

MECHANISMS OF CARBON MINERALIZATION FROM THE PORE TO FIELD
SCALE: IMPLICATIONS FOR CO₂ SEQUESTRATION

by

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Abstract

Innovative technologies to stabilize atmospheric CO₂ concentrations are essential in order to mitigate the harmful effects of anthropogenic greenhouse gas (GHG) emissions on the global climate system. Mineralization of carbon in solid, stable carbonate minerals through reaction of CO₂ with Mg-rich mining wastes is a promising CO₂ sequestration strategy that offers the potential to render certain mines GHG neutral. Here, the physical and chemical controls on rates of and capacity for CO₂ sequestration in systems representative of mine tailings are examined from the mineral-fluid interface to field scale using a combination of experimental techniques. These experimental data and existing field data are used to develop a comprehensive reactive transport model that captures the processes governing carbon mineralization in the shallow subsurface. Stirred batch reactor, microfluidic pore scale, and decimeter to meter scale column carbonation experiments using brucite [Mg(OH)₂] revealed that the primary controls on carbonation include the rate of CO₂ supply, the distribution of the reactive phase, the mineral grain size/surface area, and the availability and distribution of water. The rate-limiting step during carbonation varied from CO₂ supply to mineral dissolution depending on the experimental variables. Surface passivation and water-limited reaction resulted in a highly non-geometric evolution of reactive surface area. The extent of reaction was also limited at high water content because viscous fingering of the gas streams supplied to the columns resulted in narrow zones of highly carbonated material, but left a large proportion of brucite unreacted. More robust predictions of the CO₂ sequestration rate and capacity that can be expected at the field scale are possible due to the incorporation of water consumption, water-limited reactivity, and surface passivation functions into the reactive transport code, MIN3P. This research imparts a better understanding of fundamental mechanisms and chemical processes relevant to CO₂ sequestration in mine tailings, with implications for mineral carbonation in other settings that have greater CO₂ sequestration capacity, such as shallow subsurface formations with similar mineralogy. Aspects of this research, such as water-limited

reactivity, have broader implications for reactive transport processes in the vadose zone in general, including mineral weathering and groundwater remediation.

Preface

This thesis consists of five related manuscripts that have been published in, submitted to, or prepared for submission to peer-reviewed international academic journals and a peer-reviewed paper published in international conference proceedings.

A version of Chapter 2 is published in *Environmental Science & Technology*. This chapter is reprinted with permission from Harrison, A. L., Power, I. M. and Dipple, G. M. (2013) Accelerated carbonation of brucite in mine tailings for carbon sequestration. *Environ. Sci. Technol.* **47**: 126–134. Copyright 2012 American Chemical Society. The Supporting Information to this manuscript is reproduced in this thesis as Appendix 1: Appendix to Chapter 2. I conducted the experiments and analytical work, interpreted results, and wrote the manuscript. I.M. Power and G.M. Dipple advised on experimental design, helped with the interpretation of results, and edited the manuscript. All authors confirm that this is an accurate reflection of the author contributions and agree to the use of the *Environmental Science & Technology* paper in this thesis.

A version of Chapter 3 was published in the proceedings of the International Mine Water Association 2013 Mine Water Conference as: Harrison, A. L., Power, I. M. and Dipple, G. M. (2013) Strategies for enhancing carbon sequestration in Mg-rich mine tailings, in Brown, A., Figueroa, L., Wolkersdorfer, C. (Eds.), *Reliable Mine Water Technology* (Vol. 1). Publication Printers, Denver, Colorado, USA, pp. 593–598. It is used with permission of the International Mine Water Association. I interpreted results and wrote the manuscript. I.M. Power and G.M. Dipple advised on the interpretation of results and edited the manuscript. All authors confirm that this is an accurate reflection of the author contributions and agree to the use of this paper in this thesis.

Chapter 4 has been prepared for submission to an international peer-reviewed academic journal. The appendix to this chapter (Appendix 2: Appendix to Chapter 4) will be submitted as the supporting information to the manuscript. The manuscript is authored as follows:

A.L. Harrison, G.M. Dipple, W. Song, I.M. Power, K.U. Mayer, A. Beinlich, and D. Sinton. G.M. Dipple and I conceived the study. D. Sinton, G.M. Dipple, W. Song and I designed the experiments. W. Song and I conducted the experiments. W. Song, I.M. Power, and I performed microscopy and A. Beinlich conducted Raman spectroscopy. G.M. Dipple and I interpreted the data and discussed its implications with input from K.U. Mayer on reactive transport and geochemical modeling. I wrote the manuscript with input from all authors. All authors confirm that this is an accurate reflection of the author contributions and agree to the use of this manuscript in this thesis.

A version of Chapter 5 is published in *Geochimica et Cosmochimica Acta*. This chapter is reprinted with permission from *Geochimica et Cosmochimica Acta*, 148, Harrison, A. L., Dipple, G.M., Power, I.M. and Mayer, K. U., Influence of surface passivation and water content on mineral reactions in unsaturated porous media: Implications for brucite carbonation and CO₂ sequestration, 477-495, Copyright (2014), with permission from Elsevier. The supporting information for this manuscript is reproduced in this thesis as Appendix 3: Appendix to Chapter 5. I designed the experiments with input from I.M. Power and G.M. Dipple. I conducted the experiments, most of the sample analysis, and all of the reactive transport modeling. I.M. Power and I performed microscopy. G.M. Dipple, K.U. Mayer and I developed a new function describing surface passivation effects in the reactive transport code, MIN3P-DUSTY. K.U. Mayer provided guidance in the implementation of this function in MIN3P-DUSTY and the modeling of experiments. I interpreted the data with input from all authors, and I wrote the manuscript. G.M. Dipple, I.M. Power, and K.U. Mayer helped with revisions and editing of the manuscript. All authors confirm that this is an accurate reflection of the author contributions and agree to the use of this manuscript in this thesis.

Chapter 6 has been prepared for submission to an international peer-reviewed academic journal. The appendix to this chapter (Appendix 4: Appendix to Chapter 6) will be submitted as the supporting information to the manuscript. The manuscript is authored as follows: A.L. Harrison, G.M. Dipple, K.U. Mayer and I.M. Power. G.M. Dipple and K.U. Mayer

conceived the study. I designed the experiments with advice from all authors. I conducted the experiments and I.M. Power provided assistance in the laboratory and with sampling. I.M. Power and I performed microscopy. I interpreted the data with input from all authors. G.M. Dipple, K.U. Mayer, and I developed conceptual models to explain the observed extent of reaction in the experiments that were implemented in MIN3P-DUSTY. K.U. Mayer helped with this implementation, and the addition of a formulation in MIN3P-DUSTY to account for water loss during reaction. I wrote the manuscript, and all authors contributed to revisions and editing of the manuscript. All authors confirm that this is an accurate reflection of the author contributions and agree to the use of this manuscript in this thesis.

A version of Chapter 7 is published in *International Journal of Greenhouse Gas Control*. This chapter is reprinted with permission from *International Journal of Greenhouse Gas Control*, 25, Wilson, S. A., Harrison, A. L., Dipple, G. M., Power, I. M., Barker, S. L. L., Mayer, K. U., Fallon, S. J., Raudsepp, M. and Southam, G., Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining, 121-140, Copyright (2014), with permission from Elsevier. This manuscript was a collaborative effort with Dr. Siobhan A. Wilson, the lead author and several co-authors. As second author, I conducted reactive transport modeling and contributed to the writing and editing of the manuscript. This study consisted of three main aspects: 1) field work and analysis of field samples to quantify and verify atmospheric CO₂ mineralization within an active mine tailings storage facility, 2) reactive transport modeling to explain the observed abundance and distribution of carbonate mineral precipitates and estimate the rate of CO₂ sequestration, and 3) recommendations for tailings management and ore processing practices that could enhance CO₂ sequestration within mine tailings storage facilities to offset greenhouse gas emissions. I was not involved in part 1; this was lead by S.A. Wilson with contributions from most of the other co-authors. I.M. Power, G.M. Dipple, and G. Southam helped with fieldwork, while S.L.L. Barker, and S.J. Fallon contributed to the analysis of field samples. These parts of the manuscript were written by S.A. Wilson. I led part 2, the reactive

transport modeling, which involved developing the conceptual model for reactive transport at the site, tailoring the numerical model MIN3P-THM to apply to this conceptual framework, and testing hypotheses to describe the observed variation in tailings mineralogy at the mine site using MIN3P-THM. I wrote the sections of the manuscript describing the modeling methods, results, and interpretations. K.U. Mayer advised on the conceptual model and application of MIN3P-THM, and S.A. Wilson, G.M. Dipple, and I.M. Power advised on the conceptual framework and interpretation of results. Part 3 was a joint effort. Recommendations were made to accelerate CO₂ sequestration based on the interpretations stemming from the field and analytical work, as well as the reactive transport modeling. The reactive transport modeling provided insight into the physical constraints (e.g., hydraulic conductivity, CO₂ transport at depth) that may dictate the choice of acceleration strategy at a mine site, and helped confirm that carbon mineralization is largely restricted by the limited access of reactive minerals to CO₂. The conclusions of the paper were therefore influenced by the inclusion of the reactive transport modeling. G.M. Dipple and S.A. Wilson conceived the study, with input from G. Southam and M. Raudsepp. S.A. Wilson, G.M. Dipple, A.L. Harrison, I.M. Power, K.U. Mayer, and M. Raudsepp interpreted results. S.A. Wilson, A. L. Harrison, I.M. Power, and G.M. Dipple contributed to preparation of the manuscript. Because the modeling depended upon and complemented the field results and interpretations, my supervisory committee and I agreed that the published manuscript should be included in its entirety in this thesis. All authors confirm that this is an accurate reflection of the author contributions, and agree to the use of the *International Journal of Greenhouse Gas Control* paper in this thesis.

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List of Symbols and Abbreviations

GHG – greenhouse gas

IPCC – Intergovernmental Panel on Climate Change

MKM – Mount Keith Nickel Mine

$p\text{CO}_2$ – CO_2 partial pressure

DIC – dissolved inorganic carbon

wt.% - weight percent

XRD – X-ray diffraction

LGR – Los Gatos Research

[Mg] – aqueous magnesium concentration

$\delta^{13}\text{C}$ – delta carbon-13

$\delta^{13}\text{C}_{\text{DIC}}$ – delta carbon-13 of dissolved inorganic carbon

$\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ – delta carbon-13 of gaseous CO_2

VPDB – Vienna Pee Dee Belemnite

SEM – scanning electron microscopy

n_{xi} – initial moles of ‘x’

SA – surface area

t – time

m_{ix} – initial mass of ‘x’

m_{fx} – final mass of ‘x’

M_x – molar mass of ‘x’

C_r – reactive capacity

F_{brc} – brucite content of tailings as fraction of tailings mass

m_t – mass of tailings

FW_{brc} – gram formula weight of brucite

b – stoichiometric coefficient for carbonation of brucite

r_{CO_2} – rate of CO₂ supply

S_{brc} – surface area of brucite in tailings

r_{brc} – estimated carbonation rate of brucite with ‘flue gas’ (~10% CO₂)

USEPA – United States Environmental Protection Agency

GWI – gas-water interfacial area

GMI – gas-mineral interfacial area

MWI – mineral-water interfacial area

Da – Damköhler number

t_{res} – residence time of the fluid

k – kinetic dissolution rate constant

C_{eq} – solubility of the mineral phase

vol.% – volume percent

XRF – X-ray fluorescence spectroscopy

BET – Brunauer–Emmett–Teller

$r_{instant}$ – instantaneous carbonation rate (g CO₂ h⁻¹)

m_i – column mass at time ‘i’

r_{brc} – brucite dissolution rate

k_{eff}^0 – effective rate constant

k^0 – initial kinetic dissolution rate constant

[HCO₃⁻] – aqueous bicarbonate concentration

Ω – saturation ratio

SX – reaction stage ‘X’

brc – brucite

qtz – quartz

nsq – nesquehonite

VWC – volumetric water content

$\frac{Mg}{C}$ – ratio of moles Mg consumed to moles CO₂ sequestered during carbonation

n_{xf} – final moles of ‘x’
 φ^0 – initial brucite volume fraction
 φ^t – brucite volume fraction at time ‘t’
 φ^p – threshold brucite volume fraction
 k_{eff}^g – effective geometric rate constant
 k_{eff}^t – effective threshold rate constant
 LM – Lane Mountain
 φ_z^0 – initial volume fractions at depth ‘z’
 φ_z^p – initial volume fractions at depth ‘z’
 S_w – water saturation (fraction of pore volume occupied by water)
 CCS – carbon capture and storage
 $\delta^{18}\text{O}$ – delta oxygen-18
 $F^{14}\text{C}$ – fraction modern carbon
 TSF – tailings storage facility
 SSAMS – Single Stage Accelerator Mass Spectrometer
 MAD – median absolute deviation
 VSMOW – Vienna Standard Mean Ocean Water
 α_{A-B} – isotopic fractionation factor between substances ‘A’ and ‘B’
 $p\text{O}_2$ – O_2 partial pressure
 K_{sat} – saturated hydraulic conductivity
 AUD – Australian dollars
 EU ETS – European Union Emissions Trading Scheme
 XRPD – X-ray powder diffraction
 θ – scattering angle of X-rays
 PDF-4+ – Powder Diffraction file, version 4+
 ICP-OES – inductively coupled plasma - optical emission spectrometry
 TOC-TN – total organic carbon - total nitrogen

