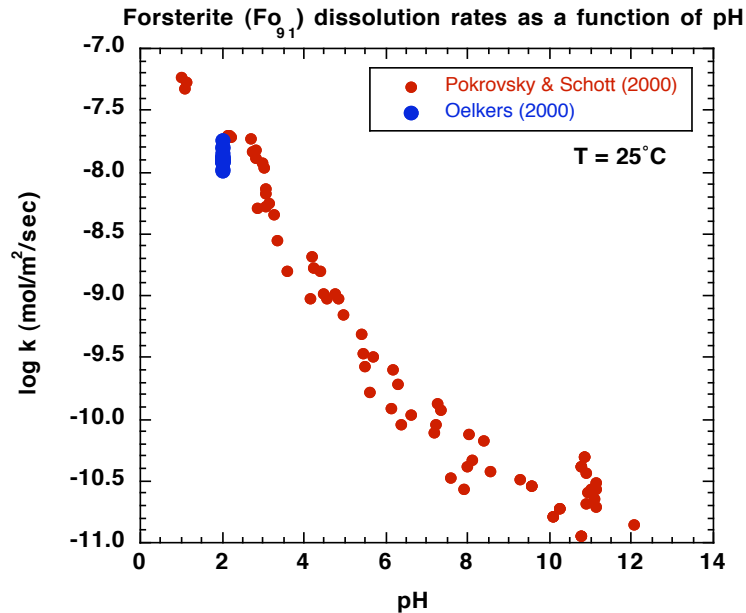
Our initial experiment was designed to be carefully controlled and simple in order to provide baseline data for comparison with future, more complex, reaction systems. Finely ground magnesium-rich olivine ((Mg,Fe)<sub>2</sub>SiO<sub>4</sub>) was combined with distilled water at a 1:10 ratio, and 0.05% NaCl by weight was added to promote ion transfer. As discussed below, parallel reactive transport simulations using Mg-rich olivine and similar reaction conditions are being carried out. The temperature was set to 77°C and enough CO<sub>2</sub> was added at 100 bars of pressure to slightly supersaturate the system. Olivine rather than serpentine was chosen for this initial experiment because of its higher reactivity and simpler chemistry. This choice was also made because of our decision to focus first on reactive transport modeling of the interaction of CO<sub>2</sub>-rich aqueous solutions with forsterite.

The apparatus used for the initial experiment consisted of a deformable, inert reaction cell held in place inside a high-pressure cylindrical furnace with the remaining interior space filled with distilled water. The reaction cell is made of a deformable gold bag with a rigid titanium top. Titanium tubing passes from the lid of the bag to a sampling valve

outside the cylindrical furnace, allowing for extraction of fluid throughout the course of the reaction. The water surrounding the gold bag is pressurized to a desired value, and when the sampling valve is opened, the pressurized water compresses the bag. Repressurizing the water after sample withdrawal ensures that the pressure of the reacting system remains constant even after multiple samples are removed. The entire furnace is fixed to a mechanical system, which continually rotates the cylinder 180 degrees, forcing convective mixing of the heterogeneous reaction mixture. A more detailed description of the experimental apparatus can be found in Rosenbauer *et al.* (2005).

Extracting fluid samples periodically during the reaction allows the extent of reaction to be monitored over time. Samples are analyzed for pH, metal content (Mg and Fe), and carbon content via ICP-MS in our labs at Stanford University. At the end of the experiment, the solids will be analyzed using x-ray diffraction and surface-sensitive spectroscopic methods to determine the amount of carbonate formed and the nature of that carbonate. After one week of reaction, initial results show that carbon dioxide concentration has decreased slightly with time after peaking 30 hours after initiation, and the pH has remained relatively constant  $\sim 7$  due to the buffering capacity of olivine.

Forsterite dissolution rate data have previously been measured by Pokrovsky & Schott (2000) and Oelkers (2000) (**Figure 5**). We will compare our new results with these earlier results and will use the *CrunchFlow* simulations discussed below to help constrain planned dissolution rate studies of forsterite, chrysotile, and the other Mg-silicate minerals discussed earlier.



**Figure 5.** Forsterite ( $\text{Mg}_{0.91}\text{Fe}_{0.09}\text{SiO}_4$ ) dissolution rate constants as a function of pH. Conditions typical for  $\text{CO}_2$  injections are identified in the square area.

## Reactive transport simulations of mineral carbonation during *in situ* CO<sub>2</sub> injection

To date, the majority of studies considering CO<sub>2</sub> injection into mafic and ultramafic rock formations have used closed system batch reactor models to understand the geochemical reaction network (Xu *et al.*, 2004; Marini, 2007; Oelkers *et al.*, 2008). No studies that we are aware of have employed an integrative reactive transport approach that combines the thermodynamics of water-rock interactions with aqueous transport considerations. Thermodynamic considerations are critical because the reaction kinetics and “mechanisms” are currently defined only to a limited extent under standard temperatures and pressures, yet must be eventually applied with confidence over a range of temperatures, pressures, and fluid and rock compositions (pH, ionic strength, porosity, etc.). Aqueous transport and, in particular, advective transport provide an additional driving force for these mineral-fluid reactions by increasing the thermodynamic departure from equilibrium. The reactive transport approach is also useful because porosity and permeability changes are distributed along a flow path as different reaction fronts move through the system.

In order to provide a consistent approach for interpreting experimental and field-based data pertaining to the reaction of CO<sub>2</sub> with serpentine and basalt mineral assemblages, we have developed an initial reactive transport modeling framework using the multi-component reactive transport software, *CrunchFlow* (Steeffel & Lasaga, 1994; Steefel, 2001; Giambalvo *et al.*, 2002; Knauss *et al.*, 2005; Maher *et al.*, 2006; Li *et al.*, 2008; Maher *et al.*, in press). The reactive transport approach has many advantages such as a complete equilibrium thermodynamic treatment, flexible kinetic rate law formulations, and a range of 3-D flow capabilities. The major disadvantages of using this model to consider CO<sub>2</sub> sequestration are that we cannot at present directly calculate the thermal energy consequences of the strongly exothermic reactions, and we cannot explicitly treat multi-phase flow. However, given the current level of understanding, the first-order challenges in developing mineral carbonation strategies are (1) reaction pathways and their associated kinetics and (2) the feedback between geochemical reactions and aqueous transport.

### *Model framework*

In support of both the modeling simulations and the experimental studies, we have compiled a consistent kinetic and thermodynamic database that can be modified to apply across a range of temperature and pressure conditions. We focused our initial simulations on the MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> system under isothermal, isobaric, and fully saturated flow-through conditions (Table 1). Using a simplified 1-D geometry, we considered the propagation of the carbonation reaction front under different boundary conditions, such as flow rate and aqueous CO<sub>2</sub> concentrations. Our numerical experiment is analogous to the flow-through experiments performed by Andreani *et al.* (2009), where we are introducing solution equilibrated with CO<sub>2</sub> into a column of homogenous material and using kinetic and thermodynamic constraints to calculate the volume changes, rates of mineral carbonation, and efficiency of CO<sub>2</sub> removal over a range of flow conditions and  $P_{\text{CO}_2}$  concentrations.

To create an initial condition for our numerical CO<sub>2</sub> flow-through experiments, we began with an idealized model rock consisting of 70% (by volume) forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)

and 30% porosity (roughly equivalent to coarse grained aggregate). We numerically reacted our initial condition with dilute fluid to form the equilibrium assemblage chrysotile (62 vol. %) and brucite (14 vol. %) (hydrolysis reactions 1 to 3 in **Table 1**). This is a common mineral assemblage associated with the alteration of ultramafic rocks to form serpentinite (Barnes & O'Neil, 1969) and leads to a reduction of the initial porosity by 26% resulting in a final porosity of 24.0% and a fluid pH of 8.2. This porosity may be more consistent with the representative elementary volume (REV) of a fracture rather than the actual matrix rock, where porosities are typically <1%. The purpose of the pre-condition computation was to arrive at a model rock assemblage and fluid composition within our numerical reactor *prior* to the influx of CO<sub>2</sub>-rich fluids. In order to avoid two-phase flow, the injection water was pre-equilibrated with CO<sub>2</sub> at 100 bars and 260 bars total pressure at a temperature of 60°C resulting in an injection fluid with a pH of 3.05.

**Table 1: Reactions and associated values used in model. Log K values not shown but are taken here (1 atm) from the EQ3/EQ6 database (Wolery & Jarek, 2003)**

	Mineral	Mineral Formula	log (25°C) (mol/m <sup>2</sup> /s)	k <sup>a</sup> E <sub>a</sub> <sup>b</sup> (kJ/mol)	Molar Volume (cm <sup>3</sup> /mol)
	Model 1: Mg-SiO <sub>2</sub> -H <sub>2</sub> O-CO <sub>2</sub> system				
1.	Forsterite	Mg <sub>2</sub> SiO <sub>4</sub> + 4H <sup>+</sup> → 2Mg <sup>2+</sup> + SiO <sub>2</sub> + 2H <sub>2</sub> O	-6.85 <sup>c</sup>	67.2	43.79
2.	Chrysotile	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 6H <sup>+</sup> → Mg <sup>2+</sup> + 2SiO <sub>2</sub> + 5H <sub>2</sub> O	-12.0	73.5	106.61
3.	Brucite	Mg(OH) <sub>2</sub> + 2H <sup>+</sup> → Mg <sup>2+</sup> + 2H <sub>2</sub> O	-8.24	42	24.63
4.	Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> + 6H <sup>+</sup> → Mg <sup>2+</sup> + 4SiO <sub>2</sub> + 4H <sub>2</sub> O	-12.0	42	136.52
5.	Magnesite	MgCO <sub>3</sub> + H <sup>+</sup> → Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>2-</sup>	-9.34 <sup>d</sup>	23.5	28.02
6.	Nesquehonite	MgCO <sub>3</sub> •3H <sub>2</sub> O + H <sup>+</sup> → Mg <sup>2+</sup> + HCO <sub>3</sub> <sup>2-</sup>	nd	nd	74.79
7.	Quartz	SiO <sub>2</sub> → SiO <sub>2</sub> (aq)	-13.4	90.9	22.69

<sup>a</sup>: kinetic rate constants (*k*) for dissolution reactions calculated from a compilation of existing experimental data by Palandri & Kharaka (2004) unless otherwise specified.

<sup>b</sup>: activation energy (*E<sub>a</sub>*) as calculated from a compilation of existing experimental data by Palandri & Kharaka (2004) unless otherwise specified.

<sup>c</sup>: for pH < 9 the dependence on *a<sub>H+</sub>*<sup>0.46</sup> (Pokrovsky & Schott, 2000), only dissolution is allowed in the model.

<sup>d</sup>: for the present study we assume that dissolution and precipitation are reversible in Δ*G<sub>r</sub>* space because precipitation rate constants are poorly defined for the majority of secondary minerals.

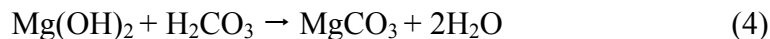
An advantage of *CrunchFlow* is that kinetic rate laws are specified uniquely for each mineral depending on the reaction mechanism. For our simulations, we rely on the theoretical framework provided by Transition State Theory (TST). A general form of the TST rate law formulation that is not restricted to the assumption of a linear dependence on the deviation from equilibrium can be written as:

$$R_l = A_{bulk} \cdot k_l \cdot \beta \cdot \left[ 1 - \exp\left(\frac{-\Delta G_r}{\sigma RT}\right)^n \right]^m \quad (3)$$

where  $R_l$  is the rate of an individual reaction pathway or mechanism (in units of mol/m<sup>3</sup> porous medium/s),  $A$  is the reactive surface area (m<sup>2</sup>/m<sup>3</sup> porous medium),  $k_l$  is the surface normalized rate constant (mol/m<sup>2</sup>/s) determined far from equilibrium,  $\beta$  is a term describing the inhibition or catalysis of the reaction,  $\Delta G_r$  is the Gibbs free energy of reaction (and the entire term in parentheses describes the dependence on reaction affinity),  $n$  and  $m$  are fitting parameters, and  $\sigma$  is Temkin's average stoichiometric coefficient. For the present numerical experiments, we are using a linear statement of eqn. 3 ( $\sigma, n, m = 1$ ) to capture the major features of reaction fronts, and will incorporate additional rate law formulations as necessary and as they are developed from our experimental studies.

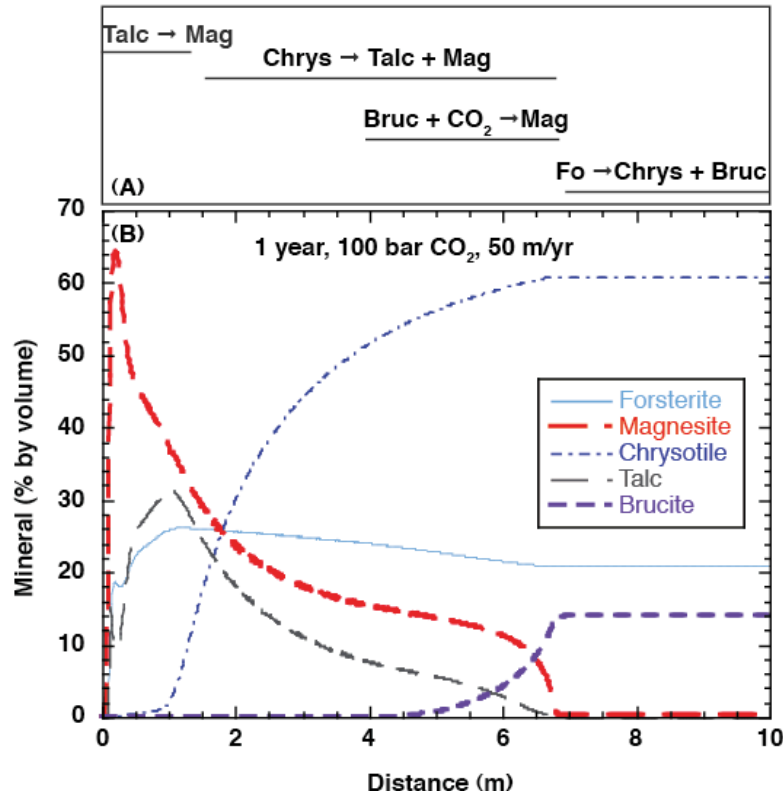
Our numerical experiments considered a 100-meter long column of saturated porous media held at 60°C and 260 bars. Updated mineral volume fractions were used to calculate porosity changes due to mineral transformations. Rate constants are as defined in **Table 1** and corrected for temperature using the established activation energies. Injection flow rates ranged from 50 m/yr to 500 m/yr and were held constant throughout the simulation. We currently use a simplified flow system and geometry in order to understand the relationship between flow rates, boundary conditions and initial conditions but plan to consider more realistic scenarios in the future. Results from our reference simulation are shown in **Figure 6** where mineral abundance as a function of distance is shown for an integrated time of 1 year. Our results show that despite the high volume changes associated with the net carbonation reaction, sufficient porosity is maintained due to the high flow rate and aggressive fluid such that “clogging” of the reactor column is not as substantial as predicted by closed system reaction path models. Most importantly, under these flow conditions the removal of the CO<sub>2</sub> from the fluid is 100% efficient, and increases in the flux of dissolved CO<sub>2</sub> would further enhance the propagation rate of the carbonation front rather than reduce the effectiveness for removing CO<sub>2(aq)</sub>.

Under all conditions in our simulations, we found that the reaction sequence followed that of **Figure 6**. The first reaction in the carbonation front was the consumption of brucite and CO<sub>2</sub> to form magnesite (*e.g.*, reactions 3 and 5 of **Table 1**):



The stoichiometric volume change of solids in this reaction is  $\Delta V/V = +13.7\%$ . As a consequence, the initial formation of magnesite rapidly consumes the available porosity in this zone of reaction (**Figure 7**). In the zone of the reaction front characterized by the transformation of chrysotile to talc plus magnesite, although this reaction also has a net positive volume change, the porosity increase is moderated by the dissolution of talc to form magnesite at the back edge of the reaction zone (**Figure 6**). In addition, we note that because the removal of CO<sub>2</sub> is nearly 99.9% efficient, the rate of magnesite precipitation is proportional to the flux of CO<sub>2</sub> (**Figure 8**). Even for the case

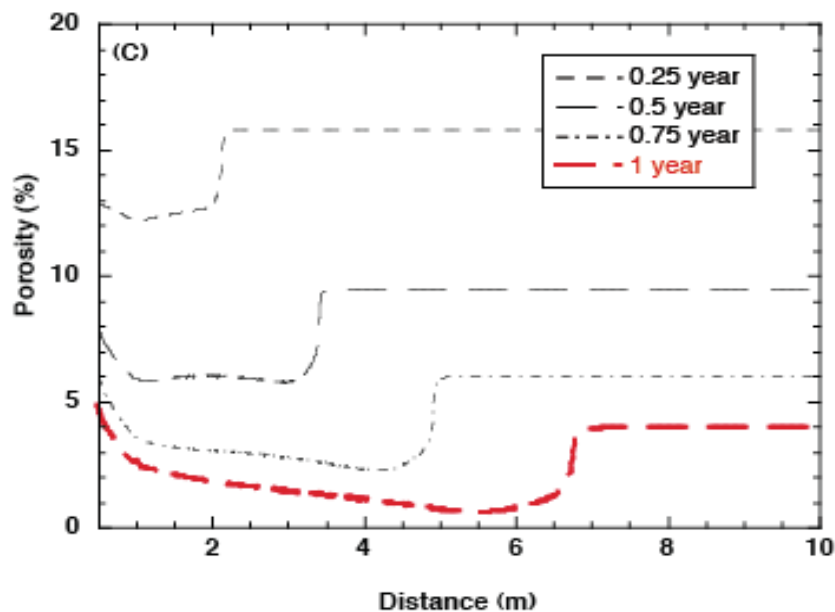
of pure seawater in equilibrium with atmospheric CO<sub>2</sub>, we find magnesite precipitation occurring in substantial quantities, albeit over slower timescales and distances.



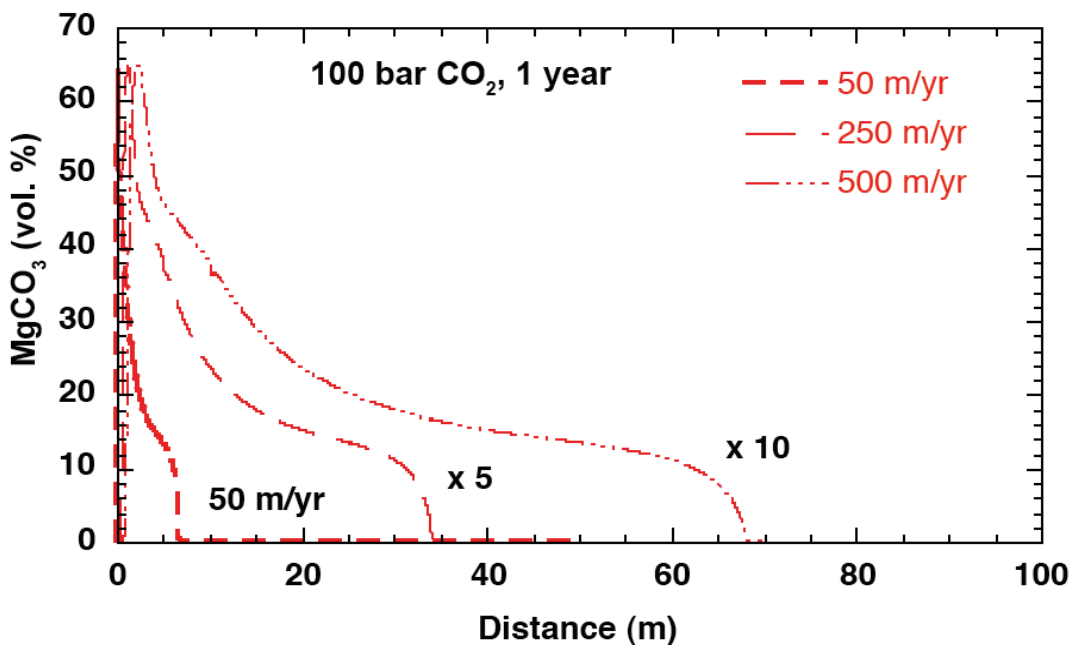
**Figure 6.** Numerical simulation of the injection of a CO<sub>2</sub>-rich fluid into a serpentinite mineral assemblage after 1 year of continuous injection at a flow rate of 50 m/yr (flow is from left to right). Initial porosity is 30%. (A) Mineral reactions occurring at different locations along the flow path; (B) changes in mineral abundance corresponding to reactions in (A). Primary minerals are shown in blue dashed lines and the magnesite (mag) carbonation front is shown in red dashed line. The leading edge of the carbonation front is due to carbonation of brucite (bruc), while the maximum magnesite abundance occurs due to the dissolution of secondary talc (grey dashed line). The peak reduction in porosity occurs due to the formation of talc from chrysotile (chrys).

Our calculations have shown that the mineral transitions that occur during alteration of basalt and serpentinites are extremely efficient and could even result in complete removal of CO<sub>2</sub> from dilute fluids such as seawater. However, these reactions do result in extremely high net volume changes and dramatic reductions in porosity. The reduction in porosity is ameliorated if chemically aggressive CO<sub>2</sub>-rich fluids are used. *Importantly, our simplified cases reflect the same processes demonstrated by the experimental work of Andreani et al. (2009), namely that the distribution of mineral transformations along a flow path is such that sufficient porosity can be maintained to enable fluids to reach the reaction front.*





**Figure 7.** Porosity evolution during the first year of injection of CO<sub>2</sub>-rich fluid. Thick dashed line corresponds to mineral abundances in **Figure 6** above.



**Figure 8.** Effect of flow on rates of CO<sub>2(aq)</sub> removal. At 50 m/yr, CO<sub>2</sub> is removed at a rate of 2.3 tons m<sup>-2</sup> yr<sup>-1</sup>, and at flow rates of 250 and 500 m/yr rates of removal are 11.3 and 22.6 tons m<sup>-2</sup> yr<sup>-1</sup>, respectively.

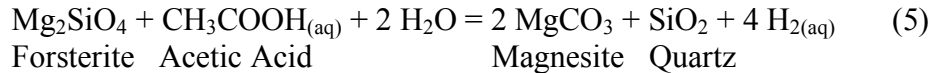
Some previous discussions of this fluid-rock system have assumed that the positive volume changes will result in hydrofracturing of the rock, thus allowing the reactions to proceed beyond limitations imposed by a constant reaction volume (Kelemen & Matter,

2008). However, no study has yet focused on the mechanism of volume expansion and/or determined the type of chemical and physical manipulations that prevent precipitation of high-volume phases, and we plan to focus on this additional aspect in both our coupled experimental and simulation studies.

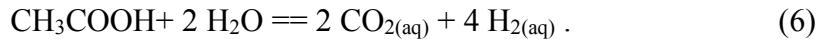
*Evaluation of the role of organic ligands in activating carbonation reactions*

An important component of our future experimental work and theoretical modeling will evaluate the potential role of organic ligands and biogeochemical environments in catalyzing carbonation reactions in ultramafic and mafic rock formations. It is well established that organic acids accelerate the dissolution rates of Mg-bearing hydroxides and silicates (Grandstaff, 1986; Wogelius & Walther, 1991; Pokrovsky *et al.*, 2005), although, as noted by Golubev & Pokrovsky (2006), unusually high concentrations of organic ligands are required to appreciably affect these rates ( $\sim 10^{-2}$  to  $10^{-3}$  m in general to triple experimental reaction rates). However, our evaluation of phase relations in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>-H<sub>2</sub> illustrated in **Figure 9** demonstrates that, in addition to the concentrations of aqueous organic acids, redox conditions (expressed here by values of aqueous H<sub>2(aq)</sub>) have an important affect on the stability Mg-silicates and on their dissolution rates (through the reaction affinity term in the rate equation 3). We also note that metal-organic complexes, such as Mg-acetate provide an additional contribution to the reaction affinity of Mg-silicates, and thus their solubility and dissolution rates (Shock & Koretsky, 1993; Schott & Oelkers, 1995; Pokrovsky *et al.*, 2005)

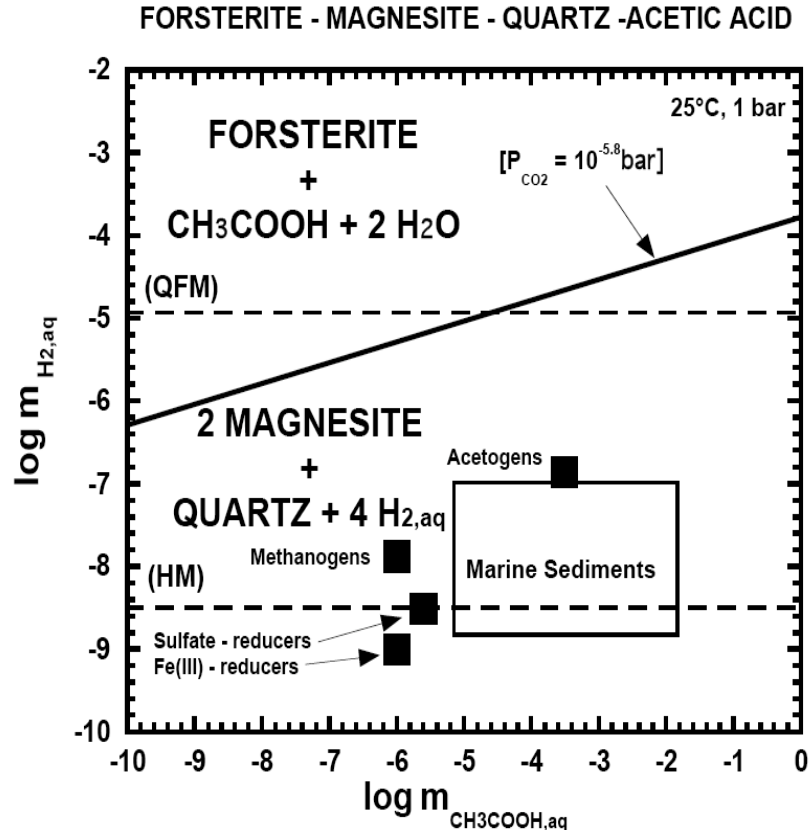
For the example provided in **Figure 9** we represent the stability of Mg-olivine (forsterite) relative to the assemblage of magnesite (MgCO<sub>3</sub>) plus quartz in terms of the concentrations of aqueous hydrogen and acetic acid (CH<sub>3</sub>COOH). The solid diagonal line shown in the figure denotes equilibrium for the reaction:



Acetic acid and aqueous hydrogen are employed as descriptive variables in **Figure 9** and reaction (5) in accord with observations reported by Helgeson *et al.* (1993) and Shock *et al.* (1997) that reduced carbon in aqueous organic acids of petroleum-field brines maintain metastable redox equilibrium with oxidized carbon in carbonate (aqueous CO<sub>2</sub>):



Similar thermodynamic analysis has been employed by Neuhoff *et al.* (2006) and Rogers *et al.* (2006), both graduate students advised by Co-PI DKB, to evaluate the evolution of porosity, CO<sub>2</sub>-metasomatism, and phase relations between zeolite, clays, and carbonates in olivine-bearing basalts infiltrated by petroleum brines at Nuussuaq, West Greenland (shown in the photo of **Figure 2B**).



**Figure 9.** The stability of forsterite (Mg-olivine) relative to magnesite ( $\text{MgCO}_3$ ) + quartz (reaction 4) as a function of the concentrations of aqueous hydrogen and acetic acid, where the latter is in redox disequilibrium with oxidized carbon in carbonate ( $\text{CO}_2$  and  $\text{MgCO}_3$ ; reaction 5). QFM denotes equilibrium for quartz, fayalite, and magnetite, and HM denotes equilibrium for hematite and magnetite. The symbols and boxes represent environmental conditions of extant niches of micro-organisms in volcanic aquifers and marine sediments (see text for details).

The diagonal line in **Figure 9** provides thermodynamic constraints on the stability of stoichiometric Mg-olivine relative to Mg-carbonate in environments where reduced carbon in aqueous organic acids are in metastable equilibrium with oxidized carbon in carbonate (in this case aqueous  $\text{CO}_2$  and magnesite). As noted in **Figure 9**, the phase boundary for reaction (4) corresponds to an isopleth of  $P_{\text{CO}_2}$  of  $10^{-5.8}$  bars as required by the equilibrium for reaction (2). For redox conditions equivalent to quartz, fayalite, magnetite (QFM) equilibrium we note that Mg-olivine reacts to form Mg-carbonate at concentrations of acetic acid  $>10^{-4.6}$  m at  $25^\circ\text{C}$ . As shown in **Figure 9**, this value decreases dramatically with decreasing concentrations of aqueous hydrogen, that is, conditions more oxidizing than QFM are detrimental to the stability of olivine.

Common niches for microorganisms, such as basaltic aquifers and deep-sea sediments, provide sufficient disequilibrium conditions to accelerate carbonation reactions (McIntosh *et al.*, 2004; Maher *et al.*, 2006). First, we note that acetogens, methanogens, and sulfate and iron reducers all compete for trace quantities of  $\text{H}_2$ ; natural

selection forces the terminal electron accepting metabolic processes of these bacteria to operate at their thermodynamic limits (Hoehler *et al.*, 1998). As shown in **Figure 9** these concentrations are 2 to 4 orders of magnitude below that required for equilibrium of reaction (5), which corresponds to reaction affinities, or Gibbs energy of reaction of  $\sim -2.7$  to  $-5.4$  kcal/mol (cf. rate equation 3). Concentrations of aqueous acetic acid shown in **Figure 9** range from low values of  $< 1$   $\mu\text{M}$  (for methanogens from Libby Hot Springs, ID, in mafic volcanic rocks,  $\sim 60^\circ\text{C}$ , Chapelle *et al.*, 2002) and  $\sim 1$  to  $2.5$   $\mu\text{M}$  for environs of iron and sulfate reducers, respectively (the latter from meteoric groundwater aquifer, NC, Chapelle & Lovley, 1992), to values exceeding  $15,000$   $\mu\text{M}$  in deep marine sediments associated with methane hydrates, burial, and diagenesis (Wellsbury *et al.*, 1997).

We conclude from this preliminary analysis that experimental and theoretical evaluation of the effects of aqueous organic ligands on the dissolution rates, solubilities, and stabilities of Mg-silicates relative to carbonate minerals are likely to be of first-order importance in optimizing the industrial utility of geologic sequestration of  $\text{CO}_2$  in ultramafic and mafic rock formations through mineral carbonation.

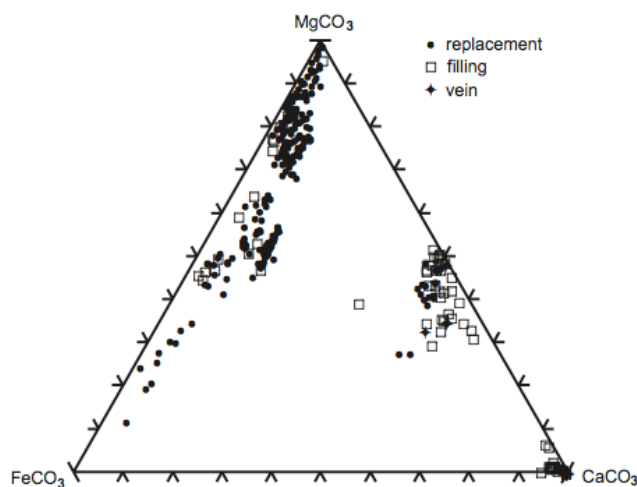
### **Field-scale characterization of natural analog sites**

Our field-scale studies provide natural analog models of geologic sequestration of  $\text{CO}_2$  in ultramafic and mafic rock formations. We have collected samples from the New Idria region in Central California where  $\text{CO}_2$ -rich fluids interacted with a serpentinite diapir resulting in large zones containing magnesite, hydromagnesite and other hydrous Mg-carbonates. We have collected samples from different zones of mineralization to characterize in thin section by petrographic microscope and electron microprobe studies and in bulk samples using XRD. This field-scale characterization is important because the reaction products may differ from what our models predict based on trace impurities and kinetic and surface area limitations. Our modeling and experiment studies to date have considered only ideal systems, whereas natural systems reflect much more diversity in reactants and products. Stanford M.S. student Pablo García Del Real is joining our research team to evaluate natural mineral parageneses of carbonation of serpentinites and to model the observations using the reactive transport code *CrunchFlow*.

Our experimental and theoretical studies have thus far focused on simple chemical systems such as  $\text{MgO-SiO}_2\text{-H}_2\text{O-CO}_2$  +/-  $\text{H}_2$ . Natural rock formations are more complex chemical systems. For example, the average compositions of ultramafic rocks and mafic rocks world wide contain, respectively, 9.9% and 8.6% (weight percent) of iron oxide, mostly as Fe(II) (Krauskopf & Bird, 1995, Table 20-3). Mafic rocks also contain significant amounts of calcium (6.7% CaO) and aluminum (8.8%  $\text{Al}_2\text{O}_3$ ). These are all important components of the common rock-forming minerals formed by metasomatic processes of mafic and ultramafic rock formations. We note that serpentine minerals are rarely the pure Mg-end member composition, but contain significant amounts of iron; the mole fraction of total iron ( $X_{\text{Fe}} = \text{Fe}/(\text{Fe}+\text{Mg})$ ) commonly is in the range of 0.02 to 0.08, and it rarely exceeds 0.1 except in some vein antigorites, which have values of up to 0.21 (Evans, 2008). In addition, Fe(III) is an important component in the serpentine minerals, especially lizardite (see reaction 1), with Fe(III) contents ranging from 33 to 88 percent of the total iron in lizardites from serpentinites formed from peridotites, dunites, and

harzburgites (O'Hanley & Dyar, 1998; Votyakov *et al.*, 1993). Iron substitution in serpentine and brucite minerals has a significant effect on their thermodynamic behavior in geologic system as summarized by Sleep *et al.* (2004).

In addition to compositional variations observed in natural serpentine minerals, carbonate minerals formed by alteration of ultramafic and mafic rock formations also can exhibit a wide range in chemical compositions. An example is illustrated in **Figure 10**, which shows the range of Mg/Fe/Ca substitutions in carbonate minerals formed during CO<sub>2</sub>-metasomatism of pricitic (olivine-bearing) basalt in the Nuussuaq region of West Greenland (see photo **Figure 2B**). The fact that multiple types of carbonate minerals can form from under different conditions within the same rock formation by reactions with CO<sub>2</sub>-rich fluids is important in both designing experiments and configuring realistic model simulations.



**Figure 10.** Ternary diagram showing the compositions of carbonate minerals in basalts at Marraat in the Nuussuaq region of West Greenland (shown in **Figure 2B**) as a function of paragenetic morphologies including replacement of mafic phyllosilicates and zeolites (solid circles), filling of primary porosity in the basalts (i.e., vesicles and brecciated flow tops; open boxes), and filling of fractures (veins; crosses). (from Rogers *et al.*, 2006)

### Progress

In our first year of this exploratory project we have conducted several experimental studies, including *in situ* ambient pressure photoelectron spectroscopy on the interaction of CO<sub>2</sub> and water with MgO surfaces and the interaction of Mg-rich olivine with CO<sub>2</sub>-rich aqueous fluids in hydrothermal rocker bombs that allow continuous sampling of the fluid phase without disruption of the experiment. Our APPES results indicate that Mg-carbonate is formed rapidly when the MgO(100) surface is exposed to 0.2 Torr of CO<sub>2</sub> under dry conditions. Interaction of H<sub>2</sub>O with the MgO (100) surface prior to its interaction with CO<sub>2</sub> appears to block CO<sub>2</sub> adsorption sites and inhibits the carbonation reaction. We also found that the polarization-dependence of NEXAFS spectra of reaction products indicates that the CO<sub>3</sub> groups are not parallel to the substrate surface. In addition, we have assembled a geochemical modeling framework that will be used to

interpret and guide experimental results and in the analysis of field-scale natural analog systems. Model development has focused on assembling relevant kinetic and thermodynamic data, analysis of reaction pathways for different host rock compositions and the evaluation of different boundary conditions (flow rate, CO<sub>2</sub> concentrations and fluid compositions) using an idealized flow-through reactor system. Key findings of our simulations to date include the following: (1) Mineral transitions that occur during alteration of basalt and serpentinites are extremely efficient and could result in complete removal of CO<sub>2</sub> from dilute fluids such as seawater. However, these reactions do result in extremely high net volume changes and dramatic reductions in porosity that could affect the flow path. (2) The effects of aqueous organic ligands on the dissolution rates, solubilities, and stabilities of Mg-silicates relative to carbonate minerals are likely to be of first-order importance in optimizing the industrial utility of geologic sequestration of CO<sub>2</sub> in ultramafic and mafic rock formations.

With the commitment of Ph.D. student Natalie Johnson and incoming M.S. student Pablo García Del Real to the experimental, modeling, and field-based tasks of this project, we expect to make rapid progress in all three of these areas over the next six months.

## **Future Plans**

**Experimental studies:** We will initiate *in situ* APPES studies of the interaction of CO<sub>2</sub>, CO<sub>2</sub> + H<sub>2</sub>O, and CO<sub>2</sub> + concentrated aqueous solutions with brucite, Mg-olivine, Mg-pyroxene, and the serpentine polymorphs. We will also begin surface science characterization studies of reaction products from the hydrothermal experiments on the interaction of CO<sub>2</sub> with olivine, pyroxene, and the serpentine polymorphs. In addition, we plan to explore the extent to which carbonation on mineral surfaces is enhanced by carbonic anhydrase, a potent Zn-metalloenzyme for CO<sub>2</sub> production in biogenic environments. The effect of surface pre-treatment by heating, exposure to organic acids, and other pre-treatment methods will be also explored. This project is intended to find more efficient pathways for carbonation reactions of Mg- and Ca-silicates and a deeper understanding of the factors controlling reaction kinetics.

**Modeling studies:** After a detailed consideration of the geochemistry, we plan to (1) develop more realistic flow scenarios that honor the geometry of an injection well and the heterogeneity of the rock formations, and (2) consider the effect of reaction kinetics, mineral surface area, and organic activators on the evolution and distribution of reactant and product phases. In order to constrain these numerical scenarios, we plan to characterize natural analog samples at different spatial scales using a variety of different techniques, including elemental mapping of the reaction fronts, XRD analyses to determine initial reactants and final products, EMP characterization to determine small scale distribution of elements, and X-ray microtomography to characterize the porosity and connectivity of pores. The compositions of spring waters emanating from alteration zones will also be used as further constraints in the model

We plan to explore the mechanism of volume expansion and to determine the type of chemical and physical manipulations that prevent precipitation of high-volume phases. This will be a key focus in our coupled experimental and simulation studies.

**Natural system studies:** A Master's student working on the project (Pablo García Del Real) will be working on characterization of the natural analog systems using the approaches mentioned above. He will be working at a number of sites in California, including the New Idria area of Fig. 2a and several other localities in the greater Bay Area. These studies, which will involve petrographic, X-ray diffraction, and electron microprobe studies, will reveal the full range of hydrated Mg-carbonate minerals that may form in such zones and their transformations.

These combined studies will guide the selection of field-scale injection sites and potential additives or pre-treatment strategies to optimize metal carbonation reactions of Mg-silicates. They will also provide some of the first detailed information on surface chemical changes during carbonation reactions of Mg-silicates, including ways of preventing surface passivation, as well as information on minimizing porosity reduction in the host rocks.

### Publications and Presentations

1. Newberg, J. T., Starr, D. E., Mysak, E., Yamamoto, S., Kaya, S., Ogasawara, H., Kendelewicz, T., Porsgaard, S., Salmeron, M., Brown, Jr., G. E., Nilsson, A., and Bluhm, H. (2009) The interaction of H<sub>2</sub>O and CO<sub>2</sub> with MgO(100) films. *2009 Gordon Research Conference on Chemical Reactions on Solids, Ventura, CA.* (presentation)
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