Silicate Mineral Dissolution and Associated Carbonate Precipitation at Conditions Relevant to Geologic Carbon Sequestration

Fei Wang
Washington University in St. Louis

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WASHINGTON UNIVERSITY
School of Engineering and Applied Science
Department of Energy, Environmental and Chemical Engineering

Dissertation Examination Committee:
Daniel E. Giammar, Chair
Jeffrey G. Catalano
John D. Fortner
Sophia E. Hayes
Young-Shin Jun
Palghat Ramachandran

Silicate Mineral Dissolution and Associated Carbonate Precipitation at Conditions Relevant to Geologic Carbon Sequestration
by
Fei Wang

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT OF THE DISSERTATION

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by

Fei Wang

Doctor of Philosophy in Energy, Environmental, and Chemical Engineering

Washington University in St. Louis, 2013

Professor Daniel Giammar, Chair

Geologic carbon sequestration (GCS) has been proposed as a means of mitigating the impacts of carbon dioxide (CO₂) emissions from fossil fuel combustion on climate change. Mineral trapping, one of the trapping mechanisms of GCS, is of great importance because it has a potentially high sequestration capacity and provides very long-term sequestration. Forsterite (Mg₂SiO₄), a magnesium-rich silicate mineral, was studied with respect to its dissolution rates and its release of dissolved magnesium for subsequent precipitation of Mg-carbonate minerals. This study was conducted at conditions relative to GCS. Under different geological conditions, the thermodynamics and kinetics of both dissolution and precipitation reactions can vary. The overall fate of injected CO₂ into porous media can be influenced by diffusive transport of aqueous species in addition to chemical reactions.
The rates and mechanisms of forsterite dissolution were studied under different temperatures, CO$_2$ pressures, and salinities that were relevant to GCS. After an initially rapid dissolution period, the dissolution rate declined significantly, an effect that is attributed to the formation of a Si-rich layer at the forsterite surface. The initial dissolution rate increased with increasing temperature and increasing CO$_2$ pressure. The effect of CO$_2$ was through its influence on the pH. The dissolution rate was enhanced by NaCl, which may have been due to its inhibition of the formation of a silica-rich surface layer.

The dissolution of a partially weathered olivine from an Indian source (Mg$_{1.84}$Fe$_{0.16}$SiO$_4$) was also studied at conditions relevant to both in situ and ex situ mineral carbonation. The release of magnesium to solution increased with increasing temperature and initial olivine concentration. The declining dissolution rate over time was also attributed to the formation of a Si-rich layer on olivine surface. The dissolution of the naturally weathered olivine was very similar to that of purer olivine at conditions relevant to mineral carbonation.

Experiments were performed to determine the effects of saturation conditions and different initial mineral substrates on magnesite precipitation from water-scCO$_2$ solutions. The critical saturation index necessary for initiating magnesite precipitation at 100 °C and 100 bar P$_{CO2}$ was approximately 2. Precipitation was fastest when solutions were seeded with magnesite to remove nucleation as a rate-limiting step. Relative to
mineral-free solutions, forsterite did not accelerate magnesite nucleation. The precipitation process did not reach equilibrium within 10 days.

At ambient $P_{\text{CO}_2}$, the influences of temperature, solution composition, and the presence of a solid substrate on the nucleation and precipitation of magnesium carbonate minerals were examined. At 25°C and 60°C the precipitates were hydrated magnesium carbonate minerals (nesquehonite or hydromagnesite), and at 100°C the solid phase was identified as brucite. Although magnesite ($\text{MgCO}_3$) was predicted to be the most thermodynamically stable magnesium carbonate phase, no magnesite precipitated and instead metastable magnesium carbonate phases formed.

The effects of diffusive transport on both silicate mineral dissolution and carbonate mineral precipitation were studied by integrating bench-scale experiments and a mathematical model that coupled chemical reactions and diffusive transport. Simulations and experiments were performed for a tubular reactor packed with forsterite powder. The diffusivities of $\text{Mg}^{2+}$ and dissolved inorganic carbon were included for quantifying rates of solute transport. The forsterite dissolution rate is a function of the pH, and the model calculated the pH at each location and time point based on the reaction rates and the transport of magnesium and inorganic carbon along the length of the tube. These simulations and experiments are relevant to diffusion-limited zones of GCS sites, and they suggest that diffusion-limitations can lead to local environmental conditions that can result in much different reaction rates and magnesite precipitation. For conditions of 100°C and 100 bar $P_{\text{CO}_2}$, magnesite precipitation was both predicted and observed to
occur after five days at a location about 1 cm below the interface of the forsterite packed bed with a well-mixed CO$_2$-rich aqueous solution.
Chapter 1. Introduction

1.1 Background

1.1.1 Carbon capture and storage

With the great consumption of fossil fuels since the industrial revolution, CO₂ has been accumulating in the atmosphere with major implications for global climate change (Albritton 2001). The ultimate goal of stabilizing the atmospheric CO₂ concentration requires a reduction of the global emission rate. To achieve this goal, there are various technological options (Pacala and Socolow 2004; IPCC 2005): increase the efficiency of energy conversion and/or utilization and decrease the overall energy needs; use energy supplies that emit less or no CO₂; improve the transfer of CO₂ to biomass; and finally introduce carbon capture and storage (CCS) technologies.

Given the current high atmospheric CO₂ concentration (around 397 ppm) (Conway and Tans 2013) and global emissions of 30.313 Gt CO₂ in 2011 (EPA 2011), carbon capture and storage (CCS) is a potentially attractive approach. It is also considered a feasible approach to scientists and engineers, because necessary technologies and systems are already available. CO₂ capture system includes capture from industrial process streams, post-combustion capture, oxy-fuel combustion capture and pre-combustion capture. Once CO₂ is captured, different storage and sequestration options are available: underground geological storage, ocean storage, and mineral carbonation and industrial uses. Among these different options, geologic storage stands out because of its great capacity.
To address doubts about this strategy and prove its feasibility, numerous full-scale and pilot-scale field studies are being conducted around the world. The Sleipner project in the North Sea was started in 1996, and it was the very first CO\textsubscript{2} storage project in deep saline aquifers (Schrag 2009). It is capable of injecting 1 million tons of CO\textsubscript{2} annually, and approximately 15 million tons have been injected already. There are also other large pilot projects in Algeria and Australia (IPCC 2005; Haszeldine 2009). In the United States, the FutureGen 2.0 Project was started in 2010, and it will equip a power plant in Illinois with oxy-combustion technology. It is planning to capture and store approximately 1.3 million tons of CO\textsubscript{2} in deep saline aquifers each year, and the facility is still under construction (FutureGen 2013).

1.1.2 CO\textsubscript{2} storage mechanisms in geological formations

CO\textsubscript{2} can be stored and sequestered in geological formations by injecting it as a supercritical fluid. Once injected, it flows above the brine, since its density is less than that of the brine. It can further dissolve into the brine, and react with the rocks. Better subsurface characterization of different types of storage sites (Figure 1.1), bridging the large spatial and temporal scales of CO\textsubscript{2} transport and geochemical reactions, and better mechanistic understanding of multiphase flow and mineral reaction kinetics are very important (Jun, Giammar et al. 2013).
There are different options for CO₂ storage in geologic formations. It can be injected into depleted oil and gas reservoirs. It can be used in enhanced oil and gas recovery or in coal bed methane recovery. Finally, storage in deep saline aquifers is a promising approach because of their large capacity, and because scientists and engineers have proposed a detailed procedure for site selection (Bachu 2000; Bachu 2002).

After being injected into geological formations, CO₂ takes the form of either a gas phase or a supercritical fluid depending on the specific temperature and pressure. There are four different storage and sequestration mechanisms as shown in Figure 1.2: (1) stratigraphic and structural trapping, in which CO₂ is trapped under low-permeability caprocks without involving any chemical reactions; (2) solubility trapping, in which CO₂ dissolves into the
aqueous phase and forms carbonate species; (3) hydrodynamic trapping, in which either the supercritical CO₂ phase or the dissolution products migrate with the deep saline aquifers; and (4) mineral trapping, in which stable carbonate minerals precipitate and permanently sequester CO₂. Among all the trapping mechanisms in geological sequestration, the most desirable one is mineral trapping, considering its permanency and large capacity. However, mineral trapping in deep saline aquifers can potentially take a thousand years or longer before mineral trapping becomes a significant sink for injected CO₂ (Bachu 2000; IPCC 2005). In addition, deep saline aquifers do not contain many Mg- or Fe-containing silicate minerals needed for mineral trapping.

Figure 1.2 Different trapping mechanisms (stratigraphic and structural trapping, solubility trapping and mineral trapping) of CO₂ in deep saline aquifers.

CO₂ sequestration in the unconventional formations of peridotite, a rock that consists mostly of olivine from the Earth’s upper mantle, and other Mg-rich formations has been
recently suggested (Kelemen and Matter 2008; Matter and Kelemen 2009; Kelemen, Matter et al. 2011). The biggest advantage of peridotite is its fast mineral carbonation rate of CO₂. The disadvantage is that they don’t have the porosity and permeability of other formations and the mineral carbonation might further fill porosity and reduce permeability (Kelemen, Matter et al. 2011).

1.1.3 Summary of recent research on mineral trapping
Different strategies for studying the mineral trapping were employed in recent investigations of water - rock - CO₂ reactions. Most researchers chose to work with pure forms of silicate minerals instead of rocks, which are multi-mineral assemblages. Relatively pure forsterite was often chosen as a model silicate mineral.

Olivine, with its chemical formula (Mg,Fe)₂SiO₄, has two end members, forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄), and can be present with any possible combination of magnesium and iron(II) because the two end members are can be mixed as a complete solution. The structure of olivine has a continuous network of isolated SiO₄ tetrahedra that are bridged by Mg and Fe atoms. Mg and Fe atoms occupy octahedral sites and form a chain structure by sharing edges of those octahedral (Deer 1992).

In the water - rock - CO₂ system, the dissolution of silicate minerals occurs. This process involves three steps. (1) Dissolution of CO₂(g) in the aqueous solution. The concentrations of more basic forms (HCO₃⁻ and CO₃²⁻) increase as the pH rises, due to dissolution of cation-rich minerals. (2) Dissolution of silicate minerals, and (3) Precipitation of
carbonate mineral (e.g., magnesite MgCO$_3$(s)). The detailed reactions are included in Chapter 2. Brief descriptions of various minerals that are relevant to GCS are summarized in Table 1.1.

For the system of water - forsterite - CO$_2$, laboratory experiments were conducted under different conditions relevant to geological formations. Both batch reactors and flow-through reactors were used. Different temperatures (25 - 150 °C) and pressures of CO$_2$ (1 - 250 bar) were studied. Experiments have been conducted over the pH range of 2 to 12.5, with or without CO$_2$ (Hanchen, Prigiobbe et al. 2006; Hächnen, Krevor et al. 2007; Hächnen, Prigiobbe et al. 2008; Prigiobbe, Costa et al. 2009; Saldi, Schott et al. 2010; Daval, Sissmann et al. 2011). It has been suggested that the dissolution of forsterite (mol/cm$^2$-s) follows the form of equation 1.1.

$$\text{Rate}_{\text{diss}} = k_0 e^{-\frac{E_a}{RT}} [H^+]^{n_H^+}$$

(1.1)

Where $k_0$ is a dissolution rate constant, and $E_a$ is the apparent activation energy, and $n_{H^+}$ is the reaction order based on the activity of $H^+$. A typical $E_a$ value is 52.9 ± 6.9 kJ/(mol-K), a typical $n_{H^+}$ value is 0.46±0.03 (Hanchen, Prigiobbe et al. 2006). As the temperature increases, the dissolution rate increases. However, when pH increases, the dissolution rate decreases, for a typical $n_{H^+}$ of 0.46. Recently, Rimstidt et. al reviewed the previous experimental studies and proposed their own forsterite dissolution rate equations for the full pH range from 0 to 150 °C. (Rimstidt, Brantley et al. 2012)
Table 1.1 Various minerals and their relevance to GCS

<table>
<thead>
<tr>
<th>mineral name</th>
<th>chemical composition</th>
<th>Relevance to GCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorphous</td>
<td>SiO$_2$(am)</td>
<td>Amorphous silica can form as a secondary phase during forsterite dissolution.</td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dypingite</td>
<td>Mg$_5$(CO$_3$)$_4$(OH)$_2$·5H$_2$O</td>
<td>Dypingite is a hydrated Mg-carbonate mineral that can precipitate and sequester CO$_2$.</td>
</tr>
<tr>
<td>forsterite</td>
<td>Mg$_2$SiO$_4$</td>
<td>Forsterite has a fast dissolution rate and can result in forming Mg-carbonate minerals.</td>
</tr>
<tr>
<td>hydromagnesite</td>
<td>Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O</td>
<td>Hydromagnesite is a hydrated Mg-carbonate mineral that can precipitate and sequester CO$_2$.</td>
</tr>
<tr>
<td>magnesite</td>
<td>MgCO$_3$</td>
<td>Magnesite is a Mg-carbonate mineral that can precipitate and sequester CO$_2$.</td>
</tr>
</tbody>
</table>

In addition, work has been dedicated to the formation of carbonate minerals in the water-forsterite-CO$_2$ systems. For example, the transformation from hydrated magnesium carbonates to dehydrated magnesium carbonates were thoroughly exploited, and the formation of pure magnesite was generally observed under partial pressure of CO$_2$ higher than atmospheric pressures (Giammar, Bruant et al. 2005; Hänchen, Prigiobbe et al. 2008; Kwak, Hu et al. 2010). However, Felmy et al. (2012) observed magensite formation at a much lower temperature (35 °C) with the dissolution of nano-sized forsterite. They suggested that the presence of a thin water film on the forsterite surface may provide unique conditions for the transformation of the intermediate nesquehonite and the magnesite growth at such a low temperature.
1.1.4 Knowledge gaps regarding mineral trapping

Although there have been numerous studies of mineral trapping, more experiments under conditions similar to those in geological formations are needed. Four important research needs are identified as the focus of this dissertation. First, the effects of high salinity on silicate mineral dissolution and carbonate mineral precipitation need to be determined. Second, the identity of carbonate precipitates needs to be determined since metastable phases may form at certain conditions, and whether precipitation is preceded by heterogeneous or homogeneous nucleation is not fully known. Third, the full ranges of possible temperature and pressure conditions that are relative to mineral trapping have not been studied. Finally, since CO$_2$-mineral-water reactions are not occurring in well-mixed systems like those often used to study the reactions, the impacts of diffusive transport on the overall processes of silicate dissolution and carbonate precipitation needs to be studied. Gradients in the pH and concentrations of aqueous species can develop in the pore space. As a result, local reaction rates and products may vary greatly.

1.2 Research objectives

The overall objective of the research presented in this dissertation was to advance the understanding of silicate mineral dissolution and related carbonate mineral precipitation at conditions relevant to geological carbon sequestration. Three specific research objectives were identified.
Objective 1: Quantify the dissolution rates of forsterite at conditions relevant to geological carbon sequestration.

Objective 2: Identify the mechanisms of carbonate mineral formation from reactions of CO$_2$ and water with forsterite and the conditions favorable for such carbonate mineral formation.

Objective 3: Determine the impacts of diffusive transport limitations on both silicate dissolution and carbonate mineral precipitation in a porous medium representative of rocks that constitute sequestration reservoirs.

1.3 Overview of dissertation

This study includes three main tasks, and all three tasks relate to each other according to their specific research objectives (Figure 1.3). When CO$_2$ dissolves into the aqueous solution, the solution becomes acidic because of carbonic acid formation. As silicate minerals (e.g. forsterite) start to dissolve, metal cations, such as Mg$^{2+}$, and aqueous SiO$_2$ are released. When the solution becomes supersaturated with respect to magnesite (MgCO$_3$(s)) and other carbonate minerals, the precipitation of these carbonate minerals is possible. Other precipitates, like amorphous silica (SiO$_2$(am)), may also form.

Corresponding to the research objectives mentioned in the previous section, the effect of environmental conditions and solution composition on the dissolution rates of forsterite was studied in Task 1. Task 1 is addressed in Chapter 2 and 3. The effects of temperature, CO$_2$ pressure and salt concentration are studied for a high-purity forsterite (Chapter 2) and for a lower-cost weathered Indian olivine (Chapter 3).
In Task 2 (Chapter 4), the precipitation of carbonate minerals in the presence of silicate or carbonate mineral substrates was investigated, and the critical saturation conditions were quantified. The effect of saturation index and initial substrates and salt concentration on nucleation and subsequent precipitation were studied.

In Task 3 (Chapter 5), experimental and modeling approaches were applied to evaluate the effects of diffusive transport limitations on silicate mineral dissolution rates and locations and extents of carbonate mineral precipitation. These processes were studied for a tubular reactor filled with forsterite. Silicate dissolution and associated carbonate precipitation are often considered the most important processes affecting mineral trapping in geologic carbon sequestration. However, the diffusive transport of the aqueous species can play a very significant role in a porous medium representative of the rocks that constitute the sequestration reservoirs. It can affect the overall rates of the reactions and the locations of products. Both simulations and experiments were performed to study the process of silicate mineral dissolution and carbonate mineral formation.
Figure 1.3 Overview of three research tasks to investigate water-forsterite-CO$_2$ interactions in mineral trapping. Task 1 investigates the dissolution rates of silicate minerals, Task 2 is focused on the formation of carbonate minerals, and Task 3 evaluates the impact of diffusive transport limitations of the aqueous species (Mg$^{2+}$, CO$_2$(aq)) on the rates of reactions and locations of precipitate (MgCO$_3$) formation.
Chapter 2. Forsterite dissolution in saline water at elevated temperature and high CO$_2$ pressure

Results of this chapter have been published in Environmental Science & Technology, 2013, 47(1): 168-173

Abstract

The rates and mechanisms of magnesium silicate dissolution can control the aqueous chemistry in ways that influence carbonate mineral precipitation during geologic carbon sequestration (GCS). A series of batch experiments was performed with forsterite (Mg$_{1.81}$Fe$_{0.19}$SiO$_4$) powder to determine the effects of pressure (10-100 bar CO$_2$), temperature (25-100 °C), and salinity (0-50,000 mg/L NaCl) on its dissolution rate at conditions relevant to GCS. Dissolution rates and products were determined by analysis of the aqueous phase, equilibrium and reaction path modeling, and solid phase characterization by scanning electron microscopy and X-ray diffraction. After an initially rapid dissolution period, the dissolution rate declined significantly, an effect that is attributed to the formation of a silica-rich layer at the forsterite surface. The initial dissolution rate increased with increasing temperature and increasing CO$_2$ pressure; the effect of CO$_2$ was through its influence on the pH. The dissolution rate was enhanced by NaCl, which may have been due to its inhibition of the formation of a silica-rich surface layer. The experimental results provide information about magnesium silicate dissolution at conditions that will be encountered during GCS that can be used to predict the fate of CO$_2$ and the evolution of subsurface geochemistry following CO$_2$ injection.
2.1 Introduction

Given increasing atmospheric CO$_2$ concentrations and annual global emission rates, geologic carbon sequestration (GCS) is a potential approach for mitigating further increases in atmospheric CO$_2$ and its implications for climate change. Once injected into geological formations, CO$_2$ can be stored and sequestered through different trapping mechanisms: (1) stratigraphic and structural trapping, in which CO$_2$ is trapped under low-permeability caprocks; (2) solubility trapping, in which CO$_2$ dissolves into the aqueous phase and forms carbonate species; (3) hydrodynamic trapping, in which either the supercritical CO$_2$ phase or the dissolution products migrate with the groundwater; and (4) mineral trapping, in which stable carbonate minerals precipitate and permanently sequester CO$_2$ (IPCC 2005). Mineral trapping is a desirable outcome because it can permanently remove CO$_2$ from the atmosphere and would not require long-term monitoring. However, it could take a thousand years or longer before mineral trapping becomes a significant sink for injected CO$_2$ (Bachu 2000; IPCC 2005).

To unravel the interactions in water-rock-CO$_2$ systems at conditions relevant to GCS, olivine with a composition close to forsterite, hereafter referred to as “forsterite”, was chosen as a model silicate mineral for this study. Forsterite is useful as model mineral for studies because it dissolves congruently under various temperature and CO$_2$ pressure conditions and because its dissolution is fast enough to allow experimental observations of dissolution and possible precipitation of Mg-carbonate minerals. (Wogelius and Walther 1991; Chen and Brantley 2000; Rosso and Rimstidt 2000; Giammar, Bruant et al. 2005; Hanchen, Prigiobbe et al. 2006) Geologic formations rich in ultramafic minerals...
like forsterite have been suggested for GCS (IPCC 2005; Shao, Ray et al. 2011), although forsterite is not found in deep saline aquifers, which are the primary geological formations currently being considered for GCS. Forsterite has also been tested for \textit{ex situ} mineral carbonation due to the low cost of mining and crushing of ultramafic rocks. (Oelkers, Gislason et al. 2008; Pronost, Beaudoin et al. 2011)

Mineral trapping in the water-forsterite-CO$_2$ system involves (1) dissolution of CO$_2$(g) into the water, (2) dissolution of forsterite, and (3) precipitation of a Mg-carbonate mineral (e.g., magnesite MgCO$_3$(s)). These reactions (equation 2.1-2.4) yield one net mineral trapping reaction (5).

\begin{align}
\text{CO}_2(g) & \Leftrightarrow \text{CO}_2(aq) \quad (2.1) \\
\text{H}_2\text{O} + \text{CO}_2(aq) & \Leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+ \quad (2.2) \\
\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ & \Leftrightarrow 2\text{Mg}^{2+} + \text{SiO}_2(aq) + 2\text{H}_2\text{O} \quad (2.3) \\
\text{Mg}^{2+} + \text{CO}_3^{2-} & \Leftrightarrow \text{MgCO}_3(s) \quad (2.4) \\
\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2(g) & \Leftrightarrow 2\text{MgCO}_3(s) + \text{SiO}_2(aq) \quad (2.5)
\end{align}

A rate equation for forsterite dissolution can account for the effects of temperature and pH (equation 2.6) (Rosso and Rimstidt 2000; Oelkers 2001):

\begin{align}
r = k_0 e^{-E_a/RT} [\text{H}^+]^{n_H^+} \quad (2.6)
\end{align}

Where $r$ represents the dissolution rate of forsterite (mol/cm$^2$-s), $k_0$ is the dissolution rate constant (mol/cm$^2$-s), $E_a$ is the apparent activation energy (J/mol), $[\text{H}^+]$ is the activity of
hydrogen ions in solution, and \( n_{H^+} \) is the reaction order with respect to \( H^+ \). This equation can hold over the pH range of 2 - 8.5. In previous research under different temperatures (25 - 150 °C) and CO\(_2\) pressures (1 - 180 bar), \( n_{H^+} \) ranges from 0.46 to 0.70 and \( E_a \) varies from 42.6 to 79.5 kJ/mol. (Wogelius and Walther 1992; Oelkers 2001; Häench, Prigiobbe et al. 2006; Prigiobbe, Costa et al. 2009) Consequently, the dissolution rate increases with decreasing pH and increasing temperature. In a recent study by Daval et al. (2011), due to the formation of a Si-rich layer on the surface, the forsterite dissolution rate became much lower after 2.95 days at 90 °C and 200 bar CO\(_2\) pressure compared to the rate predicted by Wogelius and Walther (Rosso and Rimstidt 2000). The dissolution of forsterite in aqueous solutions is initially so favorable that it will always occur far from equilibrium (Wogelius and Walther 1992; Rosso and Rimstidt 2000; Oelkers 2001; Häench, Prigiobbe et al. 2006; Prigiobbe, Costa et al. 2009). Ultimately the concentrations of dissolved magnesium and silicon released by dissolution will be controlled by either forsterite dissolution equilibrium or the precipitation of secondary phases, whichever comes first.

The objective of this study was to determine the effects of temperature, CO\(_2\) pressure, and salinity on the dissolution rate of forsterite. The study investigated the forsterite dissolution process over a range of conditions that are relevant to GCS. The results of the study can provide insights into the fate of CO\(_2\) injected into geologic formations or reacted with magnesium-rich materials in engineered reactors as part of carbon sequestration strategies.
2.2 Materials and Methods

2.2.1 Materials
Forsterite (San Carlos, Arizona, 1.59 - 4.76 mm) was obtained from Ward’s Scientific. The purest crystals of forsterite were selected by visual examination using an optical microscope, and these were then ground with an agate mortar and pestle and sieved to yield the 53-106 µm size fraction. The powder was then sonicated in ethanol for 10 minutes to remove fine particles. This process was repeated 5 times until the supernatant was clear after sonication and settling. The powder was rinsed with ultrapure water and dried at room temperature and stored in the dry atmosphere of a bench-top dessicator. The composition of forsterite was identified by X-ray diffraction (XRD) and acid digestion as Fo_{90} (Mg_{1.81}Fe_{0.19}SiO_{4}). The specific surface area (SSA) was determined to be 0.19 m^2/g by BET-N\textsubscript{2} adsorption. The morphology of forsterite powder was observed using scanning electron microscopy (SEM), and images indicated the presence of some particles smaller than 53 µm. The SSA was comparable to a predicted value of 0.21 ± 0.09 m^2/g calculated from an equation developed in a previous study for the SSA of cleaned olivine grains without fine particles (Brantley and Mellott 2000). Saline solutions were prepared by dissolution of NaCl solid (Fisher Scientific) into ultrapure (18.2 MΩ) water.

2.2.2 Methods
Forsterite dissolution experiments were carried out in 300-mL PTFE vessels with pressurized CO\textsubscript{2} in well-stirred batch reactors (Parr Instrument Company) at different temperature (25-100 °C), CO\textsubscript{2} pressures (10-100 bar) and salinities (0-50,000 mg/L
NaCl). Initially, a PTFE vessel was loaded with 0.5 g/L of forsterite powder and 200 mL of aqueous solution (dilute or salt solution). The PTFE cup was placed into a stainless steel reactor, and the whole reactor was assembled and heated to the experimental temperatures with a heating mantle. CO$_2$ was introduced to the reactor through a syringe pump (500D, Teledyne Isco) to saturate the aqueous solution as well as the pore spaces of PTFE. The pump could maintain a constant headspace CO$_2$ pressure. During each 3-week experiment, liquid samples were collected from a sampling port on the reactor after certain times (0 h, 4 h, 8 h, 1 day, 3 days, 7 days, 14 days, and 21 days). The pH of the solution was measured outside of the reactor under ambient pressure (pH$_{ex}$) within 5 minutes of collection. After 21 days the reactor was quickly cooled to ambient temperature, and the solids remaining in the reactor were collected using vacuum filtration and dried at room temperature. Liquid samples were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) for concentrations of dissolved Mg, Si, and Fe. The solid samples were characterized by XRD and SEM with energy dispersive X-ray analysis (EDX).

Geochemical equilibrium calculations were used to predict the evolution of the aqueous solution composition and pH during the dissolution of forsterite. The “React” and “SpecE8” from Geochemist’s Workbench (GWB) 8.0 were employed. (Bethke and Yeakel 2010) With the input of water composition and CO$_2$(aq) concentration at a certain temperature, “React” provided the solution composition and pH as a function of reaction progress, while “SpecE8” provided those information at equilibrium. The CO$_2$(aq) concentration was calculated according to a model by Duan and Sun (2003). The effects
of ionic strength, with a highest experimental value slightly below 1 molal, were taken into consideration in “React” with the “B-dot” equation, an extended form of the Debye-Huckel equation (Helgeson 1969), which could be used for solutions with ionic strengths up to 3 molal. The equilibrium constants in GWB are calculated using polynomial equations that give logK as a function of temperature from 0 to 300 °C. These constants at elevated temperature were only 0.1 log unit different from the equilibrium constants predicted by the thermodynamic software program SUPCRT92 (Johnson, Oelkers et al. 1992).

2.3 Results and Discussion

2.3.1 Investigation of the forsterite dissolution rate

The evolution of the concentrations of dissolved aqueous species (Mg, Si and Fe) and the pH is illustrated for the 3-week forsterite dissolution experiment in dilute solution at 50 °C and 100 bar CO₂ pressure (Figure 2.1). Initially, the aqueous solution was acidic, with an ex situ pH of 3.99, which was higher than a calculated initial in situ pH of 3.07 (Figure S2.1 of the Supporting Information). As forsterite dissolved, the Mg, Si and Fe concentrations increased and the acidity of the solution was consumed and pH increased to 5.39 after 3 weeks. The ex situ pH was usually 1 - 2 units larger than the calculated in situ pH due to CO₂ degassing from the solution under ambient conditions. At this condition, the Mg concentration was as high as 1.17 mM after 21 days (Figure 2.1 (a)), which corresponded to dissolution of 19.0% of the initial forsterite. The full data (Figures S2.2-S2.5) and the forsterite dissolution extent (%) (Table S2.1) for all experiments can be found in the Supporting Information.
Figure 2.1 Dissolved concentrations of Mg (■), Si (◆), and Fe (●), and pH_{ex} (Δ) during batch dissolution of 0.5 g/L forsterite in dilute solution at 50 °C and 100 bar CO₂ pressure for a) the entire experiment and b) the first 24 hours (only Mg results are included). The solid line is the dissolved Mg concentration for the initial dissolution rate of forsterite (5.96 × 10^{-12} mol/cm²-s). The dashed line presents the dissolved Mg concentration predicted by the rate law given in equation 2.6 with n_{H^+} of 0.46 to account for the declining dissolution rate expected from the increasing pH.

The initial dissolution rate of forsterite (R_{diss,Fo}) was determined using a linear regression of the first 8 hours of Mg concentrations and expressed in mol/cm²-s (Figure 2.1 (b)). After 8 hours the forsterite dissolution rate decreased in all 3-week experiments, even though the thermodynamic driving force for forsterite dissolution remained very favorable (Table S2.2 of the Supporting Information). Based on the established pH-dependence of forsterite dissolution (equation 2.6), some decline in the rate was expected as the solution pH increased. The pH profile calculated by “React” in GWB (Figure S2.6...
of the Supporting Information) was combined with equation 2.6 to predict the declining rate of Mg release using values of $E_a$ (52.9 kJ/mol) and $n_{H^+}$ (0.46) suggested by Hanchen et al. (Hänchen, Prigiobbe et al. 2006) and a $k_0$ value of 0.140 mol/cm$^2$-s (Supporting Information). As dissolution progresses the total surface area of forsterite was changing, due to the decreasing forsterite concentration and increasing specific surface area. After accounting for the increasing pH and changing surface area, the predicted Mg concentration does follow a declining rate of release (Figure 2.1(a)), but the measured Mg concentrations were still much lower than predicted for reaction times greater than 8 hours. This suggests that a factor other than pH, surface area (Table S2.1 of the Supporting Information) was retarding the dissolution of forsterite. The possible precipitation of secondary phases as a cause of the declining rate was ruled out by calculations that determined that the final solution composition was substantially undersaturated with respect to magnesium carbonate, hydroxide, and phyllosilicate phases (Table S2.2 of the Supporting Information). While XRD indicated that no crystalline secondary phase precipitated, SEM images showed that the crystalline surface was weathered (Figure 2.2). EDX was performed at spots where the surface was altered, but the spectra did not show any difference in the semi-quantitative elemental compositions of the reacted and unreacted surfaces.

The initial forsterite dissolution rates ($R_{\text{diss,Fo}}$) from this study can provide insights into the effects of environmental conditions on forsterite dissolution (Table 2.1). The measured initial dissolution rates ranged from $10^{-12.7}$ to $10^{-10.3}$ mol/cm$^2$-s, which were well within the range of previously reported results ($10^{-14.98}$ to $10^{-9.80}$ mol/cm$^2$-s) for
similar pH (3 - 6) and temperature (25 - 90 °C) (Wogelius and Walther 1991; Wogelius and Walther 1992; Chen and Brantley 2000; Rosso and Rimstidt 2000; Golubev, Pokrovsky et al. 2005; Hänchen, Prigiohbe et al. 2006).

![Figure 2.2](image)

**Figure 2.2** Electron micrographs of the surface of (a - b) unreacted forsterite and (c - d) the solid collected after 3 weeks of reaction at 50 °C and 100 bar CO₂ pressure.

The declining dissolution rate of forsterite was probably caused by the formation of a Si-rich layer on the forsterite surface. Previous studies have suggested that a Si-rich layer
can form on the surface of forsterite (Pokrovsky and Schott 2000; Béarat, McKelvy et al. 2006; Daval, Sissmann et al. 2011; Hellmann, Wirth et al. 2012) and peridotites (Hövelmann, Austrheim et al. 2011) during their dissolution. Daval et al. (2011) observed sharp but irregular termination of the lattice of forsterite in HRTEM images, and they suggested that the altered surface of forsterite could be either a leached layer or a precipitated layer of amorphous silica. In their study the Si-rich layer formed even when the bulk solution was slightly undersaturated with respect to amorphous silica (saturation index for amorphous silica ($SI_{SiO_2(am)}$) of -0.14) (Daval, Sissmann et al. 2011). Formation of such a Si-rich layer and its impacts on the forsterite dissolution rate are consistent with the current study in which $SI_{SiO_2(am)}$ reached as high as -0.44 at 100 °C and 50 bar CO$_2$ pressure.

Forsterite dissolution in dilute solutions was stoichiometric at all the experimental conditions in this study. The Si/Mg ratio of the dissolved phase was very close to the value of 0.55 expected for completely stoichiometric dissolution of Mg$_{1.81}$Fe$_{0.19}$SiO$_4$ (Figure 2.3). However, in saline solutions (5,000 - 50,000 mg/L NaCl) at 100 °C and 100 bar CO$_2$ pressure, Si was released preferentially to Mg with a Si/Mg ratio of 0.66. The dissolved Si concentration could not provide any evidence of a Si-rich layer on the forsterite surface if the layer had a similar thickness of 15-40 nm to that observed in a previous study. The formation of such a thin layer would only consume up to 0.01% of the Si that was released from the forsterite over three weeks.
Table 2.1 Experimental conditions and results of forsterite dissolution experiments

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>P$_{CO2}$ (bar)</th>
<th>NaCl (g/L)</th>
<th>log $R_{diss, Fo}$$^a$ (mol/cm$^2$-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>25</td>
<td>10</td>
<td>0</td>
<td>-12.71</td>
</tr>
<tr>
<td>D2</td>
<td>25</td>
<td>50</td>
<td>0</td>
<td>-11.78</td>
</tr>
<tr>
<td>D3</td>
<td>25</td>
<td>100</td>
<td>0</td>
<td>-11.89</td>
</tr>
<tr>
<td>D4</td>
<td>50</td>
<td>10</td>
<td>0</td>
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</tr>
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</tr>
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<td>D7</td>
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<td>10</td>
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<td>-11.08</td>
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<td>100</td>
<td>100</td>
<td>0</td>
<td>-11.77$^b$</td>
</tr>
<tr>
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<td>100</td>
<td>5</td>
<td>-11.35</td>
</tr>
<tr>
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<td>100</td>
<td>100</td>
<td>50</td>
<td>-10.34</td>
</tr>
</tbody>
</table>

$^a$ The initial dissolution rate ($R_{diss, Fo}$) was calculated using the Mg concentration data from the first 8 hours. Rates were normalized to surface area.

$^b$ The initial dissolution rate ($R_{diss, Fo}$) at 100 °C and 100 bar CO$_2$ pressure was calculated based on the average dissolution rate for duplicate experiments.
Figure 2.3 Stoichiometry of forsterite (Mg$_{1.81}$Fe$_{0.19}$SiO$_4$) dissolution during batch experiments in both dilute and saline solutions. The salinity of NaCl solutions was 5 - 50 g/L NaCl at 100 °C and 100 bar CO$_2$ pressure. The Si/Mg ratio of 0.55 that would correspond to stoichiometric dissolution of the forsterite is shown as a dashed line for reference.

2.3.2 Effect of temperature

The initial dissolution rate of forsterite almost always increased with increasing temperature (Figure 2.4). As suggested by the rate model (equation 2.6), the dissolution rate will be higher for higher temperature and lower pH. With increasing temperature for a fixed CO$_2$ pressure the calculated initial pH increases (Figure S2.1 of the Supporting Information), but this small effect of temperature on pH is negligible in comparison to
temperature’s effect through the activation energy term. The range of $E_a$ values is 42.6 - 104.5 kJ/mol from previous studies conducted at similar pH (3 - 6) and temperature (25 - 90 °C) (Wogelius and Walther 1991; Wogelius and Walther 1992; Chen and Brantley 2000; Rosso and Rimstidt 2000; Golubev, Pokrovsky et al. 2005; Hänchen, Prigio bbe et al. 2006). The only outlier to the trend of increasing rates with increasing temperature was the experiment at 100 °C and 100 bar CO$_2$ pressure, a system which will be discussed in more detail in the next section.

![Figure 2.4](image_url) The initial dissolution rates of forsterite in dilute solutions.
2.3.3 Effect of CO$_2$ pressure

The initial dissolution rate of forsterite did not show any direct relationship with CO$_2$ pressure (Figure 2.4). The calculated initial pH decreased with increasing CO$_2$ pressure (Figure S1 of the Supporting Information), which should have caused the initial dissolution rate to increase. At 25 and 100°C, the dissolution had a higher rate at 50 bar CO$_2$ pressure than at 10 and 100 bar CO$_2$ pressure. At 50°C the dissolution rate always increased with increasing CO$_2$ pressure.

It was surprising that the initial dissolution rate at 100 bar CO$_2$ pressure was much lower than the dissolution rates at 10 and 50 bar CO$_2$ pressure at 100°C. A duplicate experiment at 100 °C and 100 bar CO$_2$ pressure was performed after this unexpected rate was first observed and confirmed the results of the first experiment. The initial dissolution rate did not fit the overall trend with temperature either. In addition to having a lower dissolution rate, the extent of dissolution as indicated by the dissolved Mg concentration after 3 weeks was also much lower at 100 bar than at 10 and 50 bar CO$_2$ pressure at 100 °C. This significant decline in both the rate and extent of dissolution could possibly be explained by the 100 °C 100 bar experiment reaching conditions that inhibited dissolution sooner than at other conditions. A Si-rich layer may have formed so early in the dissolution process that dissolution was hindered almost from the very beginning of the experiment.

2.3.4 Effect of salinity

The initial dissolution rate of forsterite increased significantly with increasing salinity (Figure 2.5). The rate with a salinity of 50,000 mg/L (or 0.87 mol/kg) NaCl was 27 times
higher than that in dilute solution at 100 °C and 100 bar CO₂ pressure and enhancement of the dissolution rate was observed at salinities as low as 5,000 mg/L NaCl. The effect of salinity was not through any impact on the partitioning of CO₂ between the reactor headspace and the aqueous solution. Salinity is known to decrease the solubility of CO₂ in water, and calculations indicated that the CO₂ concentration in the aqueous phase decreased by 11.8% when the salt content rose from 0 to 50,000 mg/L NaCl at 100 °C and 100 bar CO₂ pressure while the calculated initial pH remained almost constant (Figure S2.7 of the Supporting Information). If salinity were affecting the dissolution rate through its effect on CO₂ dissolution, then very little if any differences should have been observed in the dissolution rates with varying salinity.

Previous studies of the dissolution of amorphous silica (SiO₂(amd)) and quartz also observed significantly higher dissolution rates with increasing concentrations of NaCl. (Dove and Crerar 1990; Dove and Elston 1992; Berger, Cadore et al. 1994; Dove 1999; Icenhower and Dove 2000; Dove and Craven 2005) For amorphous silica dissolution at 40-250 °C, the dissolution rate was about 20 times faster in 0.05 mol/kg NaCl than in dilute solution. The effect of NaCl on the dissolution rate was less significant at higher salt content (above 0.10 mol/kg NaCl). The rate-limiting step in both amorphous silica and quartz dissolution is the breaking of the Si-O bond as a result of H₂O attack. At pH higher than 3-4, the mineral surfaces are negatively charged and can attract Na⁺. The enrichment of Na⁺ at or near the mineral surface was proposed to have a steric effect that allowed H₂O more direct access to the Si-O bonds. (Dove 1999; Icenhower and Dove...
2000) It should be noted that as in the current study these earlier experiments were conducted at conditions far from equilibrium.

![Figure 2.5](image)

**Figure 2.5** The initial dissolution rates of forsterite at 100 °C and 100 bar CO$_2$ pressure.

Through similar mechanisms to those suggested for quartz and amorphous silica, salinity may affect the structure or formation of a Si-rich surface layer on the forsterite surface in ways that accelerate forsterite dissolution. The forsterite surfaces in this study (pH 3 - 6) are always negatively charged because the pH at which acid-reacted forsterite carries no net charge was found to be 2.1 at 25 °C (Pokrovsky and Schott 2000), and Na$^+$ will be attracted to the forsterite surface. The presence of Na$^+$ at or near the forsterite surface could lead to a more open structure of the Si-rich layer that allows faster access of H$^+$ to
the unreacted forsterite surface to promote the release of Mg$^{2+}$, while the overall dissolution extents after three weeks could still be similar. The presence of Na$^+$ in the near surface region may also inhibit the formation of a Si-rich layer in the first place, which is qualitatively consistent with a ratio of dissolved Si/Mg slightly greater than stoichiometric for the saline solutions. An enhanced dissolution rate in saline solutions for other temperature and CO$_2$ pressure conditions may also be expected since a Si-rich layer may form at various conditions.

### 2.4 Environmental Implications

The dissolution of magnesium- and calcium-containing silicate minerals can provide cations that are necessary for mineral trapping during GCS. For forsterite and likely for other minerals, temperature and pH are the most important properties of a GCS system that affect the dissolution rate. As temperature increases with depth according to the local geothermal gradient (20 - 60 °C/km) (Bachu 2000), the forsterite dissolution rate will increase. The CO$_2$ pressure did not directly affect the forsterite dissolution rate, but it had an indirect effect through its influence on the pH. When the pH was decreased by 0.5 due to a CO$_2$ pressure change from 10 to 100 bar after CO$_2$ injection at 25°C, the forsterite dissolution rate was 6.5 times higher. The accelerating effect of salinity on forsterite dissolution should also be taken into consideration in simulations of dissolution-precipitation reactions during GCS.

While this study provides insights into forsterite dissolution at many conditions relevant to GCS (Bachu 2000; Icenhower and Dove 2000), as a laboratory investigation it is not a
direct analog to the real GCS sites. At real GCS sites, the poorly-mixed brine, the high rock-to-brine ratio and the transport of dissolved aqueous species should be considered.

Once CO$_2$ is injected into GCS sites, the silicate dissolution rate may decrease much sooner and more extensively than would be predicted based on the established pH-dependence of forsterite dissolution (equation 2.6). Reactive transport simulations of GCS that do not account for this decreasing dissolution rate would overestimate the silicate dissolution rate and underestimate the time needed to reach conditions at which mineral trapping could occur. For example, at 50°C and 100 bar CO$_2$ pressure the 0.5 g/L forsterite suspension investigated in this study would just become saturated with respect to magnesite at pH 4.8. Based on the initial rate of forsterite dissolution (5.39×10$^{-12}$ mol/cm$^2$-s), it should take 20 days in the batch experiments to reach this value. However, if the dissolution rate based on a linear regression of Mg concentrations from 7 to 21 days is used (2.20×10$^{-13}$ mol/cm$^2$-s), then the solution would not reach saturation until almost 500 days.

The decrease of silicate dissolution rate due to the formation of a Si-rich layer on the mineral surface is not universal. It has been reported that a Si-rich layer could form on the surface of plagioclase feldspars (e.g. albite, labradorite, and anorthite) and single chain inosilicates (e.g. wollastonite). (Jordan, Higgins et al. 1999; Daval, Martinez et al. 2009; Hellmann, Wirth et al. 2012) During the dissolution of anorthite (Jordan, Higgins et al. 1999) and wollastonite (Daval, Martinez et al. 2009), the dissolution rate did not slow down even when a Si-rich layer was present. Hence, the role of Si-rich layer formation on
the dissolution of silicate minerals at real GCS sites will depend on the exact mineralogy of the site.

**Acknowledgement**

This work was supported by the Consortium for Clean Coal Utilization at Washington University. The authors thank the Center for Materials Innovation for assistance with SEM imaging and the Department of Earth and Planetary Sciences for assistance with XRD analysis. We appreciate the critical and insightful comments from three anonymous reviewers that helped improve the manuscript.
Supporting Information

Forsterite Dissolution in Saline Water at Elevated Temperature and High CO₂ Pressure

Supporting information contains 14 pages with 2 tables and 7 figures and a description of the modeling approach.
**Table S2.1** Calculated forsterite dissolution extent based on the dissolved Mg concentrations for the aqueous samples collected at the end of three weeks.

<table>
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<tr>
<th>Run</th>
<th>Temperature</th>
<th>( P_{CO_2} )</th>
<th>NaCl</th>
<th>1-day dissolution extent (%)</th>
<th>3-week dissolution extent (%)</th>
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</thead>
<tbody>
<tr>
<td>D1</td>
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<td>0</td>
<td>2.2</td>
<td>12.1</td>
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<tr>
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<td>0</td>
<td>3.2</td>
<td>11.7</td>
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<td>13.4</td>
</tr>
<tr>
<td>D4</td>
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<td>17.8</td>
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<tr>
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<td>50</td>
<td>32.8</td>
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Calculated saturation indices \(^a\) (SI) of possible secondary precipitates and forsterite for the liquid samples collected at the end of three weeks.

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<tr>
<th>Run</th>
<th>Carbonates</th>
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<th>Amorphous</th>
<th></th>
<th>Phyllosilicates</th>
<th></th>
<th>Forsterite</th>
<th></th>
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<tr>
<td></td>
<td>Magnesite</td>
<td></td>
<td>Brucite</td>
<td></td>
<td>Antigorite</td>
<td></td>
<td>Chrysotile</td>
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<td>-95.80</td>
<td>-12.71</td>
<td>-9.89</td>
<td>-12.60</td>
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\(^a\) The saturation indices (SI) of possible secondary precipitates and forsterite were calculated using the measured aqueous compositions of the samples collected at three weeks. The measured total dissolved concentrations of Mg, Si and Fe were used as the concentrations of \(\text{Mg}^{2+}\), \(\text{SiO}_2(aq)\) and \(\text{Fe}^{2+}\), respectively, in the “SpecE8” program from Geochemist’s Workbench (GWB) 8.0. With the input of water composition and fixed \(\text{CO}_2(aq)\) concentrations (Duan and Sun 2003) at different temperature and \(P_{\text{CO}_2}\) conditions, “SpecE8” provided the solution pH and the saturation indices of all possible secondary precipitates and forsterite.
Figure S2.1 Influence of temperature on the calculated initial pH ($pH_{\text{init}}$). Note that the concentration of $CO_2(aq)$ is a fixed value when the aqueous solution is at equilibrium with a headspace at a constant $CO_2$ pressure. The $CO_2(aq)$ concentration was calculated using the equations of state of Sterner and Pitzer (Sterner and Pitzer 1994) and the solubility equations of Duan and Sun (2003). The initial pH was calculated based on charge balance, using the chemical equilibrium constants calculated using SUPCRT92 with the slop98 database. Ionic strength and activity coefficient were also taken into consideration.
Figure S2.2  Dissolved concentrations of Mg (■), Si (◆), and Fe (●), and pH_{ex} (Δ), which was the pH measured under ambient pressure, during batch dissolution of 0.5 g/L forsterite in dilute solution at 25 ºC and 10 - 100 bar CO₂ pressures. The dashed lines present the dissolved Mg concentration predicted by the rate law given in equation 2.6 with n_{H+} of 0.46 and k_{app} (k_{app} = k_0 e^{-\frac{k_n}{RT}}) of 1.27×10^{-10} mol/cm^2-s to account for the declining dissolution rate expected from the increasing pH and the changing surface area.
Figure S2.3  Dissolved concentrations of Mg (■), Si (◆), and Fe (●), and pH\textsubscript{ex} (∆), which was the pH measured under ambient pressure, during batch dissolution of 0.5 g/L forsterite in dilute solution at 50 °C and 10 - 100 bar CO\textsubscript{2} pressures. The dashed lines present the dissolved Mg concentration predicted by the rate law given in equation 2.6 with n\textsubscript{H\textsuperscript{+}} of 0.46 and k\textsubscript{app} (k\textsubscript{app} = k_0 e^{-\frac{E_a}{RT}}) of $3.94 \times 10^{-10}$ mol/cm\textsuperscript{2}-s to account for the declining dissolution rate expected from the increasing pH and the changing surface area.
Figure S2.4 Dissolved concentrations of Mg (■), Si (◆), and Fe (●), and pH\textsubscript{ex} (∆), which was the pH measured under ambient pressure, during batch dissolution of 0.5 g/L forsterite in dilute solution at 100 °C and 10 - 100 bar CO\textsubscript{2} pressures. At 100 °C and 100 bar CO\textsubscript{2} pressure, a duplicate experiment was performed for 1 week, with dissolved concentrations of Mg (□), Si (◇), and Fe (○), and pH\textsubscript{ex} (▪). The dashed lines present the dissolved Mg concentration predicted by the rate law given in equation 2.6 with n\textsubscript{H+} of 0.46 and k\textsubscript{app} (k\textsubscript{app} = k_0e^{-\frac{E_0}{RT}}) of 3.19×10\textsuperscript{-9} mol/cm\textsuperscript{2}-s to account for the declining dissolution rate expected from the increasing pH and the changing surface area.
Figure S2.5  Dissolved concentrations of Mg (■), Si (◆), and Fe (●), and pH_{ex} (∆), which was the pH measured under ambient pressure, during batch dissolution of 0.5 g/L forsterite in saline solution (0 - 50,000 mg/L NaCl) at 100 °C and 100 bar CO₂ pressures. The dashed lines present the dissolved Mg concentration predicted by the rate law given in equation 2.6 with n_{H+} of 0.46 and k_{app} (k_{app} = k_{0}e^{Ea/RT}) of 3.19×10^{-9} mol/cm^{2}-s to account for the declining dissolution rate expected from the increasing pH and the changing surface area.
Figure S2.6 Predicted evolution of the aqueous phase during dissolution of 0.0036 mol/L of forsterite (0.5 g/L) in dilute solution at 50 °C and 100 bar CO₂ pressure. The calculations were performed using “React” in Geochemist’s Workbench (GWB). The concentration of CO₂(aq) was 1.15 mol/kg, according to published equations for CO₂ solubility (Duan and Sun 2003). Activity coefficients were taken into consideration in “React” with the “B-dot” equation, an extended form of the Debye-Huckel equation (Helgeson 1969), which could be used for solutions with ionic strengths up to 3 molal. The equilibrium constants (K values) were calculated using a polynomial equation that gives log K as a function of temperature from 0 to 300 °C.
Influence of NaCl concentration on the calculated initial pH ($pH_{\text{init}}$) and dissolved CO$_2$(aq) concentration. Note that the concentration of CO$_2$(aq) is a fixed value when the aqueous solution is at equilibrium with a headspace at a constant CO$_2$ pressure. The CO$_2$(aq) concentration was calculated using the equations of state of Sterner and Pitzer (Sterner and Pitzer 1994) and the solubility equations of Duan and Sun (2003). The initial pH was calculated based on charge balance, using the chemical equilibrium constants calculated using SUPCRT92 with the slop98 database. Ionic strength and activity coefficient were also taken into consideration.
Approach to Modeling the Profile of the Dissolved Mg Concentration

The “React” program from Geochemist’s Workbench (GWB) 8.0 was employed to predict the evolution of pH and dissolved magnesium as a function of time. The approach accounted for the change in pH and surface area as the dissolution reaction proceeded. The overall approach first determined the relationship between pH and dissolved magnesium as a function of reaction progress of forsterite dissolution independent of time. Then from the relationship between dissolved magnesium and pH, a dissolution rate equation (equation 2.6 of the manuscript or equation S2.1) was used to establish the relationship between dissolved magnesium and reaction time.

\[ r = k_0 e^{-\frac{E_a}{RT}}[H^+]^{n_{H^+}} = k_{app}[H^+]^{n_{H^+}} \] (2.6) or (S2.1)

Where the apparent dissolution rate constant: \( k_{app} = k_0 e^{-\frac{E_a}{RT}}. \)

To determine the relationship between pH and dissolved magnesium, the initial solution composition was defined as 0.2 kg of water, and the concentrations of dissolved Mg\(^{2+}\) and SiO\(_2\)(aq) were set to \(10^{-14}\) mol/L to indicate that Mg\(^{2+}\) and SiO\(_2\)(aq) were not initially present. The CO\(_2\)(aq) concentration was fixed to specific values, calculated according to Duan and Sun (2003), by choosing its unit as “free molal”. For only one of the experiments (25 °C and 100 bar CO\(_2\) pressure) were the conditions outside of the model range of the Duan and Sun approach, and in this case the CO\(_2\)(aq) concentration was estimated by extrapolation. The solution charge balance was met by balancing the pH. If the experiments were performed in saline solutions (experiments D10 - D12), then a certain amount of Na\(^+\) and Cl\(^-\) was set beforehand. The effects of ionic strength, with a highest value slightly below 1 molal, were taken into consideration with the “B-dot”
equation, an extended form of the Debye-Huckel equation (Helgeson 1969), which could be used for solutions with ionic strengths up to 3 molal. Second, the calculations determined the aqueous equilibrium as forsterite (close to 0.5 g/L in the experiments) dissolved. “React” could calculate the dissolved Mg\(^{2+}\) and SiO\(_2\)(aq) concentrations and the pH as a function of the amount of forsterite (mol/L) that had dissolved. These results were then used together with the dissolution rate equation (equation 2.6 or equation S2.1) to establish the relationship between dissolved magnesium and reaction time and to account for the change in forsterite mass and specific surface area that would occur over the course of the reaction.

To account for the fact that the forsterite concentration (C\(_{Fo}\), g/L) and the specific surface area (SSA) were changing, the following calculations (equations S2.2-S2.4) were used for each step, noted as subscript “\(i\)”, during forsterite dissolution.

\[
C_{Fo,i} = C_{Fo,i-1} - \Delta C_{Fo,i} \tag{S2.2}
\]

\[
r_{\text{particle},i} = \left(\frac{3C_{Fo,i}V}{\rho_{Fo}4\pi N_{\text{particle}}}\right)^{\frac{1}{3}} \tag{S2.3}
\]

\[
SSA_i = \frac{3}{\rho_{Fo} \cdot r_{\text{particle},i}} \tag{S2.4}
\]

Where the initial forsterite concentration: \(C_{Fo,0} = 0.5 \text{ g/L}\);

the initial SSA: \(SSA_0 = 1900 \text{ cm}^2/\text{g}\);

the total number of particles: \(N_{\text{particle}} = 6.21 \times 10^7\);

density of forsterite: \(\rho_{Fo} = 3.20 \text{ g/cm}^3\); (Klein and Hurlbut Jr. 1993)

solution volume: \(V = 200 \text{ mL}\).
These calculations were performed, assuming that all of the particles were spherical and dissolved at the same rates. As a result, the total number of particles ($N_{\text{particle}}$) remained constant throughout the reaction while the particle size decreases with each step in the process.

At each reaction step “i”, the forsterite dissolution rate (mol/cm$^2$-s) could be calculated using pH, based on equation 2.6 (or equation S2.1). The rate ($r_i$) could be expressed in mol/L-s, using $C_{F_0,i}$ and SSA$_i$. The reaction time ($t_i$) that would correspond to each reaction step “i” was calculated based on equations S2.6 and S2.7.

$$r_i \left( \frac{mol}{L \cdot s} \right) = r_i \left( \frac{mol}{cm^2 \cdot s} \right) \cdot C_{F_0,i} \cdot SSA_i$$  \hspace{1cm} (S5)

$$\Delta t_i = \frac{\Delta Mg_i}{r_i} = \frac{Mg_{i+1} - Mg_{i-1}}{2r_i}$$  \hspace{1cm} (S6)

$$t_i = t_{i-1} + \Delta t_i$$  \hspace{1cm} (S7)

The dissolved Mg concentrations predicted by the rate law given in equation 2.6 (or equation S2.1) with $n_{H^+}$ of 0.46 were plotted as a function of reaction time. By comparison with the experimental dissolved Mg concentration, the $k_{\text{app}}$ value that provided the optimal fit to the initial dissolution results (reaction time < 8 h) was determined for each temperature. The model results obtained following this procedure were presented as the dashed lines in Figure 2.1 and Figures S2.2-S2.5.
Chapter 3. The dissolution of olivine from Indian mines in CO$_2$-rich solutions and implications for mineral carbonation

Abstract

The dissolution of a partially weathered olivine from an Indian source (Mg$_{1.84}$Fe$_{0.16}$SiO$_4$) was studied at conditions relevant to both in situ and ex situ mineral carbonation. The dissolution process was studied in the context of magnesium-rich rocks that have been proposed as carbon sequestration reservoirs. Ex situ mineral carbonation may also be feasible because this particular material is inexpensive and accessible in large amounts. The material is primarily forsteritic olivine with a small amount of the serpentine mineral lizardite. Batch experiments were carried out at different CO$_2$ pressures (1 - 100 bar P$_{CO2}$), temperatures (25 - 100 °C) and initial olivine concentrations (0.5 and 20 g/L). Dissolved element concentrations were determined by inductively coupled plasma mass spectroscopy, and solids were characterized by scanning electron microscopy and X-ray diffraction. The dissolved Mg and Si concentrations increased with increasing temperature and initial olivine concentration. The effect of CO$_2$ pressure was through its influence on solution pH. The dissolution rate declined significantly over time, which might be attributed to the formation of a Si-rich layer on olivine surface. The dissolution of the naturally weathered olivine was very similar to that of purer olivine at conditions relevant to mineral carbonation.
3.1 Introduction

Increasing concentrations of greenhouse gases, particularly carbon dioxide (CO$_2$), in the atmosphere represent a major environmental concern due to their impacts on climate change (IPCC 2007). India’s CO$_2$ emissions in 2009 were 1.98 billion tons (United Nation Statistics Division July 2012) and they are projected to increase by 4 - 5 times by 2030 (Shackley and Verma 2008). Whereas, the CO$_2$ emissions from the United States were 5.30 billion tons in 2009 (United Nation Statistics Division July 2012). Carbon capture and sequestration (CCS) is considered as a viable option for preventing CO$_2$ accumulation in the atmosphere to levels that are dangerous to the climate (Bachu, Gunter et al. 1994; Davison 2001; Herzog 2001; Pacala and Socolow 2004; US Department of Energy, December 1999). The mineral carbonation process in which CO$_2$ reacts with suitable minerals to form stable carbonate phases is considered to be a local niche option for long-term carbon sequestration (Picot, Cassard et al. 2011). While research and pilot-scale field carbon sequestration projects are underway in the United States, carbon capture and sequestration in India is primarily at the bench-scale research stage because full-scale carbon capture and sequestration may not be a priority until a reliable electricity supply is established (Shackley and Verma 2008). Nevertheless, advances in carbon capture and sequestration can have global benefits, especially if they can be integrated into new carbon-emitting power plants from the very start of the design stage.

CO$_2$ can be transformed into carbonate minerals either by *in situ* mineral carbonation, through CO$_2$ injection into geological formations, or by *ex situ* mineral carbonation as
part of an engineered industrial process (Oelkers, Gislason et al. 2008). Mineral carbonation of CO₂ requires divalent cations (usually Mg²⁺, Fe²⁺ or Ca²⁺). The formation of Mg-carbonates is energetically favorable in the water-forsterite-CO₂ system. The carbonation process starts with the dissolution of CO₂ in water (equation 3.1), which is followed by carbonic acid formation and deprotonation (equation 3.2). As forsterite dissolves (equation 3.3), H⁺ is consumed, which brings up both pH and the CO₃²⁻ concentration. Finally, a Mg-carbonate (e.g., MgCO₃(s)) forms (equation 3.4), achieving the goal of carbonation. A net mineral trapping reaction (equation 3.5) can be obtained from these four steps.

\[
CO_2(g) \rightleftharpoons CO_2(aq) \quad (3.1)
\]

\[
H_2O + CO_2(aq) \rightleftharpoons CO_3^{2-} + 2H^+ \quad (3.2)
\]

\[
Mg_2SiO_4(s) + 4H^+ \rightleftharpoons 2Mg^{2+} + SiO_2(aq) + 2H_2O \quad (3.3)
\]

\[
Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3(s) \quad (3.4)
\]

\[
Mg_2SiO_4 + 2CO_2(g) \rightleftharpoons 2MgCO_3(s) + SiO_2(aq) \quad (3.5)
\]

Generally speaking, magnesite forms at high temperature and CO₂ pressure. Without any initial substrate, magnesite formed at 119 °C and 104 bar CO₂ pressure from solution.
saturated with respect to magnesite at a saturation index 1.32 (Hänchen, Prigiobbe et al. 2008). However, the dissolution of nano-sized forsterite could lead to the formation of magnesite at much lower temperatures (35 °C) (Felmy, Qafoku et al. 2012). At lower temperature and CO$_2$ pressure, metastable magnesium carbonates form (e.g. hydromagnesite, dypingite and nesquehonite).

*In situ* mineral carbonation of peridotite, a rock which consists mostly of olivine from the Earth’s upper mantle, has recently been suggested as an alternative to *ex situ* mineral carbonation. The peridotite massifs can also serve as an alternative geological formation to sandstone and carbonate aquifers that have received most attention for geologic sequestration (Kelemen and Matter 2008; Matter and Kelemen 2009; Kelemen, Matter et al. 2011). Although peridotite massifs can provide a much higher Mg content, the mineral carbonation of peridotite might fill porosity and reduce permeability or conversely fracture rocks and maintain permeability (Kelemen, Matter et al. 2011). The tectonic exposure of mantle peridotite at the Earth’s surface in Oman alone could be a significant sink for CO$_2$ and could consume more than 1 billion tons of CO$_2$ per year (Kelemen and Matter 2008). The dissolution and carbonation of different peridotite samples provide both experimental and computational evidence that *in situ* carbonation of peridotite may be viable as high as 200 °C and 700 bar CO$_2$ pressure (Hövelmann, Austrheim et al. 2011; Hövelmann, Austrheim et al. 2012; Paukert, Matter et al. 2012; van Noort, Spiers et al. 2013).
Ex situ mineral carbonation approaches were proposed by Seifritz (Seifritz 1990) and then advocated by Lackner and coworkers (Lackner, Wendt et al. 1995; Lackner, Butt et al. 1997). Oelkers (2008) suggested forsterite (Mg$_2$SiO$_4$), chrysotile (Mg$_3$(Si$_2$O$_5$)(OH)$_4$), wollastonite (CaSiO$_3$), anorthite (CaAl$_2$Si$_2$O$_8$) and basaltic glass as potential source minerals for carbonation, since they contain the necessary divalent cations. Picot and co-workers discussed the possibility of ex situ mineral carbonation using ore deposits related to mafic and ultramafic rocks (Picot, Cassard et al. 2011). Experiments have been conducted to study ex situ mineral carbonation with chrysotile at 300 - 1200 °C and 0.2 - 0.67 bar CO$_2$ pressure (Larachi, Daldoul et al. 2010), wollastonite at 25 - 225 °C and 1 - 40 bar CO$_2$ pressure (Huijgen, Witkamp et al. 2006), ultramafic mining residues at ambient temperature and pressure (Pronost, Beaudoin et al. 2011), and industrial wastes that contain reactive metal oxides, in particular CaO and MgO (Kelly, Silcox et al. 2011).

The dissolution of the silicate minerals can be accelerated by increasing temperature and adjusting pH (Oelkers 2001; Carroll and Knauss 2005). The net process of forsterite carbonation itself is exothermic, which can help sustain high temperature and rapid dissolution rates. The dissolution of forsterite is usually congruent and fast as compared to other Mg-containing silicates. As a result, its reaction in CO$_2$-rich solutions allows observations of both forsterite dissolution and possible precipitation of Mg-carbonate minerals (Wogelius and Walther 1991; Chen and Brantley 2000; Rosso and Rimstidt 2000; Giammar, Bruant et al. 2005; Hanchen, Prigiobbe et al. 2006; Wang and Giammar 2013). However, most of the recent studies of fosterite dissolution kinetics used very pure crystals and did not study bulk mined minerals that will be most similar to those that will
react in actual *in situ* carbon sequestration projects or engineered *ex situ* mineral carbonation processes.

The objective of this study was to investigate the water-olivine-CO$_2$ reaction at pressure and temperature conditions relevant to carbon sequestration using an inexpensive natural olivine that is commercially available in large quantities. The *ex situ* mineral carbonation process requires determination of reaction rates and extents over parameters of temperature, CO$_2$ pressure and initial olivine concentration. This knowledge can also aid in improved predictions of carbon fate and transport during *in situ* mineral carbonation as part of geologic carbon sequestration. In this study, batch reactions of the water-olivine-CO$_2$ system were carried out under different combinations of these parameters. The water chemistry was monitored to investigate the dissolution rate and pathways. The change in the composition and surface were determined through solid phase characterization.

### 3.2 Materials and methods

#### 3.2.1 Materials

The olivine used in this study was acquired from mines in Salem, Tamilnadu, India (Industrial Minerals and Refectories). It was provided in a crushed form, and the powder was then sieved to yield the 50 - 125 μm size fraction. The chemical composition (Table 3.1) was determined to be Mg$_{1.84}$Fe$_{0.16}$SiO$_4$ (Fo92) with Si deficiency by the borate fusion method; the material was dissolved in the lithium borate flux and then analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ARCOS).
Table 3.1 Composition of olivine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt %</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>49.65</td>
<td>0.6360</td>
</tr>
<tr>
<td>SiO₂</td>
<td>38.36</td>
<td>0.3290</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.78</td>
<td>0.0284</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.15</td>
<td>0.0007</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.73</td>
<td>0.0025</td>
</tr>
<tr>
<td>CaO</td>
<td>0.29</td>
<td>0.0027</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.0008</td>
</tr>
<tr>
<td>LOIᵃ</td>
<td>1.50</td>
<td>NAᵇ</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.56</strong></td>
<td><strong>1.00</strong></td>
</tr>
</tbody>
</table>

ᵃ Loss on ignition
ᵇ Not available

X-ray diffraction (XRD) pattern indexing was also consistent with this composition, and the patterns indicate that a small amount of the serpentine mineral lizardite (Mg₃Si₂O₅(OH)₄) was present in addition to the forsterite. The morphology of the olivine powder was observed using scanning electron microscopy (SEM, JEOL 7001L), which revealed that particles smaller than 50 μm adhered to the surface of the larger particles isolated by the sieving process. The specific surface area (SSA) of the powder was determined to be 1.45 m²/g by BET-N₂ adsorption, using an ASAP 2020 surface area and physisorption analyzer from Micromeritics. The SSA was larger than the value of 0.20 ± 0.09 m²/g that would be expected for cleaned olivine grains in the 50-125 μm size range.
(Brantley and Mellott 2000), which is consistent with the presence of fine particles smaller than 50 μm.

### 3.2.2 Methods

#### 3.2.2.1 Batch dissolution experiments

The dissolution of 0.5 g/L olivine was studied in well-stirred batch reactions under different temperatures (25 - 100 °C) and CO₂ pressures (1 - 100 bar). The batch reactions of 20 g/L olivine were performed over the same temperature range but only at 1 bar P\textsubscript{CO₂}. (Table 3.2) For 1 bar P\textsubscript{CO₂} experiments, storage/media bottles (250 mL) with polypropylene caps (VWR) were used. At 50 and 100 bar P\textsubscript{CO₂}, 300 mL stainless steel vessels with PTFE liners (Parr Instrument Company) were used. All the reported CO₂ pressures are gauge pressures, and the pressurized CO₂ was introduced while the initial ambient atmosphere was retained. Hence, the absolute pressure should be 1 bar bigger than the gauge pressure. For example, 1 bar P\textsubscript{CO₂} works out to be 2 bar absolute pressure.

Initially all reactors were loaded with 0.5 g/L (or 20 g/L) of olivine powder in 200 mL (or 100 mL) of ultrapure water (resistivity > 18.2 MΩ·cm), and heated to the experimental temperature using either a heating mantle or water bath (usually within 30 minutes of heating). Afterwards, CO₂ was introduced to the reactor headspace to saturate the aqueous solution. Constant CO₂ pressures in the reactor headspace were maintained by an epoxy coated pressure manifold (Ace) at 1 bar P\textsubscript{CO₂} or a syringe pump (500D Teledyne Isco) at 50 and 100 bar P\textsubscript{CO₂}. During each 1-week experiment, liquid samples of 5 mL volumes were collected at regular intervals from a sampling port. The first sample, which is referred to here as the “0 h sample”, was collected as soon as the experimental
headspace CO₂ pressure was achieved (typically within 15 minutes after introducing CO₂). Other samples were collected after 4, 8, 48, 73 and 168 hours. The solution samples were filtered using 0.22 μm mixed cellulose ester syringe filters (Millipore) and then acidified with nitric acid to yield preserved samples with 1% (by mass) nitric acid. After 168 hours the reactors were quickly depressurized and cooled to ambient temperature. The remaining solids were collected using vacuum filtration with a 0.45 μm (Millipore) membrane and air-dried at room temperature for two days.

**Table 3.2** The pH measured under ambient pressure ($pH_{ex}$) and the initial dissolution rate based on Mg and Si concentrations for batch experiment performed at different conditions.

<table>
<thead>
<tr>
<th>Run</th>
<th>T (°C)</th>
<th>$P_{CO2}$ (bar)</th>
<th>solid concentration (g/L)</th>
<th>$pH_{ex}$</th>
<th>log $R_{init. - Mg}$ (mol/cm²·Sec)</th>
<th>log $R_{init. - Si}$ (mol/cm²·Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>25</td>
<td>1</td>
<td>0.5</td>
<td>Initial</td>
<td>Final</td>
<td>-12.89</td>
</tr>
<tr>
<td>D-2a</td>
<td>50</td>
<td>1</td>
<td>0.5</td>
<td>4.90</td>
<td>5.35</td>
<td>-12.47</td>
</tr>
<tr>
<td>D-3</td>
<td>25</td>
<td>50</td>
<td>0.5</td>
<td>4.46</td>
<td>5.19</td>
<td>-12.38</td>
</tr>
<tr>
<td>D-4</td>
<td>50</td>
<td>50</td>
<td>0.5</td>
<td>4.46</td>
<td>5.73</td>
<td>-12.11</td>
</tr>
<tr>
<td>D-5</td>
<td>100</td>
<td>50</td>
<td>0.5</td>
<td>4.97</td>
<td>5.90</td>
<td>-11.91</td>
</tr>
<tr>
<td>D-6</td>
<td>25</td>
<td>100</td>
<td>0.5</td>
<td>4.56</td>
<td>5.34</td>
<td>-13.09</td>
</tr>
<tr>
<td>D-7</td>
<td>50</td>
<td>100</td>
<td>0.5</td>
<td>4.89</td>
<td>5.47</td>
<td>-12.13</td>
</tr>
<tr>
<td>D-8</td>
<td>100</td>
<td>100</td>
<td>0.5</td>
<td>4.88</td>
<td>6.00</td>
<td>-11.86</td>
</tr>
<tr>
<td>D-9</td>
<td>50</td>
<td>1</td>
<td>20</td>
<td>5.43</td>
<td>6.16</td>
<td>-13.18</td>
</tr>
</tbody>
</table>
Duplicate of experiments were carried out for this condition. The average value was reported.

3.2.2.2 Analytical methods

The pH of the aqueous samples was measured under ambient pressure (pH_{ex}) within 5 minutes of collection. The pH value corrections for non-standard temperatures were automatically performed by the pH meter with the temperature monitored by an automatic temperature compensation probe. The pH of the solutions in the reactor under 50 and 100 bar P_{CO2} would have been lower than the pH_{ex} since considerable CO_{2} degasses from the samples as they leave the reactor and come in contact with the ambient laboratory atmosphere. The solid phase was characterized by XRD to identify the crystalline phases present, and SEM was used to observe surface morphology with energy dispersive X-ray analysis (EDX) for elemental analysis of specific locations on the solids. Aqueous samples were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS) for concentrations of dissolved Mg, Si and Fe.

3.2.2.3 Geochemical modeling

The dissolution pathways of olivine under high P_{CO2} (1 - 100 bar) conditions were simulated using the “React” program from Geochemist’s Workbench (GWB) 8.0. This modeling approach took into consideration the change in solution pH. The pH values and dissolved magnesium concentrations, which could be calculated from the solution neutrality using “React”, were first determined from the extent of olivine dissolution without considering reaction time. The general rate equation for forsterite dissolution
(equation 3.6) was then employed to determine how the dissolved magnesium concentration would change with time. This equation can hold over the pH range of 2 - 8.5 under different temperatures (25 - 150 °C) and CO₂ pressures (1 - 180 bar) (Wogelius and Walther 1992; Oelkers 2001; Hanchen, Prigiobbe et al. 2006; Prigiobbe, Costa et al. 2009).

\[ r = k_0 e^{-\frac{E_a}{RT}}[H^+]^{n_{H^+}} = k_{app}[H^+]^{n_{H^+}} \]  

In equation 3.6, \( r \) represents the dissolution rate of forsterite (mol/cm²-s), \( k_0 \) is the dissolution rate constant (mol/cm²-s), \( E_a \) is the apparent activation energy (J/mol), \( \{H^+\} \) is the activity of hydrogen ions in solution, and \( n_{H^+} \) is the reaction order for \( H^+ \). The apparent dissolution rate constant (\( k_{app} \)) can be expressed as \( k_{app} = k_0 e^{-\frac{E_a}{RT}} \). The modeling results were obtained by setting \( n_{H^+} \) as 0.46, the value proposed by Hanchen et al. (2006), and different \( k_{app} \) values under different temperatures in equation 3.6. The \( k_{app} \) parameter was set to \( 3.77 \times 10^{-11} \) mol/cm²-s at 25 °C, \( 7.03 \times 10^{-11} \) mol/cm²-s at 50 °C and \( 1.45 \times 10^{-10} \) mol/cm²-s at 100 °C, to provide the optimal fit to the initial dissolution results (reaction time < 8 h).

The constant \( CO_2(aq) \) concentration under a certain \( CO_2 \) pressure was fixed according to equations published by Duan and Sun (2003). The \( CO_2(aq) \) concentration at 25 °C and 100 bar \( CO_2 \) pressure was estimated by extrapolation, since this condition is outside of the range modeled by Duan and Sun. The effects of ionic strength were taken into consideration with the “B-dot” equation, an extended form of the Debye-Huckel equation
(Helgeson 1969), which can be used for solutions with ionic strengths up to 3 molal. A step by step description of the modeling approach has been described in detail previously (Wang and Giammar 2013).

### 3.3 Results and discussion

#### 3.3.1 Water chemistry under conditions relevant to mineral carbonation

The concentrations of aqueous species (Mg, Si and Fe) and pH$_{ex}$ were monitored for 1-week olivine dissolution experiments with different initial olivine concentrations (0.5 and 20 g/L) at various temperatures (25, 50, 100 °C) and CO$_2$ pressures (1, 50, 100 bar) (Figure 3.1 and 3.2). The dashed lines in these figures illustrated how the dissolved Mg concentration was predicted to change with reaction time at 1 - 100 bar CO$_2$ pressure using geochemical modeling. The solution was initially acidic, with pH$_{ex}$ from 4.46 to 5.43 and pH$_{in}$ from 3.22 to 4.49. As olivine dissolved and released Mg and Si to measurable values, it neutralized some the acidity of the CO$_2$ and the pH increased. In addition, the olivine dissolution is congruent as seen by the data in Figure 3.3 aligning with the stoichiometric Si/Mg ratio of 0.54 in the olivine.

For all experimental conditions, forsterite dissolution was the dominant chemical reaction. The saturation indices (SI) for possible secondary precipitates and forsterite in dilute solution were calculated for 168 hours (Table 3.3). The results indicated that the dissolution of forsterite was always favorable, since its saturation index was negative under all the experimental conditions. Different Mg-carbonates were not predicted to
precipitate. The solution came close to saturation with respect to amorphous silica for all the experiments.

**Figure 3.1** Aqueous chemistry measurements from batch aqueous reactions of 0.5 g/L Indian olivine over the full range of temperature (25 - 100 °C) and P_{CO2} (1 - 100 bar) conditions studied. The dashed lines present the dissolved Mg concentration simulated by the rate law given in equation 3.6 to account for declining dissolution rate expected from the increasing pH.
Figure 3.2 Aqueous chemistry measurement of 20 g/L Indian olivine dissolution in a batch reactor at 50 °C and 1 bar $P_{CO_2}$. The dashed lines present the dissolved Mg concentration simulated by the rate law given in equation 3.6 to account for declining dissolution rate expected from the increasing pH.

For the experiments with 0.5 g/L initial olivine concentration, the initial dissolution rate of olivine ($R_{\text{init}}$) was determined by the linear regression of the elemental concentration for the first 8 hours of reaction and expressed in terms of mol/cm$^2$-s. This initial dissolution rate could be calculated based on either Mg concentration ($R_{\text{init-Mg}}$) or Si concentration ($R_{\text{init-Si}}$). At 25 °C the olivine initial dissolution rate ($R_{\text{init-Mg}}$ of $10^{-13.09} - 10^{-12.38}$ mol/cm$^2$-s) was well within the range of previously reported values ($10^{-14.34} - 10^{-12.23}$ mol/cm$^2$-s) for similar pH ($pH_{ex}$ 4 - 6) (Wogelius and Walther 1991; Golubev, Pokrovsky et al. 2005). At 50 and 100 °C, the initial olivine dissolution rate ($R_{\text{init-Mg}}$ of $10^{-12.47} - 10^{-11.86}$ mol/cm$^2$-s) was also comparable to previously reported values ($10^{-12.42} - 10^{-10.77}$ mol/cm$^2$-s) for similar pH ($pH_{ex}$ 4 - 6) (Wogelius and Walther 1992; Chen and Brantley 2000; Hanchen, Prigobbe et al. 2006). These calculated initial forsterite dissolution rates
were not compared to the rates recently predicted by Rimstidt et al. The reason is that the dissolution rates in the equation from Rimstidt et al. are based on the geometric surface area, which is on the average 5.2 times smaller than the BET surface area (Rimstidt, Brantley et al. 2012).

![Graph showing the stoichiometry of olivine dissolution](image)

**Figure 3.3** Stoichiometry of olivine (Mg$_{1.84}$Fe$_{0.16}$SiO$_4$) dissolution with an initial olivine concentration of 0.5 g/L. The dashed line shows a Si/Mg ratio of 0.54, which corresponds to stoichiometric dissolution of olivine.

The olivine dissolution rate started decreasing after 8 hours of reaction even though the olivine dissolution reaction was still very thermodynamically favorable (Table 3.3). While some decrease in rate is anticipated as the pH increases with reaction progress, the model simulation of the Mg concentration based on reaction 3.6 (shown as dashed lines
in Figure 3.1) are considerably larger than the measured values for longer reaction times. The declining rates of Mg and Si release to the solution were probably due to the loss of fine particles early on. These fine particles should dissolve much faster than the primary large particles, due to their large SSA values. After the loss of these fine particles, large particles would dissolve at a much smaller rate, because of their smaller SSA and the elevated pH due to initial dissolution. Ideally, a better simulation should account for the change in SSA with reaction time for both fine particles and large particles, while our use of equation 3.6 (dashed lines in Figure 3.1) assumed one changing SSA for all the particles. Wang and Giammar (2013) still observed a greater decline than could be explained by pH for a material that had been cleaned for removal of fine-grained particles. The formation of a Si-rich layer on the olivine surface could also contribute to the decline in the dissolution rate, although the solution was always undersaturated with respect to amorphous silica. Previous studies reported that a thin amorphous Si-rich layer (15 - 40 nm) could form on the olivine surface and render a declining dissolution rate, even when the bulk solution was slightly undersaturated with respect to amorphous silica (saturation index for amorphous silica (SI$_{SiO_2(\text{am})}$) of $-0.14$) (Pokrovsky and Schott 2000; Bearat, McKelvy et al. 2006; Daval, Sissmann et al. 2011).

XRD results (Figure 3.4) indicated that no new crystalline secondary phases formed after 1 week of olivine dissolution experiments (Figure 3.4 shown as an example). XRD did indicate that at many conditions lizardite sometimes dissolved completely after 1 week. According to XRD results, the lizardite peak (20 of 12.19°) decreased in intensity at 25 °C and disappeared completely at 50 and 100 °C (Figure 3.4). Although the dissolution
rates of serpentine minerals are generally observed to be slower than that of olivine (Krevor and Lackner 2011), the much smaller amount of serpentine present in the material could lead to its earlier disappearance in the samples. SEM images showed that dissolution pits formed on the surface (Figure 3.5 and 3.6). EDX (not shown) did not show any difference in elemental compositions of reacted and unreacted surfaces. Therefore, there was no direct evidence to prove that amorphous silica did form on olivine surface.

**Table 3.3** Calculated saturation indices \(^a\) (SI) of possible secondary precipitates and forsterite for the liquid samples collected at the end of one week.

<table>
<thead>
<tr>
<th>Run</th>
<th>Carbonates</th>
<th></th>
<th></th>
<th>Phyllosilicates</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnesite</td>
<td>Nesquehonite</td>
<td>Brucite</td>
<td>Amorphous silica</td>
<td>Antigorite</td>
<td>Chrysotile</td>
</tr>
<tr>
<td>D-1</td>
<td>-3.90</td>
<td>-6.60</td>
<td>-10.01</td>
<td>-0.90</td>
<td>-149.22</td>
<td>-19.50</td>
</tr>
<tr>
<td>D-2(^b)</td>
<td>-2.98</td>
<td>-6.09</td>
<td>-8.03</td>
<td>-1.01</td>
<td>-111.87</td>
<td>-14.75</td>
</tr>
<tr>
<td>D-3</td>
<td>-4.79</td>
<td>-7.49</td>
<td>-12.51</td>
<td>-0.69</td>
<td>-205.54</td>
<td>-26.57</td>
</tr>
<tr>
<td>D-4</td>
<td>-2.90</td>
<td>-6.01</td>
<td>-9.60</td>
<td>-0.44</td>
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<td>-18.34</td>
</tr>
<tr>
<td>D-5</td>
<td>-1.19</td>
<td>-1.19</td>
<td>-6.31</td>
<td>-0.60</td>
<td>-76.75</td>
<td>-10.31</td>
</tr>
<tr>
<td>D-6</td>
<td>-4.76</td>
<td>-7.45</td>
<td>-5.02</td>
<td>-0.64</td>
<td>-205.64</td>
<td>-26.59</td>
</tr>
<tr>
<td>D-7</td>
<td>-3.48</td>
<td>-6.59</td>
<td>-10.35</td>
<td>-0.59</td>
<td>-160.58</td>
<td>-20.89</td>
</tr>
<tr>
<td>D-8</td>
<td>-1.43</td>
<td>-5.55</td>
<td>-6.79</td>
<td>-0.60</td>
<td>-88.17</td>
<td>-11.73</td>
</tr>
<tr>
<td>D-9</td>
<td>-1.02</td>
<td>-4.13</td>
<td>-6.13</td>
<td>-0.36</td>
<td>-55.32</td>
<td>-7.76</td>
</tr>
</tbody>
</table>

\(^a\) The saturation indices (SI) of possible secondary precipitates and forsterite were calculated using the measured aqueous compositions of the samples collected at one week. The measured total dissolved concentrations of Mg, Si and Fe were used as the
concentrations of Mg$^{2+}$, SiO$_2$(aq) and Fe$^{2+}$, respectively, in the “SpecE8” program from Geochemist’s Workbench (GWB) 8.0. With the input of water composition and fixed CO$_2$(aq) concentrations at different temperature and P$_{CO2}$ conditions, “SpecE8” provided the solution pH and the saturation indices of all possible secondary precipitates and forsterite. The CO$_2$(aq) concentration was fixed to specific values, calculated according to Duan and Sun (2003) for 1 - 100 bar CO$_2$ pressure. For only one of the experiments (25 °C and 100 bar CO$_2$ pressure) its condition was outside of the model range of the Duan and Sun approach, and in this case the CO$_2$(aq) concentration was estimated by extrapolation.

b The saturation indices (SI) of possible secondary precipitates and forsterite were calculated based on the average concentrations of different elements for duplicate experiments.
Figure 3.4 XRD patterns of initial olivine mineral and the solids collected after 1 week of reactions at 100 bar $P_{CO_2}$ and different temperatures. The reference patterns for forsterite and lizardite are also included for comparison. After 1 week of reaction, the lizardite peak at $2\theta$ of 12.19° decreased in intensity at 25 °C and disappeared completely at 50 and 100 °C. The broad peak around 16° corresponds to the peak in forsterite pattern, but was broaden probably due to the poor crystallinity.
Figure 3.5 Scanning electron micrograph of olivine after 168 hours of reaction for 25 - 100 °C and 1 - 100 bar $P_{\text{CO}_2}$. The scale bar is 10 μm, and all images are presented at the same magnification.
Figure 3.6 Scanning electron micrograph of olivine after 168 hours of reaction for 25 - 100 °C and 1 - 100 bar $P_{CO_2}$. The scale bar is 1 μm.

3.3.2 Effect of temperature

The initial dissolution rate and final dissolution extent of olivine both increased with increasing temperature (Figure 3.1 and Table 3.2). The equilibrium constants for different reactions at 50 °C were listed in Table 3.4. At fixed $CO_2$ pressure and 0.5 g/L of olivine, the trend of the initial olivine dissolution rate, calculated based on both Mg and Si concentrations, agrees well with previous research and comes as expected. As indicated
in equation 3.6, with fixed dissolution rate constant \( (k_0) \), activation energy \( (E_a) \) and reaction order \( (n_{H^+}) \), the dissolution rate will increase with increasing temperature and lower pH. Even with the decreasing dissolution rate during the 1-week experiments, the final dissolution extent, which is shown by the concentration of Mg and Si at 168 hours, followed the same trend as the initial dissolution rate (i.e., greater extents of dissolution at lower pH and higher temperatures).

**Table 3.4** Equilibrium constants and solubility products for related chemical reactions under different CO\(_2\) pressure at 50 °C.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log K ) at 50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 bar</td>
</tr>
<tr>
<td>2CO(_2) + Mg(_2)SiO(_3) = 2MgCO(_3) + SiO(_2)</td>
<td>9.16</td>
</tr>
<tr>
<td>( \text{CO}<em>2) (molal) fixed by T and ( P</em>{\text{CO}_2} )</td>
<td>0.018</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{CO}_2) = ( \text{H}^+ + \text{HCO}_3^- )</td>
<td>-6.27</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{CO}_2) = 2( \text{H}^+ + \text{CO}_3^- )</td>
<td>-16.44</td>
</tr>
<tr>
<td>MgCO(_3) = Mg(^{2+}) + CO(_3^{2-})</td>
<td>-8.50</td>
</tr>
<tr>
<td>SiO(_2) = SiO(_2)</td>
<td>-2.48</td>
</tr>
<tr>
<td>( \text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 2\text{SiO}_2 + 5\text{H}_2\text{O} )</td>
<td>28.10</td>
</tr>
</tbody>
</table>

\(^a\) All values, except \( \text{CO}_2\), were calculated using SUPCRT92 with the dSLOP98 database.
\(^{b}\) \(\text{CO}_2(\text{aq})\) concentration is a fixed value when the aqueous phase is at equilibrium with a headspace at a fixed \(P_{\text{CO}_2}\). Calculations were made using the equations of state of (Sterner and Pitzer 1994) and the solubility equations of Duan and Sun (2003).

\(^{c}\) The solubility product for chrysotile is shown instead of that of lizardite dissolution, which is not available from SUPCRT92 with dSLOP98 database.

According to Kelemen and Matter (2008), the temperature for mineral carbonation of peridotite should not be higher than 185 °C, because serpentinization is slower than peridotite carbonation for temperatures between 25 and 185 °C. In serpentinization reaction (equation 3.7), olivine and pyroxene react with \(\text{H}_2\text{O}\) to form serpentine mineral, and compete for the consumption of \(\text{Mg}\) released by olivine that could have been used to capture \(\text{CO}_2\). Therefore, the temperature effect (25 - 100 °C) elucidated from the batch experiments can provide insight for both \textit{in situ} and \textit{ex situ} mineral carbonation.

\[
2\text{Mg}_2\text{Si}_4 + \text{Mg}_2\text{Si}_2\text{O}_6 + 4\text{H}_2\text{O} \leftrightarrow 2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4
\]  

(3.7)

### 3.3.3 Effect of initial olivine concentration

Increasing the olivine concentration did elevate the olivine dissolution extent. At 50 °C and 1 bar \(P_{\text{CO}_2}\), when the initial olivine concentration was increased by a factor of 40 (from 0.5 to 20 g/ L), the final dissolved \(\text{Mg}\) concentration increased by 5.5 times (Figure 3.2) and the calculated \textit{in situ} pH, using GWB 8.0, increased from 5.14 to 5.84 after 1 week of reaction. The initial dissolution rate for 20 g/L of initial olivine based on \(\text{Mg}\)
concentration (Table 3.2) is 19% of that for 0.5 g/L initial olivine. Both the initial dissolution rate and final dissolution extent at 20 g/L olivine are lower than what would be predicted from the initial dissolution rate measured with 0.5 g/L of olivine. The reason for a much smaller olivine dissolution rate for 20 g/L of olivine compared to that at 0.5 g/L is that an amorphous silica layer might have formed earlier on the olivine surface with 20 g/L olivine, therefore slowing down the olivine dissolution process much more significantly. The saturation index for amorphous silica (SI_{SiO2(am)}) reached -1.00 as soon as 8 hours and -0.28 after 1 week of experiment for 20 g/L olivine condition. In comparison, SI_{SiO2(am)} was -1.71 for 8 hours and -0.91 after 1 week of experiment for 0.5 g/L olivine condition.

3.3.4 Implications for ex situ mineral carbonation

Olivine minerals, even already weathered, are applicable for both in situ and ex situ mineral carbonation. They stand out particularly for ex situ mineral carbonation in India. According to the results reported in the previous section, the dissolution pathway of olivine at high pressure (1 - 100 bar P_{CO2}) is comparable to purer olivine, especially with respect to the dissolution rate. Consequently, insights gained from the large body of previous work with pure olivine minerals are relevant to the more abundant and less pure materials available from mines in India and elsewhere.

Magnesite precipitation is very promising at relatively low CO2 pressure when the initial olivine dosage is increased. High temperatures in engineered reactors would be needed, but pressures do not necessarily need to be much more than 1 bar P_{CO2}. For example,
using initially 20 g/L of olivine, the saturation index for magnesite (SI$_{\text{mag}}$) reached as high as -1.02 for 50 °C and 1 bar P$_{\text{CO}_2}$ after just 1 week of reaction (Figure 3.7). A dissolution rate was roughly calculated using linear regression of the Mg concentration from day 2 to 7, although the dissolution rate was obviously still declining. Using this dissolution rate, the solution is predicted to reach saturation with respect to magnesite in 18 days. This process could be accelerated even more at higher temperatures or using fine olivine mineral with a high SSA, so that it is applicable at industrial scale.

**Figure 3.7** Calculated saturation index of magnesite (SI$_{\text{mag}}$ in Table 3.3) at 25 - 100 °C and 1 - 100 bar P$_{\text{CO}_2}$. After 1 week, the dissolution of 20 g/L olivine at 50 °C and 1 bar P$_{\text{CO}_2}$ came closest to magnesite saturation.
One of the major challenges for *ex situ* mineral carbonation in India is energy input. With ore deposits within 300 km from factories and coal-fired power plants in India (Picot, Cassard et al. 2011), it was estimated that only $55 is required to capture 1 ton of CO$_2$, which was much cheaper than costs using serpentine ores ($250-427/ton$ CO$_2$) and wollastonite ($91/ton$ CO$_2$) (Gerdemann, O ’Connor et al. 2007). The costs did not include the capital costs for processing equipment and the cost of capturing and transporting the CO$_2$, which could make the total cost much higher. However, these costs are still relatively high compared to geologic storage which only goes as high as $30/ton$ CO$_2$, excluding the costs of capture, compression and transport to the site (IPCC 2005).

### 3.4 Conclusion

Naturally weathered olivine can provide Mg cations that are necessary for *ex situ* mineral carbonation. Temperature is the most important factor for accelerating the dissolution rate. CO$_2$ pressure does not directly affect olivine dissolution rate, but it indirectly accelerates dissolution by lowering the solution pH. With CO$_2$ pressure at 1 bar and above, dissolution of olivine is stoichiometric, and the initial dissolution rate is very comparable to that measured in previous studies conducted with purer olivine materials. Declines in olivine dissolution rate are very significant and need to be accounted in making predictions of *in situ* carbon sequestration or the design of *ex situ* carbonation processes. With a higher initial olivine concentration and longer reaction times, magnesite precipitation is probable at high temperatures.
Acknowledgement

This Indo-US joint project was supported by the Consortium for Clean Coal Utilization at Washington University. We thank the Center for Materials Innovations for assistance with SEM imaging and the Department of Earth and Planetary Science for assistance with XRD analysis.
Chapter 4. Precipitation of magnesite in the water-scCO$_2$ system:

Effects of supersaturation, mineral substrate and salinity

Abstract

Precipitation of magnesite from water-scCO$_2$ solutions is crucial to mineral trapping during geologic carbon sequestration. This process can transform injected CO$_2$ into carbonate minerals and permanently remove CO$_2$. Precipitation experiments were performed using batch reactors at 100 °C and 100 bar P$_{CO2}$ for up to 7 days. Forsterite and magnesite powders were used to study the effect of initial substrate on magnesite precipitation. Parallel experiments with synthetic magnesite were used to study its dissolution and the effect of salinity on magnesite dissolution. Measurements of changes in the aqueous phase were combined with solid phase characterization with scanning electron microscopy and X-ray diffraction. The critical saturation index for magnesite nucleation at 100 °C and 100 bar P$_{CO2}$ was approximately 2. Precipitation was fastest when solutions were seeded with magnesite to remove nucleation as a rate-limiting step. Relative to mineral-free solutions, forsterite did not accelerate magnesite nucleation. Magnesite dissolution extent increased with increasing salinity. Neither precipitation nor dissolution of magnesite reached equilibrium within 10 days.

4.1 Introduction

Global climate change, which is primarily caused by the increasing concentrations of greenhouse gases in the atmosphere, has been drawing the attention from both governments and public around the world. Some countries (e.g., those in the EU (EU
2013)) already have regulations on carbon emissions, and others, most notably the US (Eilperin 2013), are seriously considering developing them. To mitigate further atmospheric CO$_2$ accumulation, a brilliant idea, geologic carbon sequestration (GCS), has been proposed and widely studied, in which CO$_2$ will be stored and sequestered through injection into geologic formations. Among four different trapping mechanisms (stratigraphic and structural trapping, solubility trapping, hydrodynamic trapping and mineral trapping), mineral trapping is considered to be the most desirable mechanism, because it will permanently prevent CO$_2$ from re-entering the atmosphere. (Bachu 2000; IPCC 2005) However, mineral trapping is the trapping mechanism that will take the longest before it could become a significant sink for injected CO$_2$.

*In situ* mineral carbonation at GCS sites requires the presence of minerals that can release divalent cations (usually Ca$^{2+}$, Fe$^{2+}$ and Mg$^{2+}$) during their dissolution (Oelkers, Gislason et al. 2008). Once injected into GCS sites, CO$_2$ dissolves into the aqueous phase to form carbonic acid and lowers the aquifer pH. The mineral dissolution of these minerals helps to increase the pH from the low values promoted by high pressures of CO$_2$, and the released metal cations can form stable carbonate minerals and permanently sequester the injected CO$_2$. Peridotite massifs have recently been suggested as a candidate geological formation for *in situ* mineral carbonation. (Kelemen and Matter 2008; Matter and Kelemen 2009; Kelemen, Matter et al. 2011) With the dissolution of peridotite, which is mainly made of olivine and pyroxene, Mg$^{2+}$ is released and magnesite (MgCO$_{3(s)}$) is the most thermodynamically favorable magnesium carbonate to form. Therefore, it is necessary to study magnesite precipitation under conditions relevant to GCS. In addition,
the precipitation mechanisms of magnesite can provide insights to the precipitation of
other divalent cation containing carbonates. For example, calcite (CaCO$_3$(s)), which is
very similar to magnesite structurally, can form after the dissolution of anorthite
(CaAl$_2$Si$_2$O$_8$) in deep saline aquifers, a primary geological formation that is being
considered and tested for GCS.

The precipitation of magnesite can be complicated by the formation of several hydrated
Mg-carbonates under different environmental conditions, especially in the water-
forsterite-CO$_2$ system. These hydrated Mg-carbonates include nesquehonite
(MgCO$_3$·3H$_2$O$_{(s)}$), hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O$_{(s)}$) and dypingite
(Mg$_5$(CO$_3$)$_4$(OH)$_2$·5H$_2$O$_{(s)}$), and they can form either as the final reaction products or
intermediates (Davies and Bubela 1973; Hänchen, Prigiobbe et al. 2008; Kwak, Hu et al.
2010; Bénézeth, Saldi et al. 2011; Case, Wang et al. 2011; Felmy, Qafoku et al. 2012).
Generally speaking, magnesite precipitation requires elevated temperature (T > 60 °C) as
well as CO$_2$ pressure, while other hydrated Mg-carbonates will form under lower
temperature and pressure. One exception is that Felmy et al. (2012) observed that
magnesite could form at a much lower temperature (35 °C) with the dissolution of nano-
sized forsterite. They suggested that the presence of a thin water film on the forsterite
surface may provide unique conditions for the transformation of the intermediate
nesquehonite and the magnesite growth at such a low temperature. Even under elevated
temperature and CO$_2$ pressure, intermediate phases, such as hydromagnesite and
dypingite, form before being transformed into magnesite, the most thermodynamically
stable form. (Hänchen, Prigiobbe et al. 2008; Kwak, Hu et al. 2010)
Mineral trapping in GCS sites can become even more complicated, if the dissolution of magnesite is also considered. While most have not been at conditions relevant to GCS, numerous investigations have studied have the kinetics of magnesite dissolution and precipitation. The magnesite precipitation rate increases with increasing saturation state and temperature, but decreases with increasing CO$_3^{2-}$ activity and pH (Saldi, Jordan et al. 2009; Saldi, Schott et al. 2010). The presence of initial forsterite substrate did not significantly accelerate magnesite precipitation, but a magnesite seed did (Giammar, Bruant et al. 2005). With respect to magnesite dissolution, the rate increases with ionic strength but is weakly affected by temperature from 25 to 150 °C until it slightly decreased from 150 °C to 200 °C due to kinetics (Pokrovsky and Schott 1999; Pokrovsky, Golubev et al. 2009; Saldi, Schott et al. 2010). The dissolution process accelerated when the CO$_2$ pressure increased from 0 to 10 atm P$_{CO_2}$, but the rate remained constant from 5 to 55 atm P$_{CO_2}$ (Pokrovsky, Golubev et al. 2005; Pokrovsky, Golubev et al. 2009). Therefore, considering both dissolution and precipitation of magnesite at certain GCS conditions will provide insights to in situ mineral carbonation.

The precipitation of magnesite (equation 4.1) can only happen when the solution becomes supersaturated with respect to magnesite. The saturation index of magnesite (SI$_{mag}$) (equation 4.2) quantifies the saturation state of the solution, where K$_{sp, mag}$ is the magnesite solubility product. A critical SI$_{mag}$ has to be reached before either homogeneous nucleation or heterogeneous nucleation could occur to initiate the precipitation process. It is important to note that precipitation and nucleation are related.
but different processes. Nucleation is related to the formation of a critical cluster or nucleus from which spontaneous growth can occur. Once the nuclei are formed in the supersaturated solution, they begin to grow and form crystallites. Nucleation can occur both homogeneously and heterogeneously. Homogeneous nucleation occurs in the solution and usually requires a higher SI to overcome the energy barrier for nucleation. Heterogeneous nucleation occurs on a solid substrate and may not require a SI as high as that for homogeneous nucleation. (Stumm and Morgan 1996)

\[
\text{MgCO}_3(s) = \text{Mg}^{2+} + \text{CO}_3^{2-} \quad (4.1)
\]

\[
\text{SI}_{mag} = \log \frac{(\text{Mg}^{2+})(\text{CO}_3^{2-})}{k_{sp,mag}} \quad (4.2)
\]

The objective of this research was to investigate magnesite precipitation in the water-scCO\textsubscript{2} system. The effect of supersaturation was studied and the critical saturation index of magnesite, a number necessary for magnesite nucleation and subsequent precipitation, was determined at one specific condition (100 °C and 100 bar P\textsubscript{CO2}) that is relevant to mineral trapping. The effect of different mineral substrates on magnesite precipitation and the effect of salinity on magnesite dissolution were also investigated. The results of this study should provide insights into CO\textsubscript{2} in situ mineral carbonation at GCS sites.
4.2 Materials and methods

4.2.1 Materials

Olivine with a composition close to forsterite (San Carlos, Arizona, 1.59 - 4.76 mm), hereafter referred to as “forsterite”, was obtained from Ward’s Scientific. The purest crystals of forsterite were selected by visual examination using an optical microscope, and these were then ground with an agate mortar and pestle and sieved to yield the 53-106 µm size fraction. The powder was then sonicated in ethanol for 10 minutes to remove fine particles. This process was repeated 5 times until the supernatant was clear after sonication and settling. The powder was rinsed with ultrapure water and dried at room temperature and stored in the dry atmosphere of a bench-top dessicator. The composition of forsterite was identified by X-ray diffraction (XRD) and acid digestion as Fo$_{90}$ ($\text{Mg}_{1.81}\text{Fe}_{0.19}\text{SiO}_4$). The morphology of the forsterite powder was observed using scanning electron microscopy (SEM), and images indicated the presence of some particles smaller than 53 µm (Figure 4.1(a)).

Magnesite was also obtained from Ward’s Scientific. This commercial magnesite was prepared through a similar preparation process used for forsterite to yield a cleaned 53-106 µm size fraction. The composition was identified by XRD as MgCO$_3$, and the morphology was observed using SEM (Figure 4.2 (a)).

Synthetic magnesite was obtained by homogeneous nucleation and precipitation of magnesite during batch experiments conducted at 100 °C and 100 bar $P_{\text{CO}_2}$ for 96 hours with an initial SI$_{\text{mag}}$ of 4 (P8 experiment in Table 4.1). The solid was identified by XRD
as MgCO₃. The morphology of the powder was observed using SEM, and images indicated the synthetic magnesite powder existed as clusters of single magnesite particles, where the cluster size ranged from 10 to 40 µm and the single particle size was about 2 - 5 µm (Figure 4.2 (c)).

Figure 4.1 SEM images of the surface of (a) unreacted forsterite and (b) solid collected after 7 days of reaction at 100 °C and 100 bar Pₐ₉0, when the solution (initial SIₘₐ₉ = 2) was seeded with forsterite. (c) The clean surface of unreacted forsterite surface at a
higher magnification. (d) The precipitated magnesite on the forsterite surface at a higher magnification.

Figure 4.2 SEM images of the surface of (a) unreacted commercial magnesite and (b) solid collected after 7 days of reaction when initially seeded with commercial magnesite. The insert of (b) showed the precipitated magnesite on the surface at a higher magnification. The SEM images of surface of (c) synthetic magnesite that was obtained from 4 days of reaction with an initial $\text{SI}_{\text{mag}}$ of 2 in the solution without any substrates,
and (d) solid collected after 7 days of reaction when initially seeded with synthetic magnesite.

Stock solutions of 1 mol/L MgCl₂ and 1 mol/L NaHCO₃ were prepared by dissolution of MgCl₂·6H₂O and NaHCO₃ crystal solids (Fisher Scientific) into ultrapure (resistivity > 18.2 MΩ·cm) water. Volumes (200 mL) of aqueous solutions with different initial SI\textsubscript{mag} were prepared by diluting the MgCl₂ and NaHCO₃ stock solutions into ultrapure water to obtain a fixed 2:1 concentration ratio of [NaHCO₃]:[MgCl₂]. The 2:1 ratio of alkalinity (the same as the NaHCO₃ concentration) to Mg (the same as the MgCl₂ concentration) is the same as the ratio that would result from the dissolution of forsterite (equation 4.3). When 1 mole of pure forsterite (Mg₂SiO₄) dissolves, 4 moles of of H⁺ (the same as the generated alkalinity) is consumed and 2 moles of Mg²⁺ is released. The alkalinity to Mg ratio is always 2:1. The saline solution (0.125 mol/L NaCl) was prepared by dissolving NaCl crystal solids (Fisher Scientific) into ultrapure water.

\[
\frac{\text{Alkalinity}}{TOTA} = \frac{TOTA}{TOTA} = \frac{[\text{NaHCO}_3]}{[\text{MgCl}_2]} = 2
\]  

(4.3)

4.2.2 Experimental methods

Magnesite precipitation experiments were conducted in 300-mL PTFE vessels with pressurized CO₂ in well-stirred batch reactors (Parr Instrument Company) at 100 °C and 100 bar P\textsubscript{CO₂}. (Table 4.1) The reactor setup is similar to that was used previously to study forsterite dissolution (Wang and Giammar 2013). 200 mL solutions with SI\textsubscript{mag} of 1.0, 1.5, 2.0, 3.0 and 4.0 were prepared to test the effect of initial saturation conditions. The effect
of initial substrates were studied by adding 0.5 g/L of forsterite, commercial magnesite or synthetic magnesite powder into aqueous solutions with an initial SI$_{\text{mag}}$ of 2. These precipitation experiments were performed from 4 to 7 days. Liquid samples were collected at certain time intervals (pre-heat “0 hour”, 0 hour, 4 hours, 8 hours, 1 day, 2 days, 3 days, 5 days, and 7 days). The pre-heat “0 hour” sample was collected as soon as the solutions were prepared under ambient conditions, and the 0 h sample was collected as soon as the experimental headspace CO$_2$ pressure was achieved in the batch reactor (typically within 15 minutes after introducing CO$_2$).

Magnesite dissolution experiments were conducted in the same well-stirred batch reactors at 100 °C and 100 bar P$_{\text{CO}_2}$. Initially 3 g/L of synthetic magnesite powder was added into dilute or NaCl solutions (0.125 mol/L) and reacted for 10 days. Liquid samples were only collected at pre-heat “0 hour”, 0 hour and 10 days, since only the final Mg concentration was needed to indicate how close to equilibrium the solution would be at 10 days.

The pH of the solution was measured outside of the reactor under ambient pressure ($\text{pH}_{\text{ex}}$) within 5 minutes of collection of the liquid samples. The $\text{pH}_{\text{ex}}$ was usually 1.5 - 2 units larger than the calculated $\text{in situ}$ pH due to CO$_2$ degassing from the solution under ambient conditions. The solids were collected using vacuum filtration after the reactor was cooled to ambient temperature, and dried at room temperature. Liquid samples were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) for concentrations
of dissolved Na, Mg, Si, and Fe. The solid samples were characterized by XRD and SEM with energy dispersive X-ray analysis (EDX).

**Table 4.1** Batch experimental conditions at 100 °C and 100 bar \( P_{CO2} \)

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial substrate</th>
<th>Aqueous composition (mol/L)</th>
<th>Initial SI&lt;sub&gt;mag&lt;/sub&gt; (mol/L)</th>
<th>Time (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>None</td>
<td>0.027 0.053 0</td>
<td>1</td>
<td>1.26 168</td>
</tr>
<tr>
<td>P2</td>
<td>None</td>
<td>0.041 0.082 0</td>
<td>1.5</td>
<td>0.188 168</td>
</tr>
<tr>
<td>P3</td>
<td>None</td>
<td>0.062 0.125 0</td>
<td>2</td>
<td>0.276 168</td>
</tr>
<tr>
<td>P4</td>
<td>0.5 g/L forsterite</td>
<td>0.062 0.125 0</td>
<td>2</td>
<td>0.276 168</td>
</tr>
<tr>
<td>P5</td>
<td>0.5 g/L commercial magnesite</td>
<td>0.062 0.125 0</td>
<td>2</td>
<td>0.276 168</td>
</tr>
<tr>
<td>P6</td>
<td>0.5 g/L synthetic magnesite</td>
<td>0.062 0.125 0</td>
<td>2</td>
<td>0.276 168</td>
</tr>
<tr>
<td>P7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>None</td>
<td>0.130 0.261 0</td>
<td>3</td>
<td>0.539 96</td>
</tr>
<tr>
<td>P8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>None</td>
<td>0.233 0.466 0</td>
<td>4</td>
<td>0.910 96</td>
</tr>
</tbody>
</table>

**Magnesite dissolution experiments**

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial substrate</th>
<th>Aqueous composition (mol/L)</th>
<th>Time (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>3 g/L synthetic magnesite</td>
<td>0 0 0 0 0 240</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>3 g/L synthetic magnesite</td>
<td>0 0 0.125 0 0.133 240</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Duplicate experiments were performed for this experimental condition.
4.2.3 Equilibrium Calculations

Geochemical equilibrium calculations were performed using the “SpecE8” from Geochemist’s Workbench (GWB) 8.0 (Bethke and Yeakel 2010), to provide the calculated *in situ* solution pH (pH$_{in}$) and the saturation index of magnesite. The measured solution composition from ICP-MS served as the input of “SpecE8”. The concentrations [Mg$^{2+}$], [SiO$_2$] and [Na$^+$] could be assumed to be the total concentrations of Mg, Si and Na from ICP-MS measurement. The value of [Cl$^-$] could always be assumed to be the same as [Na$^+$], because [NaHCO$_3$]:[MgCl$_2$] was always fixed at 2 in precipitation experiments or Cl$^-$ came directly from NaCl in dissolution experiments. The CO$_2$(aq) concentration at 100 °C and 100 bar P$_{CO2}$ was calculated according to a model by Duan and Sun (2003) and then input into “SpecE8”. The effects of ionic strength, with a highest value slightly below 1.2 molal, were taken into consideration in GWB with the “B-dot” equation, an extended form of the Debye-Huckel equation (Helgeson 1969), which could be used for solutions with ionic strengths up to 3 molal. The equilibrium constants in GWB are calculated using polynomial equations that give logK as a function of temperature from 0 to 300 °C. These constants at elevated temperature were only 0.1 log unit different from the equilibrium constants predicted by the thermodynamic software program SUPCRT92 with the dSLOP98 database (Johnson, Oelkers et al. 1992).

4.3 Results and Discussion

4.3.1 Effect of supersaturation

The precipitation pathway of magnesite without any initial substrate is illustrated for the 4-day experiment with an initial SI$_{mag}$ of 4.0 at 100 °C and 100 bar P$_{CO2}$ (Figure 4.3). The
dissolved Mg concentration and the pH values were both measured under \textit{ex situ} ambient conditions (pH_{ex}), and the \textit{in situ} pH was calculated for the experimental conditions (pH_{in}). Initially, the aqueous solution was close to neutral with an average measured pH_{ex} of 7.32, while the calculated initial \textit{in situ} average pH was 5.72 (0 hour sample). As magnesite precipitated extensively during 4 days of reaction, the Mg concentration decreased and the alkalinity of the solution was consumed; associated with this reaction were decreases in pH_{ex} to 6.81 and pH_{in} to 5.19. The \textit{ex situ} pH was usually 1.5 - 2 units larger than the calculated \textit{in situ} pH due to CO\textsubscript{2} degassing from the solution under ambient conditions. After just 4 days, the Mg concentration was as low as 35.70 mM, which corresponded to precipitation of 84.7\% of the original dissolved Mg. It is worth noting that the predicted equilibrium pH is 4.60 and dissolved Mg concentration is 7.18 mM at 100 °C and 100 bar P_{CO2}. Clearly, the solution did not reach equilibrium after 4 days of reaction. The initial pH should be 8.19 if the solution is closed to CO\textsubscript{2} in the headspace or 3.22 when no NaHCO\textsubscript{3} is added at 100 P_{CO2}. The fact that the initial pH_{in} of 5.72 was between these two values indicated that pH was affected by the acidity caused by CO\textsubscript{2} dissolution from the headspace and buffering effect of added NaHCO\textsubscript{3}. The XRD indicated that magnesite was the only crystalline secondary phase precipitated (not included). SEM images showed that clusters of single magnesite particles had the size range of 10 - 40 µm and the size of the single particles was in the range of 2 - 5 µm (Figure 4.2 (c)).
Figure 4.3 Dissolved concentrations of Mg (circles), measured pH_{ex} (rectangulars) and calculated pH_{in} (triangulars) for duplicate batch experiments of magnesite precipitation with an initial SI_{mag} of 4 at 100 °C and 100 bar P_{CO2} for 4 days. The solid and hollow legends are for duplicates. The target initial Mg concentration is 0.233 mol/L.

The critical SI_{mag} for magnesite nucleation and subsequent precipitation was identified as approximately 2.0 at 100 °C and 100 bar P_{CO2}. The normalized Mg concentration \( \frac{[Mg_{diss}]}{[Mg_{disslim}]} \) was defined as the actual dissolved Mg concentration at different reaction time divided by the initial target dissolved Mg concentration. By plotting the normalized Mg concentration against the reaction time (4 - 7 days), one could easily tell how much Mg precipitated out from the aqueous solution. (Figure 4.4) The normalized Mg concentration stayed almost unchanged for the precipitation experiments with an initial
SI\text{mag} of 1.0, 1.5 and 2.0, indicating that precipitation process was barely observable. However, when the initial SI\text{mag} increased above 2.0 (SI\text{mag} of 3.0 and 4.0), extensive precipitation occurred and about 61.7% - 84.7% of the original dissolved Mg was removed from the aqueous solution. SEM indicated that only when the initial SI\text{mag} increased to 2.0 and higher one could observe magnesite crystals during SEM imaging. Although the normalized Mg concentration decreased slightly for SI\text{mag} of 1.0, it was probably not caused by magnesium carbonate precipitation since no precipitates were observed using SEM. Therefore, at 100 °C and 100 bar P\text{CO}_2, the critical SI\text{mag} was approximately 2.0, since an initial SI\text{mag} smaller than 1.5 could not trigger magnesite precipitation and a SI\text{mag} of 2.0 was sufficient.

Nucleation of carbonate minerals requires supersaturation of the solution. Without initial substrates present, nucleation occurs homogeneously. For example, a previous study found that magnesite precipitation required a critical SI\text{mag} between 0.25 and 1.14 at 95 °C and 100 bar P\text{CO}_2 (Giammar, Bruant et al. 2005). Their finding is comparable to ours, since their suggested MgCl\text{2} range (0.02 - 0.05 mol/L for their initial SI\text{mag} 0.25 - 1.14) overlaps with our MgCl\text{2} range (0.041 - 0.062 mol/L for our initial SI\text{mag} of 1.5 - 2). At 120 °C and 100 bar P\text{CO}_2, with a SI\text{mag} of 2.62 - 3.63, Hanchen et al. observed magnesite without adding initial substrates (Hänchen, Prigiobbe et al. 2008). Similarly, for calcite precipitation, a critical saturation index is observed around 0.98 - 1.30 for 25 °C (Morse and He 1993; Jiménez-López, Caballero et al. 2001; Lioliou, Paraskeva et al. 2007). Heterogeneous nucleation, which involves the nucleation of the carbonate mineral on the surface of a substrate, can potentially initiate magnesite precipitation at lower SI\text{mag}.
values. However, a previous study with forsterite as a substrate did not observe any acceleration of the overall magnesite precipitation process (Giammar, Bruant et al. 2005). To further explore the effect of initial substrates, the present study included a special set of experiments.

![Normalized Mg concentration](image)

**Figure 4.4** Normalized Mg concentration for batch magnesite precipitation experiments with an initial SI\textsubscript{mag} ranging from 1.0 to 4.0 at 100 °C and 100 bar P\textsubscript{CO2} for as long as 7 days.

### 4.3.2 Effect of mineral substrates

The evolution of Mg concentration is illustrated for 7-day magnesite precipitation experiments with an initial SI\textsubscript{mag} of 2.0 at 100 °C and 100 bar P\textsubscript{CO2} (Figure 4.5), with and
without initial mineral substrates. For seeded experiments, 0.5 g/L of forsterite, commercial magnesite, or synthetic magnesite was added into the initial solutions. The initial Mg concentrations all started at 62.4 mM, which was the target Mg concentration to achieve an initial $SI_{mag}$ of 2.0. During the 7 days of reaction, the extent of Mg concentration decrease was different for the different initial substrate conditions. When seeded with forsterite substrate, the final Mg concentration was very close to that from the experiment without any substrates, and the net precipitation process was not accelerated by the forsterite. The free energy of the magnesite-forsterite interface is probably not significantly lower than the magnesite-water interfacial free energy; a larger difference in substrate-precipitate and precipitate-water interfacial energies can drive heterogeneous nucleation. When magnesite was introduced as the initial substrate, the precipitation extent increased relative to the seed-free experiment. The rate limiting step for magnesite precipitation in experiments with a pre-existing magnesite surface is crystal growth and not nucleation, which allows for a faster overall precipitation process. Interestingly, the extent of precipitation was greater for the synthetic magnesite than for the commercial magnesite, which may be due to a higher specific surface area of the synthetic magnesite or better exposures of the crystal faces on which growth was occurring.
Figure 4.5 Dissolved Mg concentrations during 10 days of reaction for both magnesite dissolution (orange and blue symbols, experiments D1 and D2) and precipitation (experiments P3, P4, P5 and P6) at 100 °C and 100 bar P\textsubscript{CO2}. The precipitation experiments were performed for 7 days with initial solutions (initial SI\textsubscript{mag} = 2) seeded with different initial solids. The dissolution experiments were performed for 10 days. The Mg concentration at equilibrium was calculated for both dilute and saline (dashed line) solutions, using the solubility product of magnesite (\textit{K}_{sp,mag}) and the equilibrium constants calculated by SUPCRT92, and the dissolved CO\textsubscript{2} concentration calculated according to Duan and Sun (2003). The activity coefficient was assumed to be unity in dilute solution and calculated with Davies equation for salt solution.

The characterization of the solids by XRD and SEM yielded insights into the products and pathways of the reactions. The only magnesite carbonate solid identified by XRD
was magnesite (Figure 4.6), which is also consistent with the products of the homogeneous nucleation experiments. While the presence of forsterite does not appear to have accelerated magnesite precipitation by facilitating heterogeneous nucleation, the SEM images do indicate that the magnesite that precipitated in system with forsterite did so on the forsterite surface (Figure 4.1 (b), (d)). Consequently, the forsterite-magnesite interfacial energy may not be sufficiently lower than the magnesite-water interfacial energy to result in macroscopically observable acceleration of precipitation, but the difference in interfacial free energies may be sufficient to lead to any magnesite products occurring on the forsterite surface and not in solution. The SEM images of products of reactions with the two magnesite seeds yielded different observations. If seeded with commercial magnesite substrates (Figure 4.2 (a), (b)), nuclei of magnesite were observed on the surface of commercial magnesite not unlike on the surface of the forsterite; it appears as if magnesite was heterogeneously nucleating on magnesite and not just growing on existing crystal surfaces. In contrast, for the synthetic magnesite, the precipitation occurred by crystal growth of the initial magnesite particles (Figure 4.2 (c), (d)). It has been reported that magnesite precipitation occurred with a $S_{\text{mag}}$ as low as 1.30 at 100 °C, or with a $S_{\text{mag}}$ as low as 0.53 at 200 °C, with initial magnesite substrates (Saldi, Jordan et al. 2009; Saldi, Schott et al. 2012).
Figure 4.6 X-ray diffraction patterns for the precipitated solids after 168 hours (experiments P3, P4, P5 and P6) at 100 °C and 100 bar $P_{CO2}$, when the solutions (initial SI$_{mag}$ = 2) were seeded with different initial substrates or no substrate. The red arrows indicated the peaks corresponding to magnesite. The reference patterns of magnesite (01-071-1534) and forsterite (01-070-7343) are included.

4.3.3 The equilibrium for magnesite dissolution and precipitation experiments

To evaluate the degree to which magnesite precipitation approached equilibrium with the aqueous solution, equilibrium model simulations were performed and complementary dissolution experiments were conducted. The calculated equilibrium Mg concentration was used as a reference and compared to the final Mg concentration in both precipitation and dissolution experiments. The dissolution experiments of 3 g/L synthetic magnesite
were conducted in both dilute and saline solutions. For the dilute solution, as magnesite dissolved, Mg concentration increased and came close to the calculated equilibrium Mg concentration after 10 days. The equilibrium Mg concentration was predicted to be 7.18 mM, by solving the charge balance of the dissolved aqueous species. The solubility product of magnesite ($K_{sp,mag} = 10^{-9.41}$), the equilibrium constants calculated by SUPCRT92 and the dissolved CO$_2$ concentration calculated according to Duan and Sun (2003) were all used as inputs for the calculation at 100 °C and 100 bar $P_{CO2}$. The activity coefficients for all the species were assumed to be unity.

The final Mg concentrations in the precipitation experiments with an initial SI$_{mag}$ of 2.0 after 7 days were all much higher than the predicted equilibrium Mg concentration in dilute solution (dashed line in Figure 4.5). Even after accounting for the high ionic strength (0.31 - 1.17 mol/L) for experiments with initial SI$_{mag}$ of 2.0 - 4.0, the final SI$_{mag}$ calculated using “SpecE8” was 0.95 - 1.64 (day 4 for initial SI$_{mag}$ of 3.0 and 4.0, and day 7 for initial SI$_{mag}$ of 2.0). A SI value of zero would indicate that equilibrium had been reached, and these positive values indicate that the solution was still supersaturated by about an order of magnitude. Even considering the 0.1 log unit differences in the equilibrium constants (e.g., solubility product for magnesite precipitation and equilibrium constants for carbonic acid deprotonation) from different sources (SUPCRT92 and GWB), SI$_{mag}$ clearly indicated that the precipitation reaction had not reached equilibrium.

Therefore, longer reaction times (longer than 7 days) were obviously needed for magnesite precipitation to reach equilibrium. Even longer reaction time could not
guarantee that magnesite precipitation would eventually reach equilibrium. However, magnesite dissolution could easily reach equilibrium (as soon as 10 days). It indicates that precipitation rates should be considered in reactive transport models for GCS sites. For example, PHREEQC, GWB and TOUGHREACT are capable of simulating reaction and transport at the same time, but they only consider dissolution reactions as being rate-limited and assume local equilibrium for precipitation reactions (except PHREEQC) (Parkhurst 1995; Parkhurst 1999; Xu 2004). These reactive transport models also don’t include critical SI values for precipitation to occur, and they assume that precipitation occurs as soon as the solution is at all supersaturated, except for PHREEQC, which allows users to specify a target saturation index (not necessary zero) to be reached.

4.3.4 Effect of salinity

To study the effect of salinity, the dissolution pathway of 3 g/L synthetic magnesite in 0.125 mol/L (or 7.31 g/L) NaCl solution was compared to that in dilute solution. As magnesite dissolved, Mg concentration increased and came close to the calculated equilibrium Mg concentration after 10 days for the saline solution (dashed line in Figure 4.5). The equilibrium Mg concentration was predicted to be 11.68 mM, by solving the charge balance of the dissolved aqueous species. The solubility product of magnesite ($K_{sp,mag} = 10^{-9.41}$), the equilibrium constants calculated by SUPCRT92, and the dissolved CO$_2$ concentration calculated according to Duan and Sun (2003) were all used as inputs at 100 °C and 100 bar P$_{CO2}$. The activity coefficient was calculated using the Davies equation for this specific equilibrium calculation, which is applicable for ionic strength lower than 0.5 mol/L.
The released Mg concentration and the final $\text{SI}_{\text{mag}}$ both increased when the salinity of the solution increased. The final $\text{SI}_{\text{mag}}$ at 10 days, calculated using “SpecE8”, was -0.67 for dilute solution and -0.11 for saline solution. The final $\text{SI}_{\text{mag}}$ values confirmed that the high salt content pushed the solution even closer to equilibrium. The high salt content increases the ionic strength of the solution and lowers the activity of the ions. Hence, magnesite is more soluble in saline solutions than in dilute solutions. This can further increase the driving force for dissolution and it ultimately results in higher dissolved Mg concentration at equilibrium. Hence, the high salt content might lead to a decreased amount of carbon captured into the carbonate minerals, rendering a decrease in the carbon storage from \textit{in situ} mineral trapping.

4.4 Conclusions

The precipitation of magnesite was studied under 100 °C and 100 bar $P_{\text{CO}_2}$ to identify the crucial factors impacting \textit{in situ} mineral trapping at GCS sites. First and foremost, a certain degree of supersaturation with respect to magnesite (critical $\text{SI}_{\text{mag}}$) has to be achieved before magnesite precipitation can occur. At 100 °C and 100 bar $P_{\text{CO}_2}$, the critical $\text{SI}_{\text{mag}}$ was approximately 2. Second, the presence of initial magnesite substrates is much more helpful than an initial forsterite substrate for accelerating magnesite precipitation, which indicates that magnesite nucleation process is the rate-limiting step in water-forsterite-sc$\text{CO}_2$ systems and that heterogeneous nucleation does not facilitate earlier precipitation. The enhancing effect of synthetic magnesite was more significant than that of commercial magnesite. Finally, the salinity of GCS sites should be taken into
consideration, as it increases the equilibrium solubility of minerals including the carbonates needed for mineral trapping.

Acknowledgement

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Chapter 5. Effects of diffusive transport on water-mineral-CO$_2$

reactions: Rates, locations, and extents of forsterite dissolution and
magnesite precipitation

Abstract

The effects of diffusive transport on both silicate mineral dissolution and carbonate mineral precipitation are important to mineral trapping during geologic carbon sequestration (GCS). The coupling of diffusive transport and chemical reactions was examined in the context of magnesium-rich rocks that have been proposed as carbon sequestration reservoirs. A mathematical model was developed to predict the evolution of mineralogy and aqueous chemical composition in diffusion-limited zones in contact with CO$_2$-rich aqueous solutions. Experiments at relevant temperature and pressure were performed with a tube that is only open at its top to the bulk solution in a batch reactor to complement the model. The tube was packed with forsterite (Mg$_2$SiO$_4$) powder, while the bulk solution was in contact with pressurized CO$_2$ in the headspace. To model the temporal and spatial changes of various dissolved species, mass balance equations of dissolved Mg and CO$_2$(aq) (or dissolved inorganic carbon) and a charge balance equation were established for the tube. The dissolution rate of forsterite was modeled using an equation that could account for the effects of pH, temperature and saturation state of the solution. The diffusivities of Mg$^{2+}$ and CO$_2$(aq) (or dissolved inorganic carbon) were included for quantifying rates of solute transport. Chemical thermodynamic calculations considered the solubility of forsterite, amorphous silica (SiO$_2$), and magnesite (MgCO$_3$). These simulations and experiments are relevant to diffusion-limited zones of GCS sites,
and they suggest that diffusion-limitations can lead to local environmental conditions that can result in much different reaction rates than may be achieved in simulations with volume-averaged chemical compositions.

5.1 Introduction

Diffusive transport can play a key role in geological carbon sequestration. The geological formations into which CO$_2$ will be injected are porous or fractured rocks with the majority of the volume occupied by minerals. The brine is present in the pore spaces between the rocks and is always in contact with the rocks (Bachu and Adams 2003; IPCC 2005). In the previous several chapters, the focus was on the fundamental rates and products of Mg-silicate mineral dissolution and carbonate mineral precipitation. To focus on the dissolution rates, experiments were conducted in well-stirred batch reactors so that the overall reaction progress was minimally affected by transport processes. However, in real GCS sites, both minerals and the brine in the pore space can be considered stagnant. Therefore, it is very important to study the diffusive transport of solutes in the aqueous phase in the pore space and its effect on GCS.

To study the effects of diffusive transport of the aqueous species in the brine on geochemical reactions involved in carbon sequestration, several issues can be addressed using both experimental and simulation approaches. First, the impacts of diffusive transport on the dissolution rate of silicate minerals can be estimated. Second, the effects of diffusive transport on the supersaturation and precipitation of carbonate minerals can
be studied. Lastly, the location and extent of precipitation in the pore space might have a feedback effect on the diffusion of solutes in the aqueous phase.

5.2 Theory

5.2.1 Tubular reactor model system description

A tubular reactor was designed to address the effects of diffusive transport. As seen in Figure 5.1, a tubular reactor was located at the bottom of a large batch reactor, and the batch reactor is the same as that was used in the work in the previous chapters. The tube, packed with forsterite powder, was closed at the bottom and open to the bulk solution at the top. The batch reactor was initially filled with ultrapure water, and the bulk solution was always in contact with pressurized CO$_2$ in the headspace.

![Figure 5.1](image)

**Figure 5.1** Experimental system for forsterite dissolution in a tubular reactor. The tubular reactor was filled with forsterite particles with a size fraction of 10 - 44 μm and sat at the bottom of a larger batch reactor. The tubular reactor was closed at the bottom and open to
the batch reactor at the top. Liquid samples from the batch reactor could be collected from the liquid sampling tube, and at the end of an experiment the solid inside the tubular reactor could be collected and characterized to determine where precipitation occurred. In addition, the concentration of Mg ($c_{\text{Mg}}$) and pH ($pH$) in the tubular reactor were functions of both time and length, and the concentration of Mg ($c_{\text{Mg,b}}$) and pH ($pH_b$) inside the batch reactor were only functions of time.

The conceptual figure (Figure 5.2) illustrated the possible profiles of the aqueous species when forsterite dissolution occurred in a diffusion-limited zone. Initially, when the injected CO$_2$ has not reached the surface of forsterite particles, extensive dissolution process cannot start because the solution is always neutral ($pH = 7$). As a result, the concentrations of the dissolved Mg and all carbonate species are zero. It is worth pointing out that in actual GCS sites, the brine pH is usually higher than 7, and contains dissolved Mg and low amounts of dissolved inorganic carbon initially. As soon as CO$_2$ dissolves into the aqueous solution in the pore space, the dissolution of forsterite accelerates because of the lower pH from the dissolved CO$_2$, and consequently Mg$^{2+}$ ions are released. As a result, both Mg and various carbonate species develop concentration gradients along the length of the tube. The pH, which is the most important parameter in the aqueous phase, is lowest where CO$_2$(aq) is at its highest concentration (open end of the tube), and it is highest where extensive forsterite dissolution occurs (closed end of tube). As shown in Figure 5.2, in a tubular reactor which is filled with forsterite powder, it is possible to have magnesite precipitation into the deeper part of the tube (shown as the green zone).
Figure 5.2 A schematic plot of the solution composition inside the tubular reactor (a) initially and (b) after a certain reaction time. For the initial system, the Mg, DIC and CO$_3^{2-}$ concentrations are zero because neither forsterite dissolution nor the aqueous species diffusion starts, and pH is 7 because of the ultrapure water. At this time, the solution is undersaturated with respect to magnesite (MgCO$_3$(s)). After reacting for a while, profiles of Mg, DIC and CO$_2$(aq) concentrations and pH develop along the length of the tube. At this time, the solution can be supersaturated with magnesite (MgCO$_3$(s)) and precipitation might occur at the deeper part of the tube (the green zone).

5.2.2 Olivine dissolution kinetics

The forsterite dissolution rate is usually expressed as equation 5.1, where $r$ represents the dissolution rate of forsterite (mol/cm$^2$-s), $k_0$ is the dissolution rate constant (mol/cm$^2$-s), $E_a$ is the apparent activation energy (J/mol), $[H^+]$ is the activity of hydrogen ions in solution, and $n_{H^+}$ is the reaction order for $H^+$. In addition, the saturation state of the solution with respect to forsterite also affects the forsterite dissolution rate, where IAP is
the ionic activity product and $K_{sp,Fo}$ is the solubility product of forsterite. If the solution is far from equilibrium with respect to forsterite dissolution ($IAP \ll K_{sp,Fo}$), which is generally the only case for the very top of the reactor, the dissolution rate can be simplified as $r = k_0 e^{\frac{E_a}{RT}}\{H^+\}^n H^+$.

$$r = k_0 e^{\frac{E_a}{RT}}\{H^+\}^n H^+ \left(1 - \frac{IAP}{K_{sp,Fo}}\right)$$ (5.1)

A model proposed by Rimstidt et al. (2012) is based on critically reviewing and synthesizing results from other previous experimental studies and is applicable for a wide temperature range (0 - 150 °C) and the full pH range (0 < pH < 14) when forsterite dissolution is far from equilibrium (equation 5.2 and 5.3). Note that the forsterite dissolution rate for equations 5.2 and 5.3 was normalized to geometric surface area and not BET surface area. Even if some of the previous experimental work reported results using BET surface area, Rimistidt et al. corrected the reported dissolution rate based on BET surface area to values based on geometric surface area. In their examination of previous studies, BET surface area was on average 5.2 times higher than geometric surface area. As shown in Figure 5.3, for 25, 50 and 100 °C, the dissolution rate of forsterite could be plotted for the full range of pH.

$$\log r = 6.05 - 0.46\pH - 3683.0, \text{ for } \pH < 6.5 \quad (5.2)$$

$$\log r = 4.07 - 0.256\pH - 3465, \text{ for } \pH > 6.5 \quad (5.3)$$
Figure 5.3 The dissolution rate of forsterite for the whole pH range for different temperatures: 25 °C (blue line), 50 °C (green line) and 100 °C (orange line). The solid lines show the dissolution rate for \(0 < \text{pH} < 5.6\), and the dashed line shows the dissolution rate for \(5.6 < \text{pH} < 14\).

5.2.3 CO\(_2\) concentration and equilibrium constants

The constant CO\(_2\)\(_{\text{aq}}\) concentration under a certain temperature and CO\(_2\) pressure was fixed according to Duan and Sun (2003). The CO\(_2\)\(_{\text{aq}}\) concentration at 25 °C and 100 bar CO\(_2\) pressure was estimated by extrapolation, since this condition is outside of the range modeled by Duan and Sun. In addition, the solubility product of magnesite and the equilibrium constants were calculated by SUPCRT92 with the dSLOP98 database. The dissolved CO\(_2\) concentration and the equilibrium constants at 100 °C and 100 bar P\(_{\text{CO2}}\) are listed in Table 5.1 as an example. This experimental condition is also studied for forsterite dissolution and magnesite precipitation in experiments of the previous chapters.
Table 5.1 Equilibrium constants and solubility products for related chemical reactions at 100 °C and 100 bar CO₂ pressure.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>logK (^a) at 100 °C and 100 bar P(_{CO_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)(aq) (molal) (^b)</td>
<td>0.79</td>
</tr>
<tr>
<td>H(_2)O = H(^+) + OH(^-)</td>
<td>-12.22</td>
</tr>
<tr>
<td>H(_2)O + CO(_2)(aq) = H(^+) + HCO(_3)(^-)</td>
<td>-6.35</td>
</tr>
<tr>
<td>H(_2)O + CO(_2)(aq) = 2H(^+) + CO(_3^{2-})</td>
<td>-16.38</td>
</tr>
<tr>
<td>MgCO(_3)(s) = Mg(^{2+}) + CO(_3^{2-})</td>
<td>-9.41</td>
</tr>
<tr>
<td>SiO(_2)(am) = SiO(_2)(aq)</td>
<td>-2.16</td>
</tr>
<tr>
<td>Mg(_2)SiO(_4)(s) + 4H(^+) = 2Mg(^{2+}) + SiO(_2)(aq) + 2H(_2)O</td>
<td>20.51</td>
</tr>
</tbody>
</table>

\(^a\) All values, except CO\(_2\)(aq), were calculated using SUPCRT92 with the dSLOP98 database.

\(^b\) CO\(_2\)(aq) concentration is a fixed value when the aqueous phase is at equilibrium with a headspace at fixed 100 °C and 100 bar P\(_{CO_2}\). Calculations were made using the equations of state of Sterner and Pitzer (1994) and the solubility equations of Duan and Sun (2003).

5.2.4 Other parameters for describing the system

To construct a model for the tubular reactor described above, parameters other than the dissolution rate and equilibrium constants were needed (Table 5.2). First, the porosity of the forsterite powder packed in the tube was very important because it significantly affected how much forsterite was available for dissolution and the released amount of Mg. Second, the radius of the forsterite particle was included to account for the specific
surface area (assumed as 0.19 m$^2$/g), which was needed to determine Mg release from forsterite in units of mol/L-s. The radius of 4.93×10$^{-4}$ cm was calculated by assuming all the forsterite particles were spheres with the same radius. Finally, the diffusivities of both Mg$^{2+}$ ($D_{Mg}$) and dissolved CO$_2$ ($D_{CO2}$) were needed to describe the diffusion of the Mg species and the inorganic carbon. The diffusivities for these two species at 25 - 100 °C are reported in Table 5.2 (Newman and Thomas Alyea 2004). Si was not considered in diffusion, and it was always assumed to be half of the concentration of Mg$^{2+}$ based on stoichiometric dissolution of forsterite. In addition, the dimensions of the tube and batch reactor as well as the density of forsterite were also needed.

*Table 5.2* Other parameters needed to describe the reactive transport of dissolved Mg and inorganic carbon.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube length (L)</td>
<td>5.51 cm</td>
</tr>
<tr>
<td>Tube diameter (D)</td>
<td>0.635 cm</td>
</tr>
<tr>
<td>Volume of batch reactor ($V_b$)</td>
<td>200 cm$^3$</td>
</tr>
<tr>
<td>Porosity (ϕ)</td>
<td>0.44</td>
</tr>
<tr>
<td>Density of forsterite ($ρ_{Fo}$)</td>
<td>3.2 g/cm$^3$</td>
</tr>
<tr>
<td>Radius of forsterite particle $^a$</td>
<td>4.93 × 10$^{-4}$ cm</td>
</tr>
<tr>
<td>Diffusivity of Mg$^{2+}$ ($D_{Mg}$)</td>
<td>2.369 × 10$^{-8}$ $\cdot$ T (K) (cm$^2$/s)</td>
</tr>
<tr>
<td></td>
<td>1.94 × 10$^{-5}$ cm$^2$/s for 25 °C;</td>
</tr>
<tr>
<td>Diffusivity of dissolved CO$<em>2$ ($D</em>{CO2}$)</td>
<td>3.03 × 10$^{-5}$ cm$^2$/s for 50 °C;</td>
</tr>
<tr>
<td></td>
<td>3.03 × 10$^{-5}$ cm$^2$/s assumed for 100 °C.</td>
</tr>
</tbody>
</table>
The radius of forsterite particle was calculated by assuming all the particles were spheres with the same radius and a specific surface area of 0.19 m\(^2\)/g.

### 5.3 Tubular reactor model development

In order to study the diffusive transport limitations, simulations of the concentration profiles of aqueous species (e.g., Mg\(^{2+}\) and CO\(_3^{2-}\)) along the tubular reactor are of great interest. Since the top of the tubular reactor was always open and in contact with the well-mixed bulk solution that was at equilibrium with a headspace with a fixed CO\(_2\) pressure, mass balance models of both the batch reactor and the tubular reactor were established and connected through boundary conditions. At the same time, the aqueous phase must always be electrically neutral, and the pH of the solution could be calculated accordingly. The chemical reactions that could only occur inside the tubular reactor were equations 5.4 and 5.5, and the charge balance was equation 5.6. Other possible reactions of carbonate species that occurred in the tubular reactor and the well-mixed bulk solution were considered to instantaneously reach equilibrium at each point in space and time, and these were listed in Table 5.1.

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ & \iff 2\text{Mg}^{2+} + \text{SiO}_{2(\text{aq})} + 2\text{H}_2\text{O} & (5.4) \\
\text{Mg}^{2+} + \text{CO}_3^{2-} & \iff \text{MgCO}_3(\text{s}) & (5.5) \\
[\text{H}^+] + 2[\text{Mg}^{2+}] & = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] & (5.6)
\end{align*}
\]
5.3.1 Mg mass balance based on diffusion and reaction kinetics

The governing mass balance equations of dissolved Mg inside both the tubular reactor \((c_{Mg,t})\) and the batch reactor \((c_{Mg,b})\) are shown in equations 5.7 (a-c) and 5.8. Inside the tubular reactor, the magnesium concentration \(c_{Mg,t}\) (mol/L) is governed by

\[
\frac{\partial c_{Mg,t}}{\partial t} = D_{Mg} \frac{\partial^2 c_{Mg,t}}{\partial z^2} + R_{Mg,Fo} - R_{Mg,mag}
\]  

(5.7)

Boundary conditions (BCs):

At \(z=0\), \(-D_{Mg} \frac{\partial c_{Mg,t}}{\partial z} = 0\) \hspace{1cm} (5.7a)

At \(z=L\), \(c_{Mg,t} = c_{Mg,b}\) \hspace{1cm} (5.7b)

Initial condition (IC):

At \(t=0\), \(c_{Mg,t} = c_{Mg,b} = 0\) \hspace{1cm} (5.7c)

Where \(D_{Mg}\) (cm\(^2\)/s) is the diffusivity of Mg\(^{2+}\) in the aqueous phase, \(R_{Mg,Fo}\) (mol/cm\(^3\)-s) is the rate of introducing Mg due to forsterite dissolution, and \(R_{Mg,mag}\) (mol/cm\(^3\)-s) is the rate of removing Mg due to magnesite precipitation. The forsterite dissolution rate (mol/cm\(^2\)-s) is usually expressed by equation 5.1, and it can be related to \(R_{Mg,Fo}\) using specific surface area and the stoichiometry in equation 5.4. \(R_{Mg,mag}\) should only be included when magnesite is sufficiently supersaturated in the aqueous phase to start precipitating from the solution. At the top of the tubular reactor \((z=L)\), the dissolved Mg concentration is always the same as that in the batch reactor. At the bottom of the tubular reactor \((z=0)\), the flux of Mg is zero because the tube has a closed end. Initially, the Mg
concentrations in both the tubular reactor and the batch reactor are zero, because forsterite has not started dissolving.

Since the top of the tubular reactor (z=L) is open to the batch reactor, the following relationship between Mg concentration in the tubular reactor \((c_{Mg,b})\) and that in the batch reactor \((c_{Mg,b})\) can be established. Where \(V_b\) is the solution volume \((cm^3)\) in the batch reactor and \(S_t\) \((cm^2)\) is the cross-sectional area of the tubular reactor.

\[
V_b \frac{\partial c_{Mg,b}}{\partial t} = -D_{Mg} \frac{\partial c_{Mg,t}}{\partial z} \bigg|_{z=L} \cdot S_t \cdot \varepsilon \tag{5.8}
\]

**5.3.2 Inorganic carbon mass balance based on diffusion and reaction kinetics**

The governing mass balance equations of the aqueous species inside both the tubular reactor \((c_{DIC,t})\) and the batch reactor \((c_{DIC,b})\) are shown from equations 5.9 (a-c) and 5.10.

Inside the tubular reactor, the dissolved total inorganic carbon concentration \((c_{DIC}, \text{mol/L})\) is governed by

\[
\frac{\partial c_{DIC,t}}{\partial t} = D_{DIC} \frac{\partial^2 c_{DIC,t}}{\partial z^2} - R_{DIC,\text{mag}} \tag{5.9}
\]

Boundary conditions (BCs):

At \(z=0\), \(-D_{DIC} \frac{\partial c_{DIC,t}}{\partial z} = 0\) \hspace{1cm} (5.9a)

At \(z=L\), \(c_{DIC,t} = c^*\) \hspace{1cm} (5.9b)

Initial conditions (IC):
At \( t=0 \), \( c_{\text{DIC},t} = 0 \) \hspace{1cm} (5.9c)

Where \( D_{\text{DIC},t} \) (cm\(^2\)/s) is the diffusivity of dissolved inorganic carbon species in the aqueous phase and \( R_{\text{DIC,mag}} \) (mol/cm\(^3\)-s) is the rate of removing DIC due to magnesite precipitation. \( R_{\text{DIC,mag}} \) is only included when magnesite is precipitating from the solution and the form of \( R_{\text{DIC,mag}} \) has not been selected in this work. The total dissolved inorganic carbon concentration (\( c_{\text{DIC}} \)) is the total concentration of \( \text{CO}_2\text{(aq)} \), \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \). At the top of the tubular reactor (\( z=L \)), the solution is very acidic, because \( \text{CO}_2 \) dissolves into the bulk solution from the headspace and forms carbonic acid. DIC is predominantly \( \text{CO}_2\text{(aq)} \), while \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) concentrations are so small that they can be neglected. The \( \text{CO}_2\text{(aq)} \) concentration is always (\( c^* \)) in the batch reactor, since \( \text{CO}_2 \) pressure above the aqueous phase in the batch reactor is constant. At the bottom of the tubular reactor (\( z=0 \)), the flux of DIC is zero because the tube is close-ended. Initially, the DIC concentration is zero, because DIC has not started diffusing into the tube.

Since the bulk solution in the batch reactor is very acidic due to \( \text{CO}_2 \) dissolution from the headspace and the formation of carbonic acid, the following simplification for the DIC concentration in the batch reactor (\( c_{\text{DIC, b}} \)) can be established, by assuming the concentration of \( \text{CO}_2\text{(aq)} \) is much larger than that of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \).

\[ c_{\text{DIC, b}} = c^* \] \hspace{1cm} (5.10)
5.3.3 Numerical solution

One can couple the above four equations (equation 5.7 - 5.10) and solve for the concentration profiles of Mg ($c_{\text{Mg},t}$ and $c_{\text{Mg},b}$) and DIC ($c_{\text{DIC},t}$) in the tubular and batch reactors. The acid-base reactions of carbonate species and charge balance (equation 5.6) can be used to calculate the concentrations of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ and the pH. The calculated pH, which varies with time and location, changes the forsterite dissolution rate (equation 5.1) at different locations and times.

5.3.3.1 Numerical solution for Mg transport with only forsterite dissolution

To simplify the reactive transport modeling, only Mg diffusion and forsterite dissolution were included in the following governing equation. It was assumed that precipitation of magnesite did not occur. Therefore no dissolved Mg would be removed from the aqueous phase. It should be noted that the actual system will be more complicated because magnesite would start to nucleate and precipitate after a critical saturation index was reached.

$$\frac{\partial c_{\text{Mg},t}}{\partial t} = D_{\text{Mg}} \frac{\partial^2 c_{\text{Mg},t}}{\partial z^2} + R_{\text{Mg,Fo}}$$ (5.11)

This partial differential equation (PDE) can be coupled with equation 5.8, to connect the Mg concentration in the tubular reactor to that in the batch reactor.

$$V_b \frac{\partial c_{\text{Mg},b}}{\partial t} = -D_{\text{Mg}} \frac{\partial c_{\text{Mg},t}}{\partial z} \bigg|_{z=L} \cdot S_t \cdot \varepsilon$$ (5.8)
When using MATLAB to simulate the profile of Mg concentration, dimensionless forms of equations 5.11 and 5.8 are needed. The dimensionless forms of Mg concentration in the tubular reactor ($\alpha_1$), Mg concentration in the batch reactor ($\beta_1$), tubular reactor length ($\eta$), and reaction time ($\tau$) are given in equations 5.12 to 5.15.

$$\alpha_1 = \frac{c_{Mg,t}}{c_{Mg,t}^0} = \frac{c_{Mg,t}}{c_{Mg}^\infty}$$ (5.12)

$$\beta_1 = \frac{c_{Mg,b}}{c_{Mg,b}^0} = \frac{c_{Mg,b}}{c_{Mg}^\infty}$$ (5.13)

$$\eta = \frac{z}{L}$$ (5.14)

$$\tau = \frac{t}{\tau_{D1}}$$ (5.15)

Where $c_{Mg}^\infty$ is the maximum Mg concentration, $c_{Mg}^0$ is the value when forsterite dissolves completely, and it is usually set to 0.1 mol/L for convenience. The length of the tubular reactor is set to 5.51 cm. The characteristic diffusion time $\tau_{D1}$ is introduced in section 5.4, and is equal to different values under different temperatures.

Rewriting equations 5.11 and 5.8 using the dimensionless expressions above, one can get the following dimensionless forms.

$$\frac{\partial \alpha_1}{\partial \tau} = \frac{\partial^2 \alpha_1}{\partial \eta^2} + \frac{R_{Mg,F0} \tau_{D1}}{c_{Mg}^\infty}$$ (5.16)

$$\frac{\partial \beta_1}{\partial \tau} = \frac{D_{Mg} S_{t\cdot c\cdot t_{D1}}}{{v_b\cdot L}} \frac{\partial \alpha_1}{\partial \eta \eta=1}$$ (5.17)
Boundary conditions (BCs):

At $\eta=0$, $\frac{\partial a_1}{\partial \eta} = 0$ \hspace{1cm} (5.18)

At $\eta=1$, $a_1 = \beta_1$ \hspace{1cm} (5.19)

Initial conditions (IC):

At $\tau=0$, $a_1 = \beta_1 = 0$ \hspace{1cm} (5.20)

Using the method of lines, these two coupled formulae can be solved using MATLAB. Central difference is employed here to simplify the diffusion term in equation 5.16, so that it can be turned into a set of ordinary differential equations (ODE).

Suppose the length of the tubular reactor is divided into $N$ equally spaced grid points or this length is divided by two boundary points and $(N-2)$ internal points. The grid spacing, or the distance between two successive points is $\frac{1}{(N-1)}$. As a result, the concentrations along the tubular reactor are $a_{1(1)}$, $a_{1(2)}$, $a_{1(3)}$, ..., and $a_{1(N)}$. Hence, the following general form of ODE can be obtained from equation 5.16.

$$\frac{d a_{1(i)}}{d \tau} = \frac{a_{1(i+1)} - 2a_{1(i)} + a_{1(i-1)}}{(\Delta \eta)^2} + \frac{R_{Mg, Fo} \tau D_1}{c^2_{Mg}} \quad (i=2, 3, ..., N) \hspace{1cm} (5.21)$$

The corresponding boundary conditions can be rewritten as equation 5.21 (a-b).

$a_{1(1)} = a_{1(2)}$ \hspace{1cm} (5.21a)

$a_{1(N)} = \beta_1$ \hspace{1cm} (5.21b)
Applying equation 5.21b to equation 5.17, the connection between the tubular reactor and
the batch reactor turns into equation 5.22.

\[ \frac{d\alpha_{1(N)}}{d\tau} = -\frac{D_{Mg}S_{r}e^{-\tau D_1}}{V_{b}L} \frac{(\alpha_{1(N)} - \alpha_{1(N-1)})}{\Delta \eta} \] (5.22)

Hence, combining equations 5.21 and 5.22, the following differential equations in matrix
form can be obtained.

\[ \begin{bmatrix}
\alpha_{1(2)} \\
\alpha_{1(3)} \\
\alpha_{1(4)} \\
\vdots \\
\alpha_{1(N-1)} \\
\alpha_{1(N)} 
\end{bmatrix} = \frac{1}{(\Delta \eta)^2} \begin{bmatrix}
-1 & 1 & 0 & 0 & \cdots & 0 \\
1 & -2 & 1 & 0 & \cdots & 0 \\
0 & 1 & -2 & 1 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & 0 & \cdots & M\Delta \eta \\
0 & 0 & 0 & 0 & \cdots & -M\Delta \eta 
\end{bmatrix} \begin{bmatrix}
\alpha_{1(2)} \\
\alpha_{1(3)} \\
\alpha_{1(4)} \\
\vdots \\
\alpha_{1(N-1)} \\
\alpha_{1(N)} 
\end{bmatrix} + R_{d} \cdot \begin{bmatrix} 1 \end{bmatrix} \] (5.23)

Where \( M = \frac{D_{Mg}S_{r}e^{-\tau D_1}}{V_{b}L} \), and \( R_{d} = \frac{R_{Mg,Fo}}{c^{Mg}} \) for the convenience of getting numerical
solutions from MATLAB.

5.3.3.2 Numerical solution for dissolved CO\(_2\) transport without magnesite precipitation
To simplify the reactive transport modeling, CO\(_2\)\(_{aq}\) was used as a representative species
for dissolved inorganic carbon. All the other dissolved inorganic carbon species (HCO\(_3^-\)
and CO\(_3^{2-}\)) were then calculated using the equilibrium constants and the concentration of
CO\(_2\)\(_{aq}\) at each time and location. This method was considered to artificially “create”
more dissolved inorganic carbon, by creating the concentrations of HCO\(_3^-\) and CO\(_3^{2-}\)
based on the CO\(_2\)\(_{aq}\) that had transported and the pH. This issue will be further discussed
at the end of section 5.2. It was also assumed that precipitation of magnesite did not occur. Therefore no dissolved inorganic carbon would be removed from the aqueous phase. It should be noted that the actual system will be more complicated because magnesite would start to nucleate and precipitate after a critical saturation index was reached.

To investigate CO$_2$(aq) transport in the whole system, the following partial differential equations are developed together with their boundary conditions and initial condition.

In the tubular reactor, CO$_2$(aq) concentration $c_{\text{CO}_2,t}(z,t)$, which is a function of both the location along the tube ($z$) and reaction time ($t$), is only affected by diffusion ($D_{\text{CO}_2}$).

$$\frac{\partial c_{\text{CO}_2,t}}{\partial t} = D_{\text{CO}_2} \frac{\partial^2 c_{\text{CO}_2,t}}{\partial z^2} \quad (5.24)$$

The concentration of CO$_2$(aq) in the batch reactor ($c_{\text{CO}_2,b}$) is constant under a constant CO$_2$ pressure.

To obtain the dimensionless forms of the above PDE, the dimensionless forms of CO$_2$(aq) concentration in the tubular reactor ($\alpha_2$), CO$_2$(aq) concentration in the batch reactor ($\beta_2$) are given in equations 5.25 to 5.26. The dimensionless tubular reactor length ($\eta$) and reaction time ($\tau$) are already defined in equation 5.14 and 5.15 in the previous section.
\[ \alpha_2 = \frac{c_{\text{CO}_2,t}}{c_{\text{CO}_2,\text{t}}} = \frac{c_{\text{CO}_2}}{c_{\text{CO}_2,\text{b}}} \]  
\[ (5.25) \]

\[ \beta_2 = \frac{c_{\text{CO}_2,\text{b}}}{c_{\text{CO}_2,\text{b}}} = 1 \]  
\[ (5.26) \]

For our specific reactor design, the length of the tubular reactor (L) is 5.51 cm. Rewriting equation 5.24 using the dimensionless expressions above, one can get the following dimensionless forms.

\[ \frac{\partial \alpha_2}{\partial \tau} = A \frac{\partial^2 \alpha_2}{\partial \eta^2} \]  
\[ (5.27) \]

Boundary conditions (BCs):

At \( \eta = 0 \), \( \frac{\partial \alpha_2}{\partial \eta} = 0 \) \[ (5.27a) \]

At \( \eta = 1 \), \( \alpha_2 = \beta_2 = 1 \) \[ (5.27b) \]

Initial conditions (IC):

At \( \tau = 0 \), \( \alpha_2 = 0 \) \[ (5.27c) \]

Where \( A = \frac{D_{\text{CO}_2}}{\rho_{\text{Mg}}} \). Similarly, using the method of lines, the following differential equations in matrix form can be obtained.
5.3.4 Characteristic times and the importance of diffusion

Estimation is needed to determine if diffusion will affect the spatial variation in dissolved Mg concentration, before establishing any detailed model. Hence, the characteristic times for diffusion and for the dissolution of forsterite were calculated using equations 5.29 and 5.30.

\[
\tau_{\text{diff,Mg}} = \tau_{D1} = \frac{L^2}{D_{\text{Mg}}}
\]

\[
\tau_{\text{rxn,Mg}} = \frac{\Delta c_{\text{Mg}}}{R_{\text{Mg,fo}}} = \frac{c_{\text{Mg,final}}}{R_{\text{Mg,fo}}}
\]

For our specific reactor design, the length of the tubular reactor (L) is 5.51cm. The diffusivity of Mg\(^{2+}\)(D\(_{\text{Mg}}\)) of 8.84\(\cdot\)10\(^{-6}\) cm\(^2\)/s at 100 °C (Newman and Thomas Alyea 2004) is used because Mg\(^{2+}\) is the dominant Mg species in the solution. The final Mg concentration (\(c_{\text{Mg,final}}\)) was taken as 3.5 mmol/L, which is smaller than the predicted equilibrium Mg concentration of 7.18 mmol/L for magnesite (chapter 4). A forsterite dissolution rate of 1.9\(\cdot\)10\(^{-13}\) mol/cm\(^2\)-s at pH 5.6 is used (Giammar, Bruant et al. 2005). Applying equations 5.29 and 5.30, \(\tau_{\text{diff,Mg}}\) is 3.44\(\cdot\)10\(^6\) sec, and \(\tau_{\text{rxn,Mg}}\) is 9.70\(\cdot\)10\(^6\) sec. Since these two characteristic times are within the same order of magnitude, it suggests that diffusion can play an important role in the evolution of concentration profiles of
dissolved Mg during forsterite dissolution. Therefore, it is worthwhile to devote time and energy to the modeling.

5.4 Experimental approach

5.4.1 Materials

Commercial forsterite powder, with a size fraction of 10 - 44 μm, was purchased from Alfa Aesar. It was prepared using a similar procedure in the previous chapters. The specific surface area (SSA) of the powder was determined to be 1.38 m²/g by BET-N₂ adsorption. XRD was used to confirm the crystalline structure as forsterite and the morphology of the powder was observed using SEM.

5.4.2 Experimental method

The experimental setup was very similar to that described in section 5.2.1. Borosilicate glass tubes (Fisher Scientific), with a length 7.5 cm, were wet packed with commercial forsterite powder. Wet-packing method was performed so that the forsterite powder was always added to form a slurry of forsterite in water. The forsterite powder (about 7.5 g) was added and settled down to about 6.5 cm from the bottom of the tube. The porosity of forsterite in the tube was around 0.5, which was determined using the weight of the forsterite powder and the total volume of the tube. Afterwards, the tube was tied to the thermocouple that protruded from the reactor head to keep the tube vertical and away from the mixer. The reactor head was then connected with a PTFE vessel with 200 mL of ultrapure water (resistivity > 18.2 MΩ•cm) in a stainless steel reactor body. The water
level in the PTFE vessel was enough to submerge the tube completely. The bulk solution in the PTFE vessel was always well mixed. After the whole reactor was assembled, the experimental temperature and CO₂ pressure were maintained throughout the reaction. After each reaction was run for a certain period (1 day, 3 days, 5 days and 2 weeks), a liquid sample was collected from the bulk solution in the PTFE liner before the experiment was stopped. The pH of the solution was measured outside of the reactor under ambient pressure (pH_{ex}) within 5 min of collection, and the concentrations of dissolved Mg, Si and Fe were measured using ICP-MS. The tube, with the solid phase in it, was retrieved at the end of the experiment. Raman spectroscopy was used to probe for magnesite precipitation along the tube. After being air-dried, several segments of the solid were removed from the tube (each segment with a length of 1 cm). These solid samples were analyzed by XRD to confirm the presence of magnesite as a precipitate and its relative amounts along the length of the tube. To calculate the relative amount of magnesite, samples for XRD analysis were prepared using identical masses of solids from the tube. While ignoring possible effects of preferential orientation in XRD, the peak heights associated with MgCO₃ between 15° and 50° were quantitatively compared. The relative amounts of magnesite presented are then relative to the highest amount observed in any of the samples. An even more quantitative analysis could have used peak areas instead of peak heights and compared those areas with the signal from a pure magnesite material prepared with an identical amount and following the same procedures.
5.5 Results and discussion

5.5.1 Simulated reaction pathway by diffusing CO$_2$(aq) at 100 °C and 100 bar P$_{CO2}$

For a specific condition at 100 °C and 100 bar P$_{CO2}$, the concentrations of the dissolved Mg, CO$_2$(aq) and inorganic carbon in the tubular reactor were obtained as a function of both location along the tube (z) and reaction time (t) by diffusing only CO$_2$(aq), as shown in Figure 5.4. MATLAB was used to solve two series of ODEs, while the value of N was set as 10 and the time step was 0.02τ$_{D1}$ (where τ$_{D1}$=3.44∙10$^6$ sec). The total length of the tube (L) was set to 5.51 cm and the total reaction time was 191 hours (or 8 days). The porosity was set to 0.44, which was calculated according to how forsterite was wet packed in a glass tube in experiments.

At the very beginning of the reaction (t = 0 hour), the Mg concentration was zero at any location in the tubular reactor. For a reaction time of 191 hours (or 8 days), at any specific location the Mg concentration increased, with increasing time (Figure 5.4 (a) and (f)). The highest Mg concentration was the first point below the top of the tube, and it reached as high as 0.13 mol/L at the end of the reaction (t = 191 hours).

Similarly, gradients developed for pH and the concentrations of CO$_2$(aq) and DIC. The CO$_2$ concentration was highest at the top of the tube and lowest at the bottom of the tube, because only diffusion affected its amount along the tube. Initially, the pH was 6.11 for the majority of the tube (the neutral pH at 100 °C and 100 bar P$_{CO2}$), since CO$_2$ had not started dissolving into the tube yet. The pH for the very top of the tube was 3.22, because the tube was open to the batch reactor where CO$_2$ dissolved from a fixed 100 bar P$_{CO2}$
headspace. The solution pH within the tube decreased after CO₂ dissolved into the tube, but started increasing when forsterite dissolution started to consume the acidity. The total amount of dissolved inorganic carbon was calculated by summing the dissolved CO₂ (controlled by diffusion) and HCO₃⁻ and CO₃²⁻ (calculated using CO₂ concentration, equilibrium constants and pH).

The saturation index for magnesite implied that almost the whole length of the solution in the tubular reactor would become supersaturated with respect to magnesite within just 1 day of reaction (19.1 hours), with SI_{mag} at least 3.3 along the tube. For the rest of the reaction (t = 191 hours), SI_{mag} slightly increased to just below 4. According the magensite precipitation reactions in chapter 4, at 100 °C and 100 bar P_{CO₂}, magnesite could start precipitation once SI_{mag} of 2 was reached. Therefore, magensite precipitation was predicted to happen within the tube. At the very top of the tube, since the majority of the dissolved Mg concentration diffused into the batch reactor and the bulk solution was very acidic (pH 3.22 - 3.37), SI_{mag} was only -4.0 at the end of the reaction.
Figure 5.4 By diffusing only CO$_2$(aq), the concentrations of Mg (a), CO$_2$ (b), DIC (c) inside the tubular reactor, as well as the solution pH (d) and SI$_{\text{mag}}$ (e). In (f), the simulated
Mg concentration in the batch reactor connected to the tubular reactor was plotted as well as the experimentally measured Mg concentration.

5.5.2 Simulated reaction pathway by diffusing DIC at 100 °C and 100 bar $P_{\text{CO}_2}$

To find out the difference if DIC was diffused instead of $\text{CO}_2(aq)$, simulations by diffusing DIC was also performed. For a specific condition at 100 °C and 100 bar $P_{\text{CO}_2}$, the concentrations of the dissolved Mg and inorganic carbon in the tubular reactor were obtained as a function of both location along the tube ($z$) and reaction time ($t$) by diffusing DIC together, as shown in Figure 5.5. The diffusivity of DIC was set to the same order as that of $\text{CO}_2(aq)$. Other parameters were set to similar values mentioned in section 5.1. C++ was used, with the N value of 55 and the time step of 42 hours. The total length of the tube ($L$) was set to 5.51 cm and the total reaction time was 168 hours (or 7 days). The porosity was also set to 0.44, which was calculated according to how forsterite was wet packed in a glass tube in experiments.

At the very beginning of the reaction ($t = 0$ hour), the Mg concentration was set to $6.56 \times 10^{-5}$ mol/L at any location in the tubular reactor, except the very top (0 mol/L). This value was the Mg concentration at equilibrium with forsterite at 100 °C and 100 bar $P_{\text{CO}_2}$. For a reaction time of 168 hours (or 7 days), at any specific location the Mg concentration increased, with increasing time (Figure 5.5 (a) and (f)). The Mg concentration was highest at the very bottom of the tube, and it reached as high as 0.04 mol/L at the end of the reaction ($t = 168$ hours).
Similarly, gradients developed for the concentrations of DIC and pH. Since DIC was diffused instead of CO$_2$(aq), the DIC profile was very similar to that of CO$_2$(aq) in section 5.1. Initially, the pH was 8.34 for the majority of the tube, because the solution composition was set to be at equilibrium with respect to forsterite at 100 °C and 100 bar P$_{CO2}$. The pH for the very top of the tube was 3.23, because the tube was open to the batch reactor where CO$_2$ dissolved from a fixed 100 bar P$_{CO2}$ headspace. The solution pH decreased after CO$_2$ dissolved into the tube, but started increasing when forsterite dissolution started to consume the acidity. The highest pH was at the bottom of the tube, and it reached to as high as 5.59 after 168 hours.

The saturation index for magnesite implied that almost the whole length of the solution in the tubular reactor would become supersaturated with respect to magnesite, and a SI$_{mag}$ of 2 was first reached at 1.16 cm and deeper into the tube after 126 hours (5.3 days). For the rest of the reaction (t = 168 hours), SI$_{mag}$ slightly increased to just below 2.5. At the very top of the tube, since the majority of the dissolved Mg concentration diffused into the batch reactor and the bulk solution was very acidic (pH 3.23 - 3.29), SI$_{mag}$ was only -4.5 at the end of the reaction.

For both methods described in section 5.1 and 5.2, the simulated Mg concentration in the batch reactor was much lower (about 10 times) than that measured from the experiments. (Figure 5.4 (f) and Figure 5.5 (f)) It was possible that some forsterite powder (10 - 44 μm) got pulled into the batch reactor during stirring. As shown in chapter 2, 0.5 g/L of commercial olivine dissolution could result in 1.84 mM of dissolved Mg after 7 days at
100 °C and 100 bar $P_{CO_2}$. This value was at the same order of magnitude as the experimental Mg concentration (5.7 mM) after 5 days. Hence, it is possible that the dissolution of a small amount of forsterite (0.1 g of forsterite into 200 mL of batch solution) that was pulled into the batch reactor was the reason for the discrepancy between the simulated and the experimental results. In addition, the forsterite particles (10 - 44 μm) used in the tube reactions were finer than those in chapter 2 (53 - 106 μm). So its dissolution should be faster to release more Mg, given the same amount of forsterite powder in batch reactor.

The first method by diffusing $CO_2$(aq) was easy to solve using MATLAB, and the simulations were performed at Washington University. However, the second method by diffusing DIC involved much more numerical challenges, and the simulations were performed by Bin Guo at Princeton, using C++. Generally, the second method is considered closer to reality, because it transferred DIC together and then decided the concentrations of different carbonate species through charge balance. The first method would artificially “create” more dissolved inorganic carbon by creating the concentrations of $HCO_3^-$ and $CO_3^{2-}$ based on the $CO_2$(aq) that had transported and the pH. However, it was worth noting that the diffusivity of DIC was actually assumed to be that of $CO_2$(aq). To fully account for the diffusivities of all three DIC species ($CO_2$(aq), $HCO_3^-$ and $CO_3^{2-}$), an effective diffusivity could be used to further improve the second approach (Li, Peters et al. 2006).
Figure 5.5 By diffusing DIC, the concentrations of Mg (a), CO$_2$ (b), DIC (c), pH (d) and SI$_{mag}$ (e) inside the tubular reactor. (f) The simulated Mg concentration in the batch
reactor connected to the tubular reactor was plotted as well as the experimentally measured Mg concentration.

5.5.3 Experimental analysis for a 5-day tubular experiment at 100 °C and 100 bar P_{CO2}

Raman spectroscopy was employed to identify the presence of different Mg-carbonate precipitates along the length of the tube. Raman spectroscopy allows one to perform non-destructive analysis by shining the laser through the glass tube, even when the solid was still wet. However, sometimes the solid had to be removed from the tube before performing Raman analysis, because of the high background caused by trace impurities in the glass that fluoresced. This was true for the tubular experiment for 5 days at 100 °C and 100 bar P_{CO2}. No Mg-carbonates were identified until about 1 cm into the solid. In addition to the forsterite that was initially added to the tube, magnesite and hydromagnesite were both present at that location. (Figure 5.6) Hydromagnesite might act as an intermediate for magnesite precipitation. (Hänchen, Prigiobbe et al. 2008) The three major bands at 964, 855 and 824 cm\(^{-1}\) wavenumbers are indicative of the Si-O stretching modes of forsterite (Mohanan 1993). The major band at 1094 cm\(^{-1}\) is indicative of the CO\(_3^{2-}\) stretching of magnesite, and the major band at 1119 cm\(^{-1}\) is indicative of the CO\(_3^{2-}\) stretching of hydromagnesite (Edwards, Villar et al. 2005).
Figure 5.6 Raman spectra from about 1 cm into the tube after 5 days of reaction at 100 °C and 100 bar P$_{CO_2}$. (a) Forsterite was present as well as some Mg-carbonates. The three major bands at 964, 855 and 824 cm$^{-1}$ are from forsterite. (b) Both hydromagnesite and magnesite were present. The major band at 1094 cm$^{-1}$ is from magnesite, and the major band at 1119 cm$^{-1}$ is from hydromagnesite.

XRD was used to analyze the different segments of the final solid (from 0.5 cm to 1 cm in length) after they were air-dried and removed from the tube. The MgCO$_3$ signal strength from XRD of each solid sample was adjusted so that the amplitudes of the peaks between 15° and 50° of 2θ were comparable to those of a MgCO$_3$ standard that was collected. Finally, the sample-to-sample signal strength of the MgCO$_3$ phase in the sample was each scaled to the layer of the sample with the most MgCO$_3$ signal and then their relative signal strength, or the relative amount of magnesite, was calculated for the whole length of the tube (Figure 5.7). This results from this XRD approach indicated that magnesite did not form until about 1 cm into the tube. The amount of magnesite was highest at about 1 cm into the tube, and decreased by 75.6% at about 3 cm into the tube. No magnesite was found from 3 cm further down the tube.
The location of magnesite precipitation (about 1 cm into the tube) was consistent with the Raman spectroscopy measurements. It also agrees with the $SI_{mag}$ prediction in the second approach where DIC was diffused into the tube. $SI_{mag}$ in Figure 5.5 (e) implied that almost the whole length of the solution in the tubular reactor would become supersaturated with respect to magnesite, and a $SI_{mag}$ of 2 was first reached at 1.16 cm and deeper into the tube after 126 hours (5.3 days). Based on the finding that a critical $SI_{mag}$ of 2 has to be reached before magnesite can precipitate at 100 °C and 100 bar $P_{CO2}$ (chapter 4), the second approach successfully predicted that magnesite precipitation should not happen until day 5 at about 1 cm deeper into the tube.

![Graph showing relative amount of magnesite](image)

**Figure 5.7** Relative amount of magnesite formed in a tubular reactor after 5 days of reaction at 100 °C and 100 bar $P_{CO2}$. Magnesite did not form until about 1 cm into the tube, and its relative amount was highest there. Deeper into the tube, the magnesite amount decreased and finally no precipitation happened after 3 cm into the tube.
5.6 Conclusions

Diffusion-limited zones in geologic formations can lead to local reaction rates and products much different for different locations, which did not happen in well-mixed laboratory batch reactors (chapter 2). As for the forsterite system in a diffusion-limited tubular reactor at 100 °C and 100 bar $P_{\text{CO}_2}$, magnesite was predicted to precipitate about 1 cm into the tube only when a critical magnesite saturation index of 2 was reached. When diffusing total DIC instead of $\text{CO}_2$ alone, the simulated results agreed very well with experimental observations. Both Raman spectra and XRD analysis proved that the extent of Mg carbonation changed with the length of the tube. The model successfully served as a guide and suggested when and where magnesite would precipitate. Future work could be devoted into including magnesite precipitation rate in the mass balance governing equations after a critical saturation state is reached, and considering the effect of precipitation on the transport properties of the diffusion-limited zone.
Chapter 6. Conclusions and recommendations for future work

6.1 Conclusions

This study was devoted to reactions occurring in the water-forsterite-CO$_2$ system, because mineral trapping for such a system has a potentially high sequestration capacity and could provide very long-term sequestration. The dissolution of forsterite and the release of dissolved magnesium for subsequent precipitation of Mg-carbonate minerals were two very important parts of this study. In addition, investigations of the overall fate of injected CO$_2$ into porous media considered both diffusive transport of aqueous species and chemical reactions.

6.1.1 The dissolution of forsterite and partially weathered olivine

For both forsterite and partially weathered olivine, temperature and pH are the most important properties of a GCS system that affect their dissolution rate. The CO$_2$ pressure did not directly affect the dissolution rate, but it had an indirect effect through its influence on the pH. After an initially rapid dissolution period, the dissolution rates for both materials declined significantly, an effect that is attributed to the formation of a Si-rich layer at the mineral surface. The presence of NaCl increased the forsterite dissolution rate. A higher initial olivine concentration also increased the release of Mg but not in a linear manner; this information can be helpful in extending results to the high solid:water ratios that will be encountered in geologic formations and for ex situ mineral carbonation.
6.1.2 The precipitation of magnesite and hydrated magnesium carbonates

Under high temperature and \( \text{CO}_2 \) pressure, magnesite was the only precipitate. Most importantly, the aqueous solution has to reach a certain degree of supersaturation with respect to magnesite before magnesite precipitation can occur. At 100 °C and 100 bar \( P_{\text{CO}_2} \), the critical \( S_{\text{mag}} \) was approximately 2. In addition, magnesite precipitation was accelerated when the solution was seeded with magnesite to remove nucleation as a rate-limiting step. Relative to mineral-free solutions, forsterite did not accelerate magnesite nucleation, but magnesite was still observed on the forsterite surface.

6.1.3 Forsterite dissolution and magnesite precipitation in a diffusion-limited zone

Diffusion-limited zones in geologic formations can lead to local reaction rates and products that vary significantly from location to location. Both bench-scale experiments and a mathematical model that coupled chemical reactions and diffusive transport have illustrated this point. For a tubular reactor packed with forsterite powder, the simulation included the diffusion of \( \text{Mg}^{2+} \) and dissolved inorganic carbon, as well as the forsterite dissolution rate, which is a function of the pH. For 100°C and 100 bar \( P_{\text{CO}_2} \), the model successfully served as a guide and suggested that magnesite would first form after five days at a location about 1 cm below the interface of the forsterite packed bed with a well-mixed \( \text{CO}_2 \)-rich aqueous solution. The model results agreed with both Raman and XRD analysis.
6.2 Recommendations for future work

The dissolution rate of both forsterite and weathered olivine decreased significantly with reaction time. The formation of a Si-rich layer was regarded as the cause of the declining dissolution rate. Reactive transport simulations of GCS that do not account for this decreasing dissolution rate would overestimate the silicate dissolution rate and underestimate the time needed to reach conditions at which mineral trapping could occur. Hence, the role of the Si-rich layer formation on the dissolution of silicate minerals at real GCS sites will need to be considered.

Different Mg-carbonate minerals precipitated under different temperatures and CO$_2$ pressures. Even when magnesite did form under higher temperature and CO$_2$ pressure, hydrated Mg-carbonate intermediates (e.g. hydromagnesite) formed first and then transformed to magnesite. Hence, how to account for the formation of the intermediates and their transformation into magnesite in the reactive transport modeling of real GCS sites will need to be considered.

Magnesite precipitation cannot occur until a critical saturation index with respect to magnesite was reached. Researchers will need to implement such a parameter into their reactive transport models of GCS sites. Second, it should be noted that even when a critical saturation index with respect to magnesite was reached, Mg might not be removed as much as thermodynamically expected from the aqueous solution. Many reactive transport simulations of GCS sites only assume that the silicate mineral dissolution is the rate-limiting reaction and that relative to this silicate mineral dissolution rate carbonate
precipitation can be assumed to reach equilibrium instantaneously. Therefore, the precipitation rate of magnesite may need to be determined and implemented into reactive transport models. Finally, experiments of magnesite precipitation for longer reaction times (longer than 1 week) would help determine if Mg could eventually approach magnesite equilibrium and if so how fast the precipitation rate is.

For modeling of the tubular reactor, the current simulation only considered the dissolution rate of forsterite as the reaction kinetics. The precipitation kinetics of magnesite were not included in the governing mass balance equations for either Mg or dissolved inorganic carbon. Future work could incorporate the magnesite precipitation rate into simulations. In addition, once magnesite precipitation occurred, the transport properties of the diffusion-limited zone (e.g. porosity and permeability) would be further affected. Therefore, a more advanced model should consider the precipitation of magnesite and its effect on transport properties of the porous media and allow the transport properties to change with reaction progress.

Finally, although the current simulations agreed well with the experimental results of the tubular reactions, long term experiments and even more detailed analysis are needed. Given longer reaction time, one can find out if hydrated Mg-carbonate intermediates would eventually disappear and completely transform into magnesite. When, where and how much magnesite would precipitate are also of great interest for a longer reaction time. More tubular experiments could be conducted to study the effects of temperature and CO$_2$ pressure and the dimension of the tubular reactor. In addition, the transport
properties of the porous media before and after the tubular reaction could be studied using CT imaging, which yields information regarding the pore network structure that includes the size, connectivity, and morphology of pores. This information will help integrate the heterogeneity of the porous media into the model.
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