R_{sample} – $^{13}\text{C}/^{12}\text{C}$ ratio in a sample

$R_{standard}$ – $^{13}\text{C}/^{12}\text{C}$ ratio in a standard

FE-SEM – field emission scanning electron microscopy

IAP – ion activity product

K – equilibrium constant

k_{Mg} – brucite dissolution rate constant in the absence of ligands at pH 8.5

$K_{\text{Mg-HCO}_3^-}$ – adsorption constant of HCO_3^- on brucite surface sites

$k_{\text{HCO}_3^-}$ – rate constant in the presence of HCO_3^-

nd – no data

LLNL – Lawrence Livermore National Laboratories

NIST – National Institute of Standards and Technology

EDS – energy dispersive spectroscopy/spectrum

α – van Genuchten parameter

n – van Genuchten parameter

m – van Genuchten parameter

S_{rl} – residual water saturation

q_g – Darcy flux

k_{rg} – relative permeability with respect to the gaseous phase

μ_g – viscosity of gaseous phase

k – intrinsic permeability

p_g – gaseous phase pressure

ρ_g – density of the gaseous phase

g – acceleration due to gravity

z – vertical distance

S_{ea} – effective saturation

q_{g_0} – initial Darcy flux at residual saturation

ΔV_s – solid volume change

v_x – stoichiometric coefficient of a given reactant or product

ρ – density

ΔV_w – water volume change

ΔV_p – gas-filled pore volume change

mbgs – meters below ground surface

A – cross-sectional area

Q – volumetric flow rate

$\frac{dh}{dl}$ – head gradient

r_{CO_2} – CO₂ sequestration rate (mol s⁻¹)

List of Supplementary Materials

- Video AM1. Brucite carbonation in a micromodel. The video consists of time lapse images taken at 5 minute intervals using a light microscope played at two frames per second. The entire duration shown is ~7.3 h with a field of view of 3.4 mm × 2.2 mm. Black frames replace frames that have been removed due to technical problems with the microscope. Red arrows indicate two occurrences of nesquehonite precipitation in the brucite-rich zone. This video can be found in the Accompanying Materials located in the Supplementary Thesis Materials and Errata Collection: <http://hdl.handle.net/2429/51487>
- Video AM2. Carbonate precipitation and brucite carbonation in a micromodel. The video consists of time lapse images taken at 5 minute intervals using a light microscope played at two frames per second. The entire duration shown is ~10 h with a field of view of 1.9 mm × 1.3 mm. Black frames replace frames that have been removed due to technical problems with the microscope. This video can be found in the Accompanying Materials located in the Supplementary Thesis Materials and Errata Collection: <http://hdl.handle.net/2429/51487>

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*This work is dedicated to my parents, Jed and Dawn, and to my brother,
Nigel.*

1. Introduction

1.1 CO₂ sequestration via carbon mineralization

The accumulation of anthropogenic greenhouse gases (GHGs), mainly CO₂, in the atmosphere has been identified as a cause of global climate change (IPCC, 2007). Carbon sequestration is one of many strategies necessary to stabilize CO₂ concentrations and prevent irreversible climate change while transitioning to alternative energy sources (Hoffert et al., 2002; Pacala and Socolow, 2004; Broecker, 2007). Carbon mineralization, also known as mineral carbonation, is a promising option for CO₂ sequestration as the reaction products are environmentally benign and stable, providing little possibility of accidental release and reducing the need for post-storage monitoring (Seifritz, 1990; Lackner et al., 1995; Lackner et al., 1997; Lackner, 2003; Sipilä et al., 2008). Research in mineral carbonation has largely focused on industrial processes that use high temperatures and pressures (e.g., 185°C, 150 atm) to accelerate reaction rates (Béarat et al., 2002; Gerdemann et al., 2007; Sipilä et al., 2008; Zevenhoven et al., 2008; Fagerlund et al., 2009; Krevor and Lackner, 2009; Koukoulas et al., 2009), however the financial and energy costs of such methods has limited their implementation. Alternatives to this approach include injection of supercritical CO₂ or CO₂-rich gases or fluids into subsurface mafic and ultramafic formations (Kelemen and Matter, 2008; Alfredsson et al., 2008; Oelkers et al., 2008; Matter and Kelemen, 2009; Schaef et al., 2010; Gislason et al., 2010; Kelemen et al., 2011; Schaef et al., 2011; Van Pham et al., 2012; Paukert et al., 2012; Schaef et al., 2013a; Hellevang et al., 2013; Schaef et al., 2013b; Galeczka et al., 2014; Gislason and Oelkers, 2014), or alkaline industrial waste stockpiles (Bobicki et al., 2012; Power et al., 2013b and references therein), and direct air capture at Earth's surface conditions via enhanced weathering of pulverized rock or wastes (Wilson et al., 2006; Renforth et al., 2009; Schuiling and Boer, 2010; Pronost et al., 2011; Renforth et al., 2011; Assima et al., 2012; Washbourne et al., 2012; Assima et al., 2013a; Assima et al., 2013b; Wilson et al., 2014).

Although of lower capacity than natural rock, carbonation of industrial wastes such as steel and blast furnace slag, waste from alumina production, alkaline and saline waste water, and mine tailings is a promising CO₂ sequestration option, as it exploits available waste materials that tend to be inherently more reactive than natural minerals (Huijgen and Comans, 2006; Wilson et al., 2006; Dilmore et al., 2008; Eloneva et al., 2008; Ferrini et al., 2009; Khaitan et al., 2010; Power et al., 2010; Gunning et al., 2010; Wilson et al., 2010; Pronost et al., 2011; Morales-Flórez et al., 2011; Back et al., 2011; Mignardi et al., 2011; Power et al., 2011b; Bobicki et al., 2012; Power et al. 2013a; Power et al., 2013b; Power et al., 2014a; McCutcheon et al., 2014). The study of controls on reactivity of these materials provides valuable insight into reaction mechanisms that may also operate in natural mafic and ultramafic rock formations that have greater total sequestration capacity, while providing a meaningful offset of GHG emissions at the industry level (Power et al. 2013c; Power et al., 2013b). For example, Power et al. (2013b) estimate that conscription of mining wastes produced globally for carbon mineralization could offset approximately 1.5% of annual global CO₂ emissions.

1.2 Carbon mineralization in ultramafic mine tailings

It has been well documented that surface weathering of ultramafic mine tailings sequesters atmospheric CO₂ under normal mining conditions via formation of hydrated Mg-carbonate phases (Wilson et al., 2006; Wilson, 2009; Wilson et al., 2009a; Wilson et al., 2011; Bea et al., 2012; Pronost et al., 2012; Beinlich and Austrheim, 2012; Oskierski et al., 2013). This passive process has been observed at historic Canadian and Australian chrysotile mines (Wilson et al., 2006; Wilson et al., 2009a; Pronost et al., 2012; Oskierski et al., 2013), in historic chromite mine shafts (Beinlich and Austrheim, 2012), and at the active Australian Mount Keith Nickel Mine (MKM) (Wilson, 2009; Bea et al., 2012) and Canadian Diavik Diamond mine (Wilson et al., 2011). Passive carbon mineralization reactions in these environments are facilitated by the high surface areas of the tailings minerals (Wilson et al., 2009a), yet are limited by the uptake

of CO₂ into solution (Wilson et al., 2010). Although the carbon sequestration potential of ultramafic tailings is significant, it remains largely under-utilized. Large mines, such as MKM, have the capacity to offset the GHG emissions of their mining operations, and potentially emissions from other sources. Complete carbonation of tailings produced annually at MKM (~11 Mt; BHP Billiton, 2005) exceed total annual mine emissions by more than a factor of ten. Yet, Wilson (2009) estimates that passive carbonation rates at MKM currently offset annual mine emissions by only ~15%. In order to exploit the full CO₂ sequestration capacity at mine sites, current carbon mineralization rates must be accelerated.

A growing body of research has provided insight into the rates and mechanisms of passive carbon mineralization in mine tailings and wastes (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2011; Bea et al., 2012; Pronost et al., 2012; Beinlich and Austrheim, 2012; Oskierski et al., 2013), and several recent experimental studies have elucidated controls on the sequestration capacity and rate of reaction of bulk tailings (Pronost et al., 2011; Assima et al., 2012; Assima et al., 2013a; Assima et al., 2014a; Assima et al., 2014b). Recent developments in reactive transport modeling have also provided insight into the controls on passive carbonation rates (Bea et al., 2012). However, the development of strategies to accelerate carbonation rates at mine sites is still in its infancy (e.g., Power et al., 2014a), and the capability of reactive transport models to capture the governing reaction mechanisms and to predict the fate of CO₂ under accelerated carbonation scenarios remains untested. Here, strategies that accelerate carbon mineralization reactions by increasing the supply of CO₂ were investigated experimentally (Chapters 2-6). These experimental trials were supplemented by a collaborative study of the mechanisms of passive carbon mineralization in the active tailings storage facility at the Mount Keith Nickel Mine (Chapter 7). Experimental studies were focused on reaction of brucite [Mg(OH)₂], a mineral commonly present at low abundance (~1-15 wt.%) in ultramafic mine tailings and residues (Wilson, 2009; Chrysochoou et al., 2009; Pronost et al., 2011; Assima et al., 2012; Bea et al., 2012; Assima et al., 2013a; Assima et al., 2013b; Assima et al., 2014a). Brucite is highly reactive in comparison to the more abundant silicate

phases such as forsterite [Mg_2SiO_4] and serpentine-group minerals [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$] (Bales and Morgan, 1985; Pokrovsky and Schott, 2000; Pokrovsky and Schott, 2004; Pronost et al., 2011; Assima et al., 2013a; Daval et al., 2013; Thom et al., 2013; Power et al., 2013b; Assima et al., 2014a) and its carbonation could provide immediate and significant CO_2 offsets at mine sites (e.g., up to ~60% offset of annual mine emissions at MKM). To better predict the fate of CO_2 in tailings storage facilities and to estimate CO_2 sequestration capacity, the capabilities of the existing reactive transport code, MIN3P (Mayer et al., 2002; Molins and Mayer, 2007; Bea et al., 2012), were extended to include new processes that were experimentally observed to govern carbonation. The insight provided by the experiments and improved modeling capabilities will help guide implementation of accelerated carbonation strategies at mine sites, with implications for carbonation of other industrial wastes and natural rock of similar mineralogical composition.

1.3 Fundamental processes of water-rock interaction in the Earth's shallow subsurface

As a naturally occurring process, carbon mineralization is also an important part of the global carbon cycle that regulates atmospheric CO_2 concentrations over geologic time (Berner et al., 1983). However, identification of rate-controlling mechanisms is challenging in natural systems due to the multitude of factors that may concurrently affect reaction rates (Maher et al., 2006). The prediction of reaction rates in water unsaturated porous media is hindered by difficulties in accurately quantifying reactive surface area, capturing the effect of pore scale chemical and physical heterogeneities on reaction rates, and the response of these variables to dynamic wetting and drying processes. For instance, secondary precipitates may coat the surfaces of reacting minerals with the potential to passivate reactive surfaces, but the effect of these coatings is variable (c.f., Hodson, 2003; Park and Fan, 2004; Cubillas et al., 2005; Béarat et al., 2006; Lekakh et al., 2008; Andreani et al., 2009; Huntzinger et al., 2009; Daval

et al., 2009a; Daval et al., 2009b; Daval et al., 2011; Stockmann et al., 2011; Stockmann et al., 2013). Pore scale heterogeneities in water distribution may also reduce the surface area available for reaction by leaving some mineral surfaces unexposed to reactive fluids (e.g., Pačes, 1983). Wetting and drying cycles may alter the reactivity over time, particularly for reactions that involve hydrous minerals whose dissolution and precipitation also modify the local water content. The experimental investigation of carbon mineralization reactions, and brucite carbonation in particular, is a fitting approach to study water-rock-gas interactions in general, due to the coupled nature of the reactions and rapid reaction rates that permit significant reaction progress on experimental timescales. The experimental studies conducted for this thesis therefore provided insight into fundamental controls on reactivity during coupled dissolution-precipitation reactions in the shallow subsurface that are addressed in Chapters 4-6. The experiments spanned reaction scales from the fluid-mineral interface to pore to porous media scale using batch and microfluidic reactors, and decimeter and meter scale column apparatus (Fig. 1.1). The broad range of reaction scales studied provided important insight into the effects of water saturation, the evolution of reactive surface area, and the previously unheralded process of evaporative-driven particle movement on mineral reactivity in conditions representative of the Earth's shallow subsurface. The experimental results are presented in the context of their application to CO₂ sequestration and the broader implications for mineral dissolution-precipitation reactions in natural and anthropogenic porous media.

1.4 Objectives and organization

The objectives of this thesis are to elucidate the controlling reaction mechanisms during carbonation of brucite in order to help design CO₂ sequestration strategies employing carbon mineralization in near surface environments, namely ultramafic mine tailings, and to ameliorate the fundamental understanding of mineral dissolution-precipitation reactions in unsaturated porous media. A combination of experimental, analytical, and reactive transport

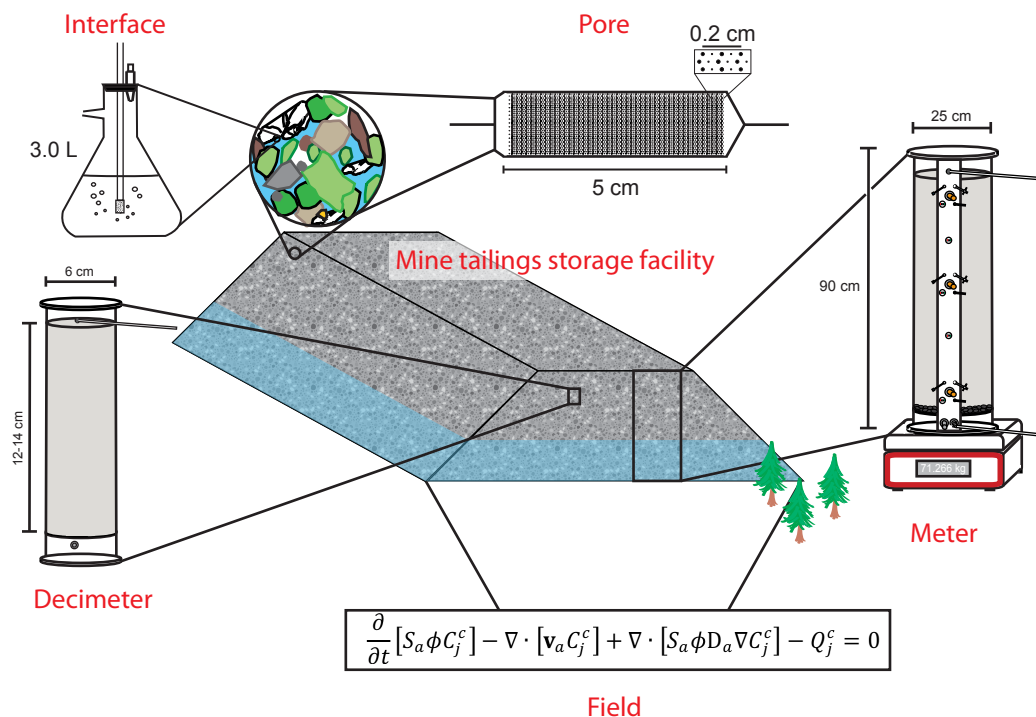


Figure 1.1. Conceptual diagram of the scales of processes studied in this thesis. Batch reactors were used to explore reactions at the mineral-solution interface, as detailed in Chapter 2, and extrapolated from in Chapter 3. Microfluidic reactors were employed to study reactions at the pore scale in Chapter 4. Decimeter and meter scale column reactors were used to elucidate reactive transport processes at the porous medium scale (Chapters 5 and 6). Numerical reactive transport modeling helped the interpretation of reaction mechanisms and determination of rates from the porous medium to field scale (Chapters 5-7).

modeling techniques are used to investigate brucite and mine tailings carbonation from the mineral-solution interface to field scale (Fig. 1.1).

Five manuscripts and a conference proceedings article have been assembled that describe these investigations. The second chapter of this thesis (Chapter 2) presents an experimental study conducted using “zero-dimensional” stirred batch reactors to ascertain the effect of increased CO₂ supply on brucite carbonation rates. The zero-dimensional nature of these experiments allowed the surface controlled reactions at the mineral-water interface to be examined. This chapter presents a ‘proof-of-concept’ study that demonstrates the potential to accelerate mineral carbonation rates in mine tailings by supplying gas streams with elevated

CO₂ concentrations. This manuscript was published in *Environmental Science & Technology* in 2013.

Chapter 3 is a follow-up to the work presented in Chapter 2, which uses the experimental results to evaluate potential CO₂ sequestration strategies that could be employed at mine sites. The experimentally determined carbonation rates are applied to estimate rates of CO₂ sequestration achievable at the Mount Keith Nickel Mine in Western Australia, compared to rates of CO₂ supply. The rate at which CO₂ could be injected into tailings as a function of brucite content and tailing deposition rates were estimated to outline conditions under which CO₂ leakage to the atmosphere could be avoided. All calculations were conducted assuming rates from the zero-dimensional reactors would be portable to field scale, an assumption fraught with uncertainty. This manuscript was published in the peer-reviewed conference proceedings for the International Mine Water Association 2013 Mine Water Conference.

The fourth chapter is a study that investigated the fundamental controls on rates and distribution of mineral dissolution-precipitation reactions at the pore scale. Microfluidic techniques were applied to elucidate the impact of evaporative processes on CO₂ dissolution and fixation in the unsaturated zone at the pore scale and revealed a number of previously unheralded processes that exert considerable influence on reaction rates. It is demonstrated that the dynamic evolution of the gas-water interface, water content, and mineral to water ratio may significantly alter reaction rates as the volume of water filled pore space evolves.

Chapter 5 presents an experimental examination of the reproducibility of the reaction rates achieved in the homogeneous batch reactors to a porous medium with one-dimensional flow, and the scaling-up of reaction processes observed at the interface and pore scale. The objective of this study was to evaluate the effect of water saturation and precipitation of hydrous Mg-carbonates at the brucite surface on reaction progress in an environment physically representative of natural and anthropogenic porous media, such as mine tailings. Decimeter scale column experiments containing brucite were supplied with 10% CO₂ gas streams. Numerous studies have investigated the effect of surface coatings on mineral dissolution rates

but have reported conflicting results (c.f., Hodson, 2003; Park and Fan, 2004; Cubillas et al., 2005; Béarat et al., 2006; Lekakh et al., 2008; Andreani et al., 2009; Huntzinger et al., 2009; Daval et al., 2009a; Daval et al., 2009b; Daval et al., 2011; Stockmann et al., 2011; Stockmann et al., 2013). Such studies typically employ zero-dimensional, fluid dominated batch reactors (Park and Fan, 2004; Daval et al., 2009a; Daval et al., 2009b; Stockmann et al., 2011; Stockmann et al., 2013), and are often complicated by concomitant precipitation of both silicate and carbonate minerals (e.g., King et al., 2010), hampering unambiguous identification of the passivating effects of carbonates alone. The experiments conducted for this thesis used brucite, a silica-free mineral. Therefore, the effect of Mg-carbonate precipitates could be assessed directly, without the complication of silica layer formation. Moreover, passivating effects may differ in the mineral dominated columns compared to batch reactors, due to the limited pore volume in which secondary phases can form, and the relative scarcity of water. Experiments of varying water saturation were conducted in order to distinguish between surface passivation-limited and water-limited reaction at conditions relevant for the shallow subsurface, with additional insight from reactive transport modeling using MIN3P-DUSTY. A version of this chapter is currently under review for publication in a peer-reviewed journal.

In Chapter 6, the results of larger (meter-scale), instrumented column experiments are presented. The objectives of this study were to ascertain the impact of water saturation on the availability of reactive surface area and reactive capacity of a porous medium, and to investigate the evolution of the effective reactive surface area of brucite during reaction. The larger size of the experimental apparatus compared to those conducted for Chapter 5 allowed for installation of instrumentation and sampling ports at multiple locations along the flow path without significant disruption of gas flow. This provided better constraints for the further development of the reactive transport model used in Chapter 5, in particular, by providing spatial and temporal evolution of the gas phase CO_2 concentration and pore water chemistry, important indicators of reaction progress. Moreover, the greater range in water saturation achieved along the flow path permitted a more in depth investigation of the effects of water

saturation on both brucite reactivity and gas flow. These data allowed for better assessment of the effect of water saturation on reactive surface area and CO₂ sequestration capacity.

Chapter 7 was a collaborative effort that studied carbon mineralization reactions at field scale in the active tailings storage facility at the Mount Keith Nickel Mine in Western Australia. The objective of this study was to identify mechanisms of carbon mineralization and quantify the rate of passive CO₂ sequestration. My contribution was to conduct reactive transport modeling using MIN3P (Bea et al., 2012) to describe the observed variation in tailings mineralogy and to estimate rates of CO₂ fixation. Results of the modeling were used to make recommendations for tailings management and ore processing practices that would maximize CO₂ sequestration at mine sites. Siobhan A. Wilson conducted most of the fieldwork at Mount Keith and the analyses of field samples, with contributions from several co-authors. These field data were used to constrain the reactive transport modeling. The modeling depends upon and complements the field data, therefore the entire manuscript, which includes Dr. Wilson's contributions, is included as Chapter 7 in this thesis. Chapter 7 was published in *International Journal of Greenhouse Gas Control* (Wilson et al., 2014).

In combination, this thesis provides new information on some of the fundamental controls on mineral dissolution-precipitation reactions in conditions representative of the Earth's shallow subsurface, using brucite carbonation as a model reaction (refer to conclusions in Chapter 8). Owing to the relevance of brucite carbonation for CO₂ sequestration strategies, this thesis makes a meaningful contribution towards the development of technologies to offset greenhouse gas emissions, with particular implications for CO₂ sequestration in ultramafic mine tailings.

2. Accelerated carbonation of brucite in mine tailings for carbon sequestration¹

2.1 Introduction

The accumulation of anthropogenic greenhouse gases (GHGs), predominantly CO₂, in the atmosphere has been identified as a cause of climate change (IPCC, 2007). Carbon sequestration is one of many strategies necessary to stabilize CO₂ concentrations while transitioning to alternative energy sources (Hoffert et al., 2002; Lackner, 2003; Pacala and Socolow, 2004; Broecker, 2007). Carbon mineralization involves dissolution of non-carbonate minerals (e.g., silicates, hydroxides, and oxides) and subsequent precipitation of carbonate minerals, which sequesters CO₂ (Seifritz, 1990; Lackner et al., 1995; Lackner et al., 1997; Lackner, 2003). This is a promising option for carbon sequestration as carbonate minerals are environmentally benign and stable, providing little possibility of accidental release and reducing the need for post-storage monitoring (Lackner et al., 1995; Sipilä et al., 2008). Research in carbon mineralization has largely focused on industrial processes that use elevated temperatures and pressures to accelerate carbonation reaction rates (e.g., 185°C, 150 atm; Béarat et al., 2002; Gerdemann et al., 2007; Sipilä et al., 2008; Zevenhoven et al., 2008; Fagerlund et al., 2009; Krevor and Lackner, 2009; Koukoulas et al., 2009), however, the financial and energy costs of such methods limits their viability. To avoid such costs, research has been directed towards developing carbon mineralization strategies at low temperature and pressure conditions (Manning, 2008; Power et al., 2009; Wilson et al., 2009a; Renforth et al., 2009; Schuiling and Boer, 2010; Pronost et al., 2011; Wilson et al., 2011). Carbonation of industrial wastes such as steel and blast furnace slag, and alkaline and saline waste water is advantageous as it exploits available waste materials (Huijgen and Comans, 2006; Wilson et al., 2006; Dillmore et al., 2008; Eloneva et al., 2008a; Ferrini et al., 2009; Power et al., 2010; Gunning et al., 2010;

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Wilson et al., 2010; Morales-Flórez et al., 2011; Back et al., 2011; Mignardi et al., 2011; Power et al., 2011b; Bobicki et al., 2012).

Passive carbon mineralization in mine tailings under normal mining conditions has been well documented (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2010; Wilson et al., 2011; Pronost et al., 2012). This process has been recognized at historic and active Canadian chrysotile and diamond mines (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2011), and at the active Mount Keith Nickel Mine (MKM) in Western Australia (Wilson, 2009). Carbonation of tailings is facilitated by high surface areas (Wilson et al., 2009a) yet at MKM, reaction rates are limited by the uptake of CO₂ into solution (Wilson et al., 2010; Bea et al., 2012). If passive carbonation of bulk tailings were accelerated at large mines, it could more than offset the GHG emissions of mining operations. Supplying elevated (above atmospheric) partial pressures of CO₂ ($p\text{CO}_2$) into tailings may accelerate carbonation both by enhancing mineral dissolution due to increased acidity (Vermilyea, 1969; Pokrovsky and Schott, 2000; Pokrovsky and Schott, 2004) and promoting carbonate mineral precipitation due to elevated dissolved inorganic carbon (DIC) concentration.

Carbonation of brucite [Mg(OH)₂], a common but minor component of ultramafic mine tailings, offers significant sequestration potential. It has been documented at between 1-15 wt.% in chrysotile tailings, nickel tailings and deposits, and in chromite ore processing residue (Wilson, 2009; Chrysochoou et al., 2009; Pronost et al., 2011). In Québec, Canada, there is an estimated 2 Gt of chrysotile mining residue (Larachi et al., 2010), some of which contains 1.8 wt.% brucite (Pronost et al., 2011). If these brucite contents are representative of the entire chrysotile stockpile, up to 27 Mt of CO₂ could be sequestered via brucite carbonation alone. At active mine sites, accelerated carbonation of brucite in tailings provides the potential to significantly offset the annual GHG emissions of mining operations. At MKM, ~11 Mt of tailings are produced annually, containing 0.11-0.28 Mt brucite (BHP Billiton, 2005; Wilson, 2009). Carbonation of the brucite produced annually would offset mine emissions (370 kt yr⁻¹ CO₂ equivalent; BHP Billiton, 2005) by 22-57%. Yet, passive carbonation rates at MKM and the

Black Lake chrysotile mine in Québec are estimated at only ~ 56 and ~ 0.6 kt yr⁻¹, respectively (Wilson, 2009; Pronost et al., 2012). Incorporation of accelerated carbonation methods in the design of prospective mines offers the potential to significantly offset emissions throughout the lifetime of mining operations. At the Dumont Nickel deposit in Québec, for instance, assuming homogeneous brucite distribution in processed nickel ore of 10-15 wt.% (Pronost et al., 2011) and a similar scale of operations as MKM, accelerated brucite carbonation could exceed that predicted for MKM. Therefore, despite its minor abundance, brucite carbonation could provide a meaningful CO₂ sink on the scale of mine emissions.

The goal of this study was to investigate the mechanisms of brucite carbonation in mine tailings and to identify the rate-limiting steps in order to design methods for accelerating carbon sequestration in tailings. The effect of elevated $p\text{CO}_2$ at 1 atm total pressure on the carbonation rate of brucite was investigated experimentally in batch reactors. Investigation of brucite carbonation may also guide ongoing work to accelerate carbonation of Mg-silicate minerals in tailings, which constitute the majority of ultramafic tailings and offer greater total sequestration capacity.

2.2 Methods

Brucite slurries (3.0 L) were prepared in side arm flasks (A1 Fig. A1.1). The solution composition mimicked that of pore water at MKM (1.0 M NaCl, and 0.1 M MgCl₂·6H₂O; Stolberg, 2005). High purity pulverized brucite ore (150 g; grain size = 2-40 μm diameter; surface area = 6.6 m² g⁻¹) from Brucite Mine, Nevada was added to each solution just prior to supplying CO₂ gas. Rietveld refinement of X-ray diffraction (XRD) data indicated the brucite ore was between 90-95 wt.% brucite with minor dolomite and trace lizardite. Mixtures of CO₂ and N₂ gas were bubbled into continuously stirred slurries using glass sparge tubes. Gases were blended using a two-tube gas blender. CO₂ concentration of the supplied gas stream was varied between experiments for values of 10%, 50%, and 100% CO₂ at a total flow rate

of 540 mL min^{-1} , which was divided evenly between duplicate experiments that were run simultaneously. Duplicate experiments are henceforth referred to as ‘X% CO_2 1 and 2.’ Three experiments were run using laboratory air ($p\text{CO}_2 \approx 0.04\%$) supplied at $\sim 270 \text{ mL min}^{-1}$ using a peristaltic pump to act as experimental controls and establish the carbonation rate at low $p\text{CO}_2$. Slight differences in the reactivity of duplicate reactors occurred due to imperfect mixing that resulted in occasional settling of brucite particles, which were re-suspended manually when observed.

Flasks were vented through the side arm to maintain atmospheric pressure. The exhaust of high $p\text{CO}_2$ experiments was directed into a Los Gatos Research (LGR)[®] off-axis integrated cavity output laser spectrometer for continuous measurement of CO_2 concentration (Barker et al., 2011). All gas composition data represent the combined exhaust from duplicate, simultaneous, high $p\text{CO}_2$ reactors.

Slurry temperature and pH were measured routinely and water samples for DIC and Mg concentrations ($[\text{Mg}]$), and $\delta^{13}\text{C}_{\text{DIC}}$ (Craig, 1957) were collected regularly. Solid samples were taken at the same time for mineralogical analysis using XRD, $\delta^{13}\text{C}$ and carbon abundance ($\%C$) analysis, and imaging using scanning electron microscopy (SEM). System mass before and after sampling and the mass of each sample were measured. At the end of each experiment, slurries were filtered to collect and weigh all solids.

The experimental durations were 198, 56, and 72 h for the 10%, 50%, and 100% CO_2 experiments, respectively. Two short-term experiments using atmospheric CO_2 were run for 56 and 72 h to serve as experimental controls (i.e., systems with negligible carbonation). A third atmospheric CO_2 experiment was conducted for 2856 h to establish background carbonation rates. The high $p\text{CO}_2$ experiments were terminated upon achievement of steady-state conditions. For further details regarding experimental setup and analytical techniques, refer to Appendix 1 (A1).

2.3 Results and discussion

2.3.1 Chemical environment

There are three main requirements to allow carbonation to occur *in situ* in tailings facilities: (1) CO_2 is available in solution as DIC, (2) cations are available, and (3) the chemical environment promotes both tailings mineral dissolution (cation leaching), and carbonate mineral precipitation (Fig. 2.1).

In all reactors, initial pH values following brucite addition were between 9.3 and 9.4 and initial DIC concentration ranged from 15 to 26 mg L^{-1} . Initial DIC content is attributed to dissolution of laboratory air into the saline solutions prior to sparging of gas. In the 10% and 50% CO_2 reactors, an abrupt initial drop in pH was followed by a period of relatively constant pH before declining to a final stable pH of ~ 7.6 and ~ 7.1 in the 10% and 50% experiments, respectively (Fig. 2.2A). In the 100% CO_2 reactors pH declined rapidly to a minimum stable value of ~ 6.9 after 10 h. Initial drops in pH were coincident with rapid increases in both DIC and $[\text{Mg}]$ in all high $p\text{CO}_2$ reactors owing to $\text{CO}_{2(g)}$ and brucite dissolution, respectively (Figs. 2.2A, 3A and B). The pH value and duration of the first pH stabilization and final pH were dependent on the $p\text{CO}_2$ in the reactor atmospheres (Fig. 2.2A). During the first 6-8 h in the 10% CO_2 experiments, DIC and $[\text{Mg}]$ increased, before declining to reach near constant values during the period of 12-46 h (Fig. 2.3A-B). The relatively stable DIC during this period is

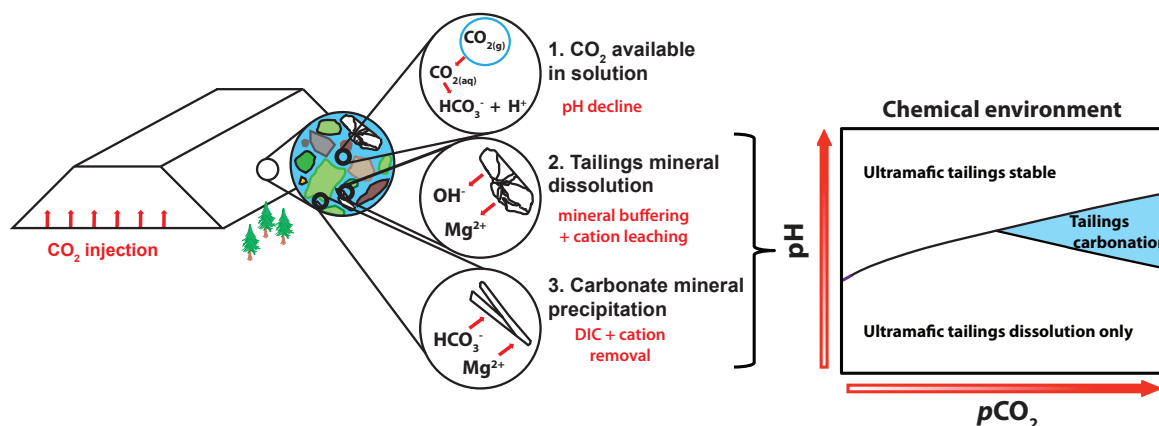


Figure 2.1. Schematic of carbon mineralization *in situ* in a tailings storage facility.

indicative of a quasi-steady-state wherein brucite carbonation was balanced by CO_2 uptake into solution. The final stable pH value was lower at higher $p\text{CO}_2$, resulting in a greater proportion of Mg and DIC remaining in solution (Figs. 2.2A, 2.3A-B, Table 2.1). Final DIC and [Mg] stabilized approximately at equilibrium with the hydrated carbonate mineral, nesquehonite $[\text{MgCO}_3 \cdot 3\text{H}_2\text{O}]$, as calculated with PHREEQC (Parkhurst and Appelo, 1999) using the Pitzer database (Fig. 2.3A-B).

In the long-term atmospheric CO_2 experiment, pH reached a minimum of 9.0. An initial increase in DIC in this experiment to 80 mg L^{-1} after 192 h was followed by a decline to 33 mg L^{-1} after 2856 h (Fig. 2.2B). This implies DIC was removed faster than it was replaced by uptake of $\text{CO}_{2(\text{g})}$ into solution, with the converse true at early time. A 0.02 M increase in [Mg] in this experiment was consistent with evapoconcentration, with no significant change in [Mg] in the controls (A1 Fig. A1.2). This implies brucite dissolution was slow in the controls, and was balanced by the rate of Mg-carbonate precipitation in the long-term experiment.

In all high $p\text{CO}_2$ experiments, the decline in pH from alkaline to circumneutral conditions was driven by the uptake of CO_2 . Although low pH accelerates brucite dissolution (Pokrovsky and Schott, 2004), carbonate precipitation is generally favored at higher pH values (Teir et al., 2007; Eloneva et al., 2008b; Ferrini et al., 2009; Krevor and Lackner, 2011). As such, some mineral carbonation processes have been designed such that cation extraction and carbonate precipitation are achieved in separate steps (Park and Fan, 2004; Teir et al., 2007; Sipilä et al., 2008; Eloneva et al., 2008b). *In situ* carbon mineralization in mine tailings requires these processes to occur concurrently. The chemical environment must promote tailings mineral dissolution yet permit carbonate precipitation. The high $p\text{CO}_2$ experiments indicated that both brucite dissolution and carbonate precipitation are promoted with elevated $p\text{CO}_2$ at atmospheric pressure and temperature, suggesting that accelerated *in situ* carbonation of brucite may be achieved in ultramafic tailings, provided the brucite content is sufficient.

CO_2 concentration in the exhaust gas from duplicate reactors in the 10% CO_2 and 50% CO_2 experiments was reduced by up to 45% and 44%, respectively at the onset of each

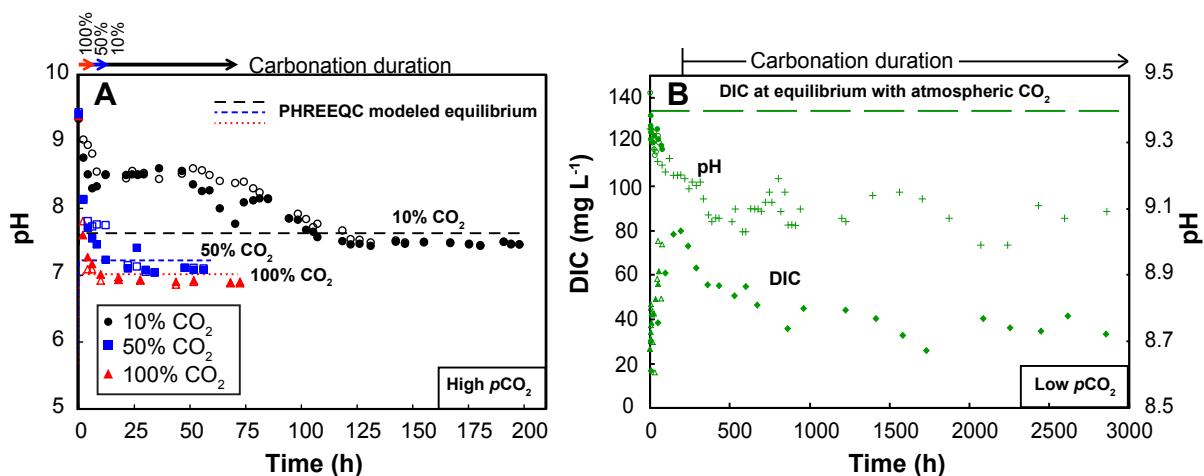


Figure 2.2. Plots of pH (A) in high $p\text{CO}_2$ experiments versus time. Dashed lines are results from PHREEQC (Parkhurst and Appelo, 1999) models assuming kinetically controlled brucite dissolution and equilibrium $\text{CO}_{2(\text{g})}$ dissolution. Dissolved inorganic carbon (DIC) (diamonds) and pH (+) in the long-term atmospheric CO_2 experiment, and DIC (triangles) and pH (circles) in controls versus time (B). The dashed line in (B) indicates the DIC concentration at equilibrium with atmospheric CO_2 . Open symbols and solid symbols in (A) represent duplicates 1 and 2, respectively. Arrows above the graph in (A) represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

experiment, implying carbonation began immediately (A1 Fig. A1.3). No change in gas composition was measurable in the 100% CO_2 experiment as the entire volume of gas consisted of CO_2 . In all high $p\text{CO}_2$ experiments, 43-51% of CO_2 supplied during the carbonation reaction was sequestered (Table 2.1).

Owing to the exothermic nature of the reaction, an increase in slurry temperature in high $p\text{CO}_2$ reactors over that of experimental controls was noted throughout carbonation, although the experiments were not insulated (A1 Fig. A1.4). Diurnal temperature variations in the laboratory resulted in periodic fluctuations in slurry temperature in all experiments (A1 Fig. A1.4). Control temperature was exceeded by a maximum of $5.4 \pm 0.5^\circ\text{C}$. The enthalpy of reaction for brucite carbonation is $-75.1 \text{ kJ mol}^{-1}$ (Konigsberger et al., 1999), corresponding to a total of $\sim 129 \text{ kJ}$ of energy released in the 100% CO_2 experiments based on the average mass of nesquehonite formed, providing the potential to heat the 3.0 L of water by 10.3°C .

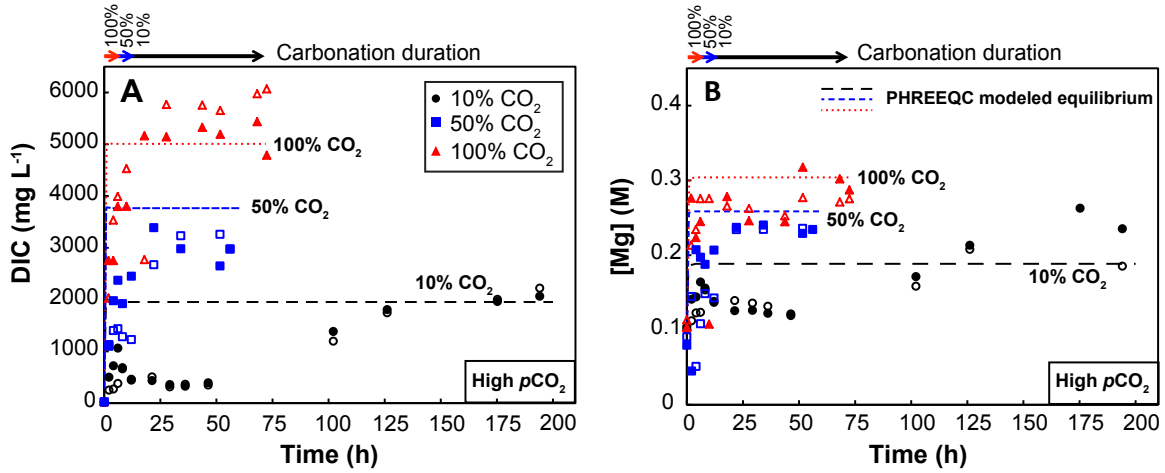


Figure 2.3. Plots of dissolved inorganic carbon concentration (DIC) (A), and Mg concentration (B) in high $p\text{CO}_2$ experiments versus time. Dashed lines are results from PHREEQC (Parkhurst and Appelo, 1999) models assuming kinetically controlled brucite dissolution and equilibrium $\text{CO}_{2(g)}$ dissolution. Open symbols and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graphs represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

This suggests heat was lost to the surroundings. Temperature may provide a useful indicator for reaction progress and be utilized to monitor and map carbonation in tailings facilities that contain sufficient brucite (Pronost et al., 2012).

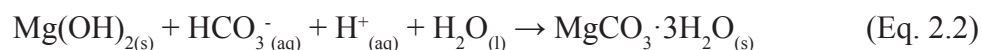
2.3.2 Brucite dissolution and carbonation rates

The rates of brucite dissolution and carbonation were accelerated linearly with $p\text{CO}_2$, resulting in a ~2400-fold increase in carbonation rate with an increase from atmospheric $p\text{CO}_2$ (~0.04%) to 100% CO_2 (Fig. 2.4). Both dissolution and carbonation rates were calculated as averages over the entire reaction, making comparison with published dissolution rates difficult, as the instantaneous rate of reaction may change with time. Brucite dissolution was calculated as follows (Eq. 2.1):

$$\text{Rate} = n_{\text{ibrc}} / (SA_{\text{ibrc}} \times t_c) \quad (\text{Eq. 2.1})$$

Where n_{ibrc} is the initial moles of brucite, SA_{ibrc} is the total initial brucite surface area (m^2), and t_c is the time for complete carbonation (s) as estimated with XRD, %C, and pH data (Fig. 2.2A, A1 Figs. A1.5-A1.6). Reaction end times of 75 h for 10% CO₂ 1 and 2, 14 and 12 h for 50% CO₂ 1 and 2, respectively, and 7 h were estimated for both 100% CO₂ experiments. Average dissolution rates in duplicate reactors were 9.7×10^{-9} , 5.6×10^{-8} and 1.0×10^{-7} mol m^{-2} s^{-1} with 10%, 50%, and 100% CO₂, respectively. The brucite dissolution rates with atmospheric CO₂ were too slow to be estimated.

XRD results indicated brucite was replaced by nesquehonite [MgCO₃·3H₂O] (Eq. 2.2) in all high pCO_2 reactors (A1 Fig. A1.6):



Nesquehonite was first detected within 8 h in 10% CO₂ 1 and within 6 h in 10% CO₂ 2 using carbon abundance analysis. It was detected within 2 h in the 50% and 100% CO₂ experiments. Minor amounts of phases that were not identifiable by XRD were formed in all high pCO_2 reactors and the atmospheric CO₂ experiment (A1 Fig. A1.6-A1.7). In the atmospheric CO₂ experiment, carbon abundance in the solids increased by 2.6%, identifying this phase as a carbonate. The unidentified phase was replaced by dypingite [Mg₅(CO₃)₄(OH)₂·5H₂O] as the reaction progressed in 10% 1 and 2. XRD and %C data indicated carbonation was completed within 102 h in the 10% CO₂ reactors, by the 22 h and 12 h sampling points in 50% CO₂ 1 and

Table 2.1. CO₂ mass balance and brucite dissolution and carbonation rates.^a

pCO_2 (% of 1 atm)	Dissolution rate ^b (mol brucite h ⁻¹)	Carbonation rate ^b (mol CO ₂ h ⁻¹)	CO _{2(g)} supplied (g)	CO ₂ in aqueous phase (g)	CO ₂ in solid (g)	Total CO ₂ sequestered (g)	Efficiency ^d (%)
0.04	nd ^c	1.1×10^{-4}	1768	8×10^{-2}	14	14	0.8%
10	0.03	0.03	223	6	91	97	43%
50	0.22	0.15	180	9	83	92	51%
100	0.36	0.27	211	16	76	92	44%

^a All values are averages for duplicate reactors.

^b Dissolution and carbonation rates have been converted to mol h⁻¹ for ease of comparison.

^c nd = no data

^d Efficiency calculated as Mass CO₂ sequestered in solid ÷ Mass CO_{2(g)} supplied during carbonation.

2, respectively, and between 6 and 10 h in both 100% CO₂ reactors (A1 Fig. A1.6). Reaction end points between these times were inferred by the final decline in pH indicative of brucite removal.

As observed by SEM, precipitates from the 10% and 50% CO₂ experiments included elongate crystals consistent with the morphology of nesquehonite (Ferrini et al., 2009), along with flaky, poorly crystalline material and pseudo-rosettes (A1 Fig. A1.8). This morphology is typical of dypingite (Power et al., 2007; Power et al., 2009), and is likely representative of both dypingite and the unidentified carbonate phase in the high *p*CO₂ experiments. Precipitates from the 100% CO₂ experiments were dominated by nesquehonite crystals (A1 Fig. A1.8).

Other experimental studies have used elevated CO₂ concentrations to precipitate nesquehonite by replacement of brucite or carbonation of MgCl₂ in solution (Hänchen et al., 2008; Ferrini et al., 2009; Zhao et al., 2010; Back et al., 2011), which is consistent with this study. With a Mg:C ratio of 1:1, nesquehonite optimizes the amount of carbon stored per cation, an advantage for sequestration purposes. Dypingite and the unidentified carbonate phase may be reaction intermediates (Hopkinson et al., 2011) or products of nesquehonite dehydration (Ballirano et al., 2010) between sampling and analysis, as depicted in SEM images, wherein flaky material armors nesquehonite crystals (A1 Fig. A1.8).

Initial %C values of solids ranged from 0.76-1.10% owing to the presence of primary dolomite [CaMg(CO₃)₂]. Carbon abundance in solid samples increased with time in each high *p*CO₂ experiment, followed by stabilization between 7.85% and 8.29% within 100, ~12, and 10 h in the 10%, 50%, and 100% CO₂ experiments, respectively (A1 Fig. A1.5). This is consistent with formation of nesquehonite, which ideally contains 8.68% carbon. Carbon abundance increased to 3.6% after 2856 h in the atmospheric CO₂ experiment. The mass of CO₂ sequestered in the high *p*CO₂ experiments was calculated using %C data assuming that dolomite mass remained constant and that CO₂ was stored primarily within nesquehonite. A total of 317 g of nesquehonite (~101 g CO₂) and 253 g (~81 g CO₂) were formed in 10% CO₂ 1 and 2, respectively. In 50% CO₂ 1 and 2, 275 g of nesquehonite (~88 g CO₂) and 244 g of

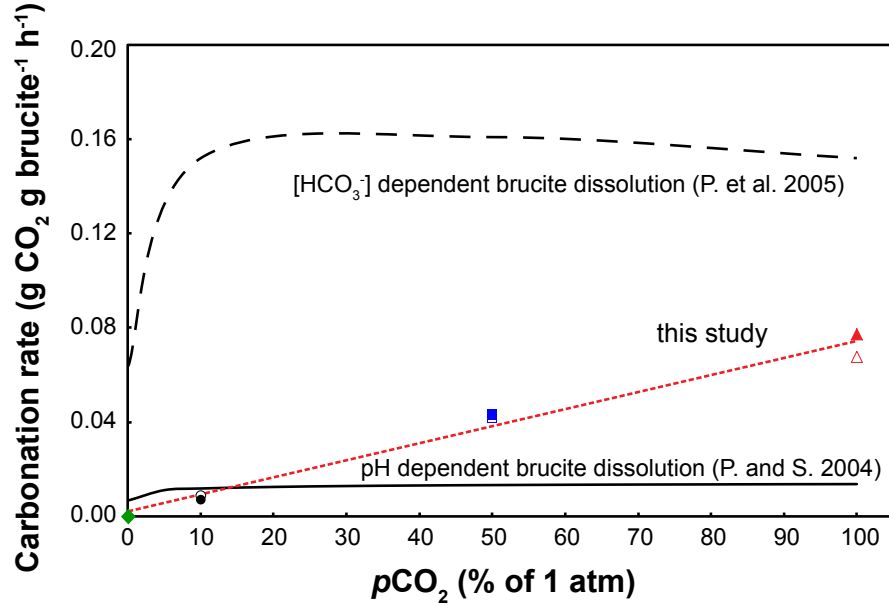


Figure 2.4. Experimentally determined and modeled (PHREEQC; Parkhurst and Appelo, 1999) brucite carbonation rate versus $p\text{CO}_2$ in experiments using ligand (Pokrovsky et al., 2005b) and pH (Pokrovsky and Schott, 2004) dependent brucite dissolution rate laws. Open symbols and solid symbols represent duplicates 1 and 2, respectively.

nesquehonite ($\sim 78 \text{ g CO}_2$) were formed, respectively. A total mass of 223 g of nesquehonite ($\sim 71 \text{ g CO}_2$) and 254 g of nesquehonite ($\sim 81 \text{ g CO}_2$) was precipitated in 100% CO_2 1 and 2, respectively. Discrepancies between duplicate reactors are attributed to imperfect mixing causing minor amounts of brucite to remain uncarbonated. The mass of carbon mineralized in the atmospheric CO_2 experiment was calculated using %C data assuming that brucite mass remained relatively unchanged, which is justified by the relative peak heights in the XRD data. A total of $\sim 14 \text{ g CO}_2$ was captured over 2856 h.

Carbonation rates in the high $p\text{CO}_2$ experiments were calculated as follows (Eq. 2.3):

$$\text{CO}_2 \text{ sequestration rate (g CO}_2 \text{ g brucite}^{-1} \text{ h}^{-1}) = [(m_{fnsq} / M_{nsq}) \times M_{\text{CO}_2}] / [m_{ibrc} \times t_h] \quad (\text{Eq. 2.3})$$

Where m_{fnsq} is the final mass of nesquehonite (g), m_{ibrc} is the initial brucite mass (g), t_h is

the time of reaction completion (h), and M_{nsq} and M_{CO_2} are the molar masses of nesquehonite and CO_2 ($g\ mol^{-1}$), respectively. In the atmospheric CO_2 experiment, the carbonation rate was calculated based on the rate of increase of %C in the solids. The rates of CO_2 sequestration using laboratory air, and average rates between duplicate 10%, 50%, and 100% CO_2 experiments were $\sim 3.30 \times 10^{-5}$, 7.78×10^{-3} , 4.26×10^{-2} , and $8.00 \times 10^{-2}\ g\ CO_2\ g\ brucite^{-1}\ h^{-1}$, respectively. Dissolution and carbonation rates and CO_2 mass balances are summarized in Table 2.1.

2.3.3 Reaction mechanism

Brucite dissolution is a surface controlled reaction (Vermilyea, 1969; Jordan and Rammensee, 1996; Pokrovsky and Schott, 2004) that is accelerated with increased acidity and concentration of certain organic and inorganic ligands, such as HCO_3^- (Vermilyea, 1969; Pokrovsky and Schott, 2004; Pokrovsky et al., 2005b). Proton and ligand promoted dissolution occur in parallel; their effect is additive (Pokrovsky et al., 2005b). Ligands that promote brucite dissolution are those that form protonated ions at neutral to weakly alkaline pH (e.g., HCO_3^-), whereas those that are deprotonated inhibit dissolution (e.g., CO_3^{2-} ; Vermilyea, 1969; Pokrovsky et al., 2005b). Therefore, aqueous carbonate species may enhance or inhibit brucite dissolution depending on the solution pH. Previous studies have documented a dependence of brucite and MgO dissolution rate on HCO_3^- concentration (Pokrovsky et al., 2005b; Back et al., 2011). As HCO_3^- is the dominant aqueous carbonate species in the experimental pH range (Langmuir, 1997), dissolution and hydration of CO_2 may accelerate brucite dissolution via the direct effect of increasing HCO_3^- concentration and the indirect effect of increasing acidity. These effects cannot be separated in the high pCO_2 experiments, as neither pH nor DIC were fixed. Increased DIC concentration should also promote brucite carbonation by facilitating carbonate precipitation at lower Mg concentration, as suggested by Chen et al. (2006) to account for enhanced carbonation of olivine in $NaHCO_3$ solutions.

To discern the effect of elevated pCO_2 on brucite carbonation rate, experimental conditions were modeled using PHREEQC (Parkhurst and Appelo, 1999). Experimentally

determined, steady-state, far from equilibrium rate laws dependent on pH (Pokrovsky and Schott, 2004) and ligand (HCO_3^-) concentration (Pokrovsky et al., 2005b) were used, and are provided in Appendix 1. Nesquehonite precipitation and CO_2 uptake were simulated as equilibrium processes. Modeling revealed that experimental dissolution and carbonation rates exceeded those predicted with proton promoted dissolution and high DIC promoted carbonate precipitation alone. With 100% CO_2 , the experimental carbonation rate is 6-fold faster than predicted due to acidity promoted dissolution (Fig. 2.4). Comparison of experimental dissolution rates with the pH-dependent rate law of Pokrovsky and Schott (2004) highlights the discrepancy between the experimental rates and those predicted due to proton promoted dissolution (A1 Fig. A1.9). In this study, dissolution rate is calculated based on the time to dissolve brucite of a specified mass, rather than an instantaneous rate based on the flux of Mg^{2+} ; this could in part explain the divergence from the Pokrovsky and Schott rate law (Pokrovsky and Schott, 2004) as the instantaneous rate was likely not constant. Experimental carbonation rates fell between those predicted by pH and HCO_3^- promoted dissolution (Fig. 2.4), implying that HCO_3^- promoted brucite dissolution is likely an important mechanism enhancing brucite carbonation, yet the CO_2 supply was insufficient to achieve the maximum predicted rates.

2.3.4 Rate limitation

The fractionation of carbon stable isotopes can be used to infer the relative rates of processes that involve CO_2 and thus help identify rate limitations (Wilson et al., 2010). All isotopic data are reported in δ -notation relative to Vienna Pee Dee Belemnite (VPDB) in units of per mil (‰). The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values of the gas supply for the 10%, 50%, and 100% CO_2 experiments were -35‰, -37‰, and -32‰, respectively. Differences in initial $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are due to the use of different CO_2 tanks for each experiment. Equilibrium fractionation between $\text{CO}_{2(\text{g})}$ and HCO_3^- is +7.9‰ at 25°C (Mook et al., 1974), therefore, the equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ values for the high $p\text{CO}_2$ experiments should be between ~-24‰, to -29‰. Divergence from the equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ value increased in the first 36 h in 10% CO_2 1 and 2, before rising to

reach equilibrium composition after ~175 h (Fig. 2.5A). Wilson et al. (2010) observed a similar negative trend in $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation of a MgCl_2 solution using atmospheric CO_2 , which was attributed to a kinetic isotope fractionation effect due to slow uptake of $\text{CO}_{2(\text{g})}$ into solution (Wilson et al., 2010). In the 50% and 100% CO_2 experiments, equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ composition was obtained after 56 and 43 h, respectively (Fig. 2.5A). Yet, mineralogical data indicated carbonation was complete within 75, 12, and 7 h in the 10%, 50% and 100% CO_2 experiments, respectively. This implies that isotopic equilibrium between CO_2 in the gas and aqueous phase was not achieved during the carbonation reaction, but is only approached when the DIC sink, carbonate mineral precipitation, is ceased.

Due to the presence of dolomite in the initial material, early time $\delta^{13}\text{C}$ values of solids are not representative of precipitated carbonate (~-4.4‰). A cut off of a minimum of 4% carbon in the solids (at least 80% of carbon in nesquehonite) was chosen to be representative of nesquehonite stable isotopic composition. Nevertheless, the presence of minor dolomite results in the solids being enriched relative to the precipitated nesquehonite. The $\delta^{13}\text{C}$ values of the solids (primarily nesquehonite) remained between -28.3‰ to -30.8‰, and -29.6‰ to -32.6‰ in 10% CO_2 1 and 2, respectively. A greater range in $\delta^{13}\text{C}$ values was recorded in the 50% CO_2 experiment, with values between -29.6‰ to -37.4‰, and -31.2‰ to -36.1‰ in 50% CO_2 1 and 2, respectively. In 100% CO_2 1 and 2, $\delta^{13}\text{C}$ values were between -25.0‰ to -30.1‰, and -25.6‰ to -31.0‰, respectively. Fresh carbonate could not be sampled therefore $\delta^{13}\text{C}$ values are cumulative for carbonate formed throughout each experiment. Insufficient carbonate precipitation occurred in the atmospheric CO_2 experiment to determine the ^{13}C composition of the carbonate.

The equilibrium $\delta^{13}\text{C}$ fractionation factor between nesquehonite and HCO_3^- has not been determined. However, the observed fractionation is consistent with the equilibrium carbon isotopic fractionation factor estimated by Wilson et al. (2010) for dypingite and HCO_3^- ($3.8 \pm 1.3\text{‰}$ at 25°C). The $\delta^{13}\text{C}$ values of solids generally deviate between 0-5‰ from values predicted assuming isotopic equilibrium is maintained with the average $\delta^{13}\text{C}_{\text{DIC}}$ value during

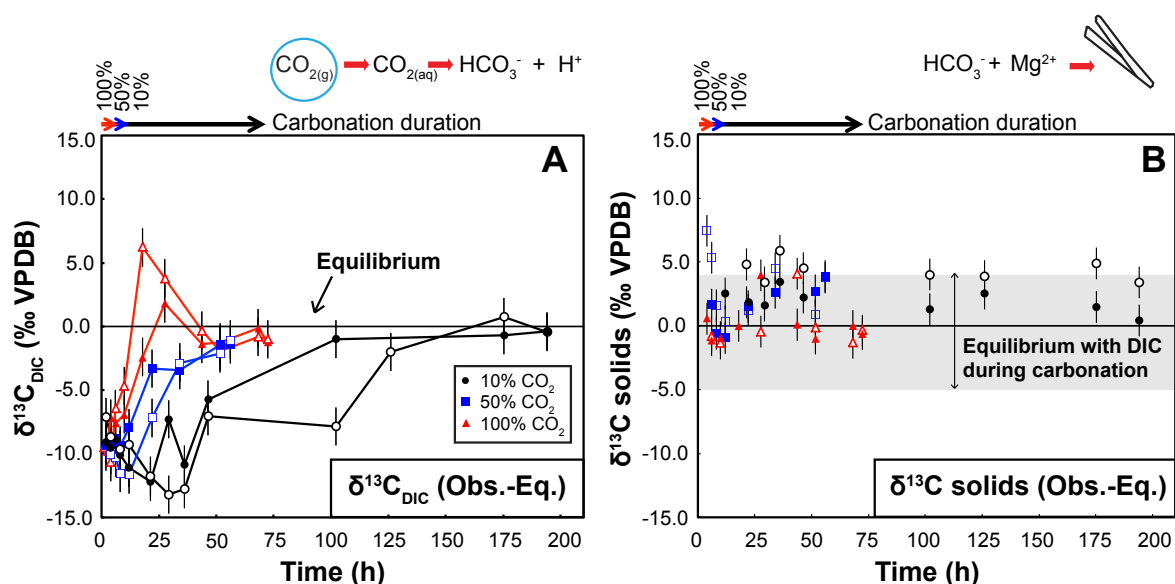


Figure 2.5. Deviation from calculated equilibrium $\delta^{13}\text{C}_{\text{DIC}}$ values in high $p\text{CO}_2$ experiments versus time using the fractionation factor of Mook et al. (1974) (A). Deviation from calculated equilibrium $\delta^{13}\text{C}$ values of solids with the average $\delta^{13}\text{C}_{\text{DIC}}$ during carbonation using the fractionation factor of Wilson et al. (2010) in high $p\text{CO}_2$ experiments versus time of sampling (B). Shaded area represents the range of equilibrium $\delta^{13}\text{C}$ values of solids with the observed range in $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation. Open and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graphs represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

carbonation (Fig. 2.5B). The majority of $\delta^{13}\text{C}$ values of solids fall within the range of equilibrium composition estimated with the observed range of $\delta^{13}\text{C}_{\text{DIC}}$ values during carbonation (shaded area in Fig. 2.5B). This suggests that nesquehonite precipitated approximately at isotopic equilibrium with DIC throughout carbonation. Moreover, nesquehonite saturation indices calculated using PHREEQC (Parkhurst and Appelo, 1999) indicate nesquehonite precipitated near chemical equilibrium (A1 Fig. A1.10). This implies carbonate mineral precipitation is not rate limiting for carbonation, rather the slow approach to isotopic equilibrium between $\text{CO}_{2(\text{g})}$ and DIC indicates uptake of CO_2 is the limiting step for brucite carbonation.

During carbonation, DIC concentrations in experiments were consistently below $\text{CO}_{2(\text{g})} \leftrightarrow \text{DIC}$ equilibrium levels as predicted by PHREEQC (Parkhurst and Appelo, 1999) modeling (Fig. 2.3A). This further indicates equilibrium between CO_2 in the gas and aqueous

phase was not obtained during carbonation. Experimental carbonation rates were generally lower than predicted by modeling due to HCO_3^- promoted dissolution, with divergence increasing at lower $p\text{CO}_2$ (Fig. 2.4). This is consistent with a kinetic limitation to uptake of CO_2 into solution, as equilibrium DIC concentrations were not achieved in the experiments, and divergence from $\text{CO}_{2(\text{g})} \leftrightarrow \text{DIC}$ equilibrium was greatest at lower $p\text{CO}_2$. This is in agreement with the stable isotopic data, indicating that uptake of CO_2 into solution is rate limiting for brucite carbonation even at elevated $p\text{CO}_2$. The implication is that if $\text{CO}_{2(\text{g})} \leftrightarrow \text{DIC}$ equilibrium could be attained, the brucite carbonation rate would be further accelerated. CO_2 uptake into solution is divided into two steps: (1) $\text{CO}_{2(\text{g})}$ dissolution and (2) $\text{CO}_{2(\text{aq})}$ hydration. $\text{CO}_{2(\text{g})}$ dissolution involves the phase transfer from gaseous to aqueous CO_2 , whereas $\text{CO}_{2(\text{aq})}$ hydration is the subsequent formation of H_2CO_3 or HCO_3^- depending on solution pH, which dissociate to form CO_3^{2-} (Stumm and Morgan, 1996). It is well understood that dissociation is rapid, whereas the hydration of $\text{CO}_{2(\text{aq})}$ is relatively slow (Sullivan et al., 1993; Stumm and Morgan, 1996; Lasaga, 1998). An option for further enhancing CO_2 uptake into solution is to accelerate CO_2 hydration, which may be achieved through use of biological catalysts such as the carbonic anhydrase enzyme (Mirjafari et al., 2007; Favre et al., 2009; Sharma and Bhattacharya, 2010).

2.3.5 Implications for carbon sequestration in mine tailings

Experimental data show a linear increase in brucite carbonation rate with $p\text{CO}_2$, resulting in a ~2400-fold acceleration with an increase from atmospheric $p\text{CO}_2$ (~0.04% CO_2) to 100% CO_2 . Conversely, modeling using PHREEQC (Parkhurst and Appelo, 1999) reveals a non-linear relationship between carbonation rate and $p\text{CO}_2$ with both proton and HCO_3^- promoted dissolution (Fig. 2.4). This implies that use of 100% CO_2 may not be necessary to achieve maximum carbonation rates if CO_2 uptake into solution were enhanced (Fig. 2.4). Direct use of flue gas (e.g., ~17% CO_2 ; Kikkinides et al., 1993) from mine site power plants could be sufficient to achieve similar carbonation rates as use of purified CO_2 . This is highly advantageous as it eliminates the cost of purifying CO_2 .

Despite a kinetic limitation for uptake of CO₂ into solution, brucite carbonation rates achieved in experiments exceed that required to carbonate all the brucite produced annually at MKM. MKM produces ~0.11-0.28 Mt of brucite in tailings annually, and emits 370 kt yr⁻¹ of CO₂ equivalent GHGs (BHP Billiton, 2005; Wilson, 2009). Carbonation of brucite produced annually would offset mine emissions by ~22-57% (Fig. 2.6), which is up to 4-fold faster than estimated passive carbonation rates (Wilson, 2009). A tax on carbon emissions implemented in July 2012 in Australia implies tailings carbonation may offer a significant financial benefit for Australian mines such as MKM (e.g., up to \$4.8 million saved annually; Australian Government, 2011). Complete carbonation of brucite accumulated in tailings stockpiles at MKM would sequester a total of 1-3 Mt of CO₂. This is a comparable sequestration rate to what is currently achieved at the largest geologic carbon sequestration demonstration projects (~1-2.8 Mt CO₂ yr⁻¹; Michael et al., 2009; Whittaker et al., 2011).

Brucite is present in ultramafic tailings from other deposit types, such as chrysotile. In Québec, Canada, there are approximately 2 Gt of chrysotile mining residues (Larachi et al., 2010). At the Black Lake mine in Québec, chrysotile milling residues contain ~1.8 wt.% brucite (Pronost et al., 2011). If these brucite contents are representative for the entire stockpile, up to 27 Mt of CO₂ could be sequestered via brucite carbonation alone.

Brucite carbonation represents only a small proportion of the total sequestration potential of ultramafic tailings, which consist primarily of Mg-silicate minerals. At MKM, accelerated carbonation of Mg-silicate minerals has the potential to sequester much more CO₂ than is emitted annually (Fig. 2.6). Accelerated dissolution of silicate tailings minerals such as serpentine [Mg₃Si₂O₅(OH)₄] and forsterite [Mg₂SiO₄] is predicted with increased *p*CO₂ owing to proton promoted dissolution (Bales and Morgan, 1985; Pokrovsky and Schott, 2000). The effect of inorganic carbon ligands on silicate mineral dissolution is less certain (c.f., forsterite, wollastonite, and anorthite; Berg and Banwart, 2000; Golubev et al., 2005), and the effect on serpentine dissolution is not well understood under conditions prevalent in mine tailings. The presence of ligands such as citrate have been found to enhance serpentine dissolution by several

orders of magnitude over that predicted by pH promoted dissolution, and can be significant in pH ranges appropriate for carbonate precipitation (Krevor and Lackner, 2011). If serpentine dissolution were similarly affected as brucite by surface reactions involving the HCO_3^- ligand, total carbonation rates in tailings may be underestimated based on pH effects alone.

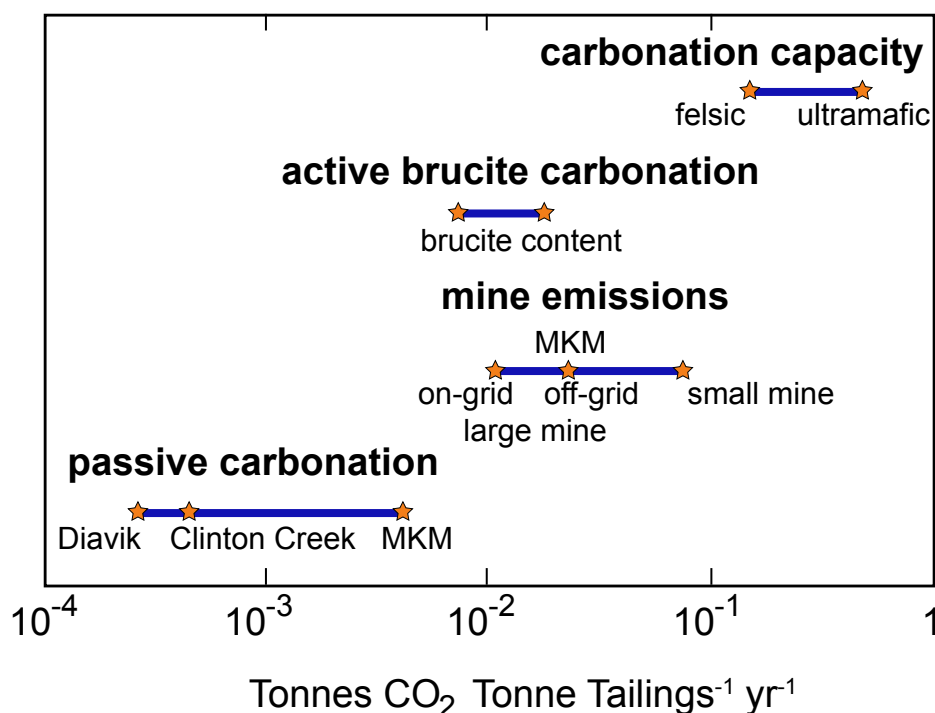


Figure 2.6. Comparison of range of passive annual carbonation rates at Diavik Diamond Mine, Northwest Territories, Canada (Wilson et al., 2011), Clinton Creek Chrysotile mine, Yukon Territory, Canada (Wilson et al., 2009), and the Mount Keith Nickel Mine (MKM), Western Australia (Wilson, 2009) with annual GHG emissions at various mine sites, total sequestration capacity, and potential annual carbonation rates at MKM via accelerated brucite carbonation.

3. Strategies for enhancing carbon sequestration in Mg-rich mine tailings²

3.1 Introduction

Anthropogenic greenhouse gas (GHG) emissions, particularly CO₂ emissions, have been identified as a cause of global climate change (IPCC, 2007). Carbon sequestration is one of many potential strategies to stabilize CO₂ concentrations and prevent irreversible climate change while we transition to non-fossil fuel based energy sources (Pacala and Socolow, 2004; Broecker, 2007). Mineral carbonation, or carbon mineralization, is a method of carbon sequestration that involves dissolution of non-carbonate minerals (e.g., silicates, hydroxides, and oxides) to release cations, and the binding of these cations with CO₂ in carbonate minerals (Seifritz, 1990; Lackner et al., 1995; Lackner et al., 1997; Lackner, 2003). Many industrial wastes, including mine tailings, are rich in minerals that provide suitable feedstock for mineral carbonation such as brucite [Mg(OH)₂], forsterite [Mg₂SiO₄], and serpentine group minerals [Mg₃Si₂O₅(OH)₄] (e.g., Wilson et al., 2009a; Renforth et al., 2011; Bobicki et al., 2012). Carbonation of industrial wastes is advantageous as it exploits available waste materials that are typically fairly reactive under ambient conditions, and it may decrease the hazardous nature of wastes such as asbestos mine tailings (Renforth et al., 2011; Bobicki et al., 2012). Carbon mineralization in mine wastes has been documented to occur passively under normal mining practices at both historic and active asbestos, diamond, chromite, and nickel mines globally (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2010; Wilson et al., 2011; Bea et al., 2012; Pronost et al., 2012; Beinlich and Austrheim, 2012). Carbonation reactions are facilitated by high surface areas (Wilson et al., 2009a), yet are limited by the uptake of CO₂

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into solution (Wilson et al., 2010). Although the carbon sequestration capacity of ultramafic tailings is significant, rates of passive carbonation are insufficient to take full advantage of the carbon sequestration potential. For instance, complete carbonation of tailings produced annually at the Mount Keith Nickel Mine (MKM) in Australia (~11 Mt tailings per year; BHP Billiton, 2005) would exceed annual mine emissions by more than a factor of ten. Yet passive carbonation rates currently offset annual emissions by only ~15% (Wilson, 2009). Carbon mineralization in mine tailings could be accelerated by increasing the exposure of tailings to CO₂, such as by injection of CO₂-rich gas streams into tailings storage facilities. Here, we generalize the experimental results from our previous work (Harrison et al., 2013a; Chapter 2) investigating the potential for accelerated carbonation of brucite, a common and highly reactive tailings mineral, to evaluate CO₂ injection as a carbon sequestration strategy in mine tailings. Brucite is a Mg-hydroxide mineral that is typically present between 1 and 15 wt.% in ultramafic mine tailings and residues (Chrysochoou et al., 2009; Pronost et al., 2011; Bea et al., 2012). It is far more reactive than the more abundant silicate phases such as serpentine (e.g., Bales and Morgan, 1985; Assima et al., 2013a), and therefore provides a useful starting point for investigation of accelerated tailings carbonation strategies.

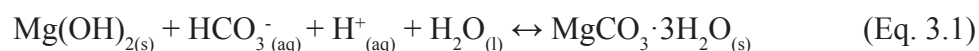
3.2 Methods

The effects of supplying CO₂-rich gas streams at ambient temperature and pressure (~21°C; 1 atm) on the carbonation rate of brucite was investigated experimentally in batch reactors, with geochemical conditions emulating those at MKM. Alkaline 3.0 L slurries containing 150 g brucite were supplied with gas streams with a range of CO₂ content (~0.04%, 10%, 50%, 100% CO₂ by volume) at a rate of ~270 mL min⁻¹ (Harrison et al., 2013a; Chapter 2). Slurry samples were extracted periodically for measurement of pH, the stable carbon isotopic composition ($\delta^{13}\text{C}$) of dissolved inorganic carbon (DIC), and cation and DIC concentrations. Solid samples were collected for measurement of mineralogical compositions and $\delta^{13}\text{C}$. For

further details regarding the experimental setup, refer to Harrison et al. (2013a; Chapter 2).

3.3 Results and discussion

The experimental results indicated that brucite (brc) was carbonated to produce the hydrated Mg-carbonate mineral nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] at a rate that increased linearly with CO_2 partial pressure ($p\text{CO}_2$) according to the following reaction (Harrison et al., 2013a; Chapter 2):



A 2400-fold increase in CO_2 sequestration rate was achieved with an increase from atmospheric composition ($\sim 0.04\% \text{CO}_2$) to pure CO_2 . Increasing the $p\text{CO}_2$ serves to enhance both brucite dissolution and carbonate precipitation. However, even at elevated $p\text{CO}_2$ the rate of CO_2 uptake into solution was found to be rate limiting. This is attributed to the relatively slow transformation from gaseous CO_2 to an aqueous form that can be mineralized (i.e., HCO_3^- and CO_3^{2-}) as indicated by chemical and isotopic disequilibrium between gaseous CO_2 and DIC during the carbonation reaction (Harrison et al., 2013a; Chapter 2). Nevertheless, the experimental carbonation rates would be sufficient to carbonate all the brucite produced annually at MKM (0.1-0.3 Mt brucite), offsetting total mine emissions by 20-60% (Harrison et al., 2013a; Chapter 2). Therefore accelerated carbonation of tailings minerals by supplying CO_2 -rich gas streams is a promising method for reducing GHG emissions at mine sites with tailings that contain brucite. Power generation at mine sites often occurs at on-site power plants, which could provide a local point source of CO_2 emissions. Flue gas from power plants typically contains between 10-20% CO_2 (Kikkinides et al., 1993; Uibu et al., 2011). These emissions provide a readily available source of CO_2 -rich gas that could be injected into tailings storage facilities to accelerate brucite carbonation (Harrison et al., 2013a; Chapter 2). An alternative

would be to circulate CO₂-rich water, which could help to avoid the issue of slow CO₂ uptake into solution. However, the use of CO₂-rich gas has the advantage that it would not increase the water consumption at mine sites, which can be an important concern particularly for mines in arid locations with high evaporative losses. A potential concern regarding CO₂ injection is its effect on the mobility of hazardous metals. Metals could be mobilized via dissolution of primary tailings minerals, yet secondary precipitates can incorporate these metals and limit their mobility depending on solution pH (Power et al., 2010). Therefore further investigation is warranted to determine the potential side effects of CO₂ injection on tailings geochemistry.

If brucite carbonation via CO₂-rich gas injection were implemented at a mine site, tailings storage facilities would need to be designed to minimize leakage of injected CO₂ to the atmosphere. This requires that the rate of carbon mineralization in the tailings keep pace with the rate of CO₂ supply. The rate of CO₂ injection will be limited by the availability of the highly reactive phases such as brucite, as these will consume the majority of the CO₂ in the short term. Greater brucite content will accommodate higher injection rates, as well as provide greater total sequestration capacity. The sequestration or ‘reactive capacity’ (Eq. 3.2) of brucite is calculated by assuming complete conversion to nesquehonite; this equates to 0.75 g CO₂ stored per gram brucite. In order to prevent CO₂ leakage, the rate of CO₂ supply must not exceed the reactive capacity at any given time, and should therefore balance the rate of brucite deposition according to the reaction stoichiometry.

The rates achieved in the brucite carbonation experiments employing 10% CO₂ were considered representative of reaction in mine tailings. The predicted brucite carbonation rate using flue gas is thus ~0.3 mol CO₂ m⁻² brucite yr⁻¹ (after Harrison et al., 2013a; Chapter 2). Due to the relatively high reactivity of brucite, it is assumed that the rate of CO₂ mineralization is dictated primarily by the brucite carbonation rate rather than carbonation of the less reactive silicates. The reactive capacity provided by brucite and the time before CO₂ venting at a given CO₂ injection rate can then be calculated according to Equations 3.2 and 3.3. Carbonation rates in the field will be affected by water content distribution (e.g., Assima et al., 2013a), surface

passivation effects (e.g., Jeon et al., 2006), and the hydraulic properties of the porous medium. Quantification of the extent to which these effects will alter carbonation rates requires further experimentation. As such, for the purposes of this study, it is assumed that CO₂ supply is the primary rate-limiting factor; therefore Equation 3.3 applies only when the maximum rate of carbonation (Eq. 3.4) is less than the rate of CO₂ supply.

$$\text{Reactive capacity } (C_r) = \frac{m_t F_{brc}}{GFW_{brc}} b \quad (\text{Eq.3.2})$$

$$\text{Time to CO}_2 \text{ venting} = \frac{C_r}{r_{CO_2}} \quad (\text{Eq.3.3})$$

$$\text{Maximum brucite carbonation rate} = m_t F_{brc} S_{brc} r_{brc} \quad (\text{Eq.3.4})$$

Where, C_r is the reactive capacity (mol CO₂), m_t is the mass of tailings (g), F_{brc} is the brucite content of the tailings as a fraction of tailings mass, b is a stoichiometric coefficient for the carbonation of brucite, GFW_{brc} is the molar mass of brucite (g mol⁻¹), r_{CO_2} is the rate of CO₂ supply (mol CO₂ yr⁻¹), S_{brc} is the surface area of brucite (m² g⁻¹), and r_{brc} is the ‘flue gas’ rate of brucite carbonation measured in batch reactors (mol CO₂ m⁻² brc yr⁻¹).

At MKM, approximately 0.5 m of tailings are deposited annually, assuming they are evenly distributed across the ~16.6 km² tailings storage facility, with historic tailings reaching depths of up to ~19 m (Wilson, 2009). The total annual CO₂ equivalent emissions at MKM are reported to be 0.37 Mt CO₂ (BHP Billiton, 2005). GHG emissions from mining operations are typically divided between fossil fuel combustion from distributed sources like trucks and mining equipment, and emissions from electricity generation. It is estimated that ~64% of emissions are from electricity generation, and ~36% are from distributed sources (USEPA, 2008). This suggests that at MKM, approximately 0.24 Mt CO₂ yr⁻¹ is produced from point sources. If CO₂ were injected at a rate equal to the rate of point source CO₂ emissions (~328 mol CO₂ yr⁻¹ m⁻² tailings; after BHP Billiton, 2005), current brucite production rates are nearly

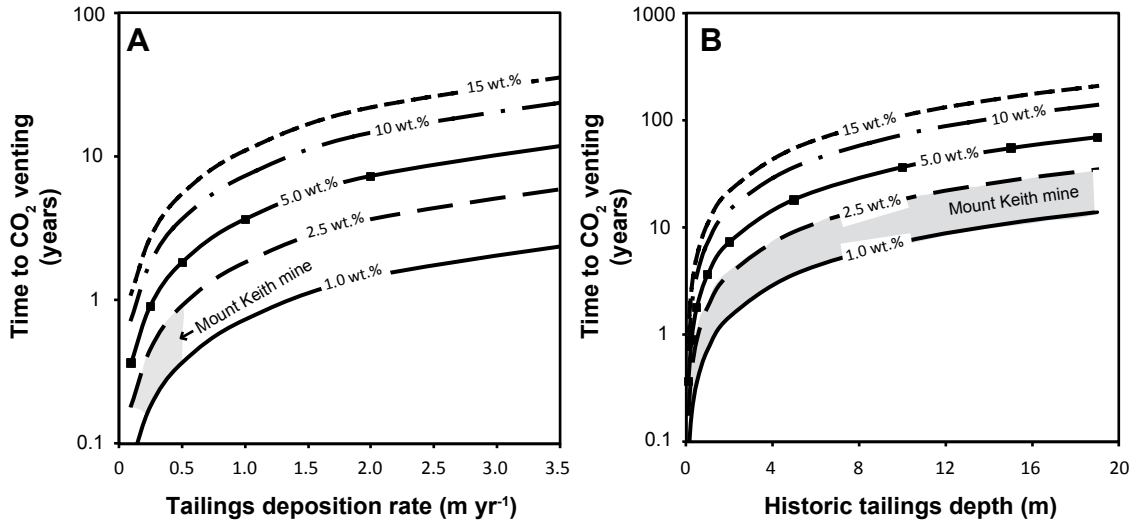


Figure 3.1. Time to CO₂ venting versus tailings deposition rate (A) and historic tailings depth (B) at various brucite contents with a CO₂ injection rate equal to the estimated rate of point source CO₂ emissions at the Mount Keith Nickel Mine (~328 mol CO₂ yr⁻¹ m⁻² tailings; after BHP Billiton, 2005). Shaded areas indicate range of brucite content and tailings depth and deposition rate applicable to the Mount Keith Nickel Mine.

sufficient to offset point source CO₂ emissions (Fig. 3.1A). Higher injection rates could be initially applied to carbonate historic tailings. For instance, it would take up to 20 years for CO₂ to vent from the deepest tailings at MKM at this CO₂ injection rate (Fig. 3.1B). For highly reactive minerals like brucite, the reactive capacity rather than the mineral carbonation rate will likely limit the maximum CO₂ injection rate.

At mines with high tailings production rates that produce power on-site, such as MKM, it is estimated that a minimum brucite content in tailings of ~3 wt.% would be required to offset point source mine emissions, or ~64% of total emissions, if brucite is the primary sink for CO₂ (Figs. 3.1A and 3.2). Smaller ‘off-grid’ mines produce greater CO₂ emissions per tonne of tailings produced, and would require in excess of 6.5 wt.% brucite to offset estimated point source emissions (Fig. 3.2). Regardless of electricity source or mine size, accelerated carbonation of even minor amounts of brucite (e.g., 2.5 wt.%) could provide >4-fold acceleration over passive carbonation rates (Fig. 3.2). In the case of a carbon tax or cap-and-trade system, offsetting GHG emissions would be financially beneficial for mining companies. Economically marginal

deposits that possess significant carbon capture potential, such as high brucite content, may therefore become financially viable (e.g., Bobicki et al., 2012).

Although accelerated brucite carbonation would provide significant offsets of mine emissions, in order to take full advantage of the sequestration capacity offered by mine tailings, Mg-silicate carbonation must also be enhanced (Fig. 3.2). Passive carbonation of serpentine has been documented in tailings with and without brucite (Wilson et al., 2006; Wilson, 2009; Wilson et al., 2009a). This demonstrates that despite being less reactive than brucite, Mg-silicate carbonation is possible in a tailings environment. Injection of CO₂-rich gas into tailings

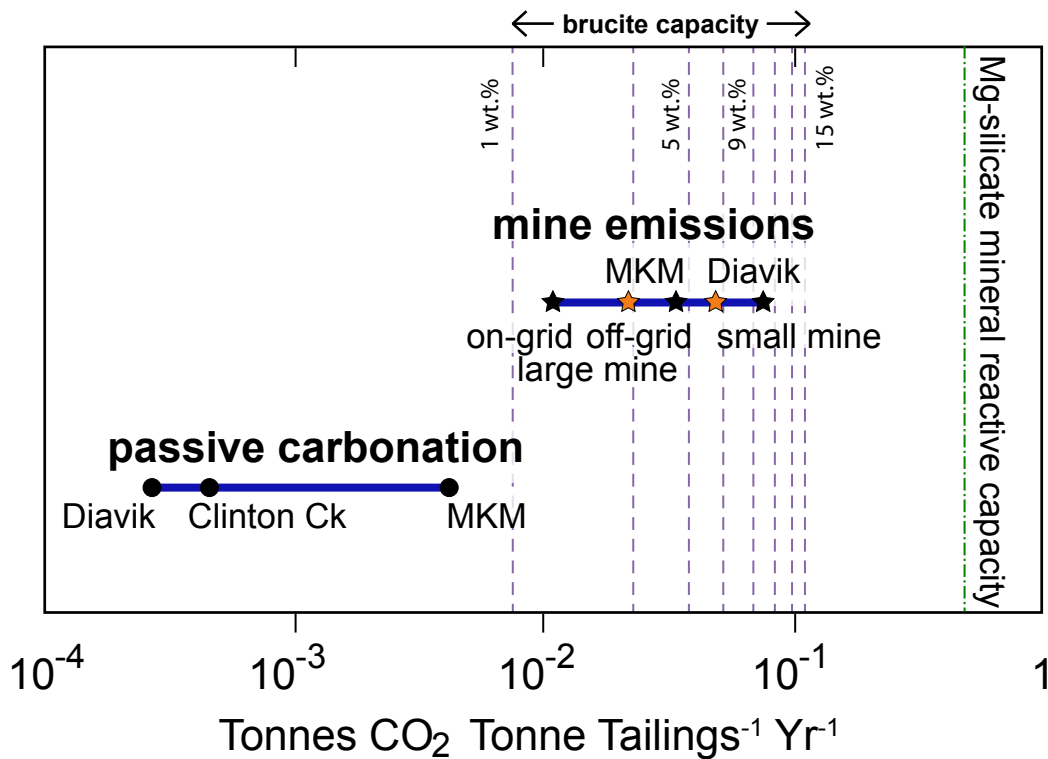


Figure 3.2. Comparison of range of passive annual carbonation rates at Diavik Diamond Mine, Northwest Territories, Canada, Clinton Creek Chrysotile mine, Yukon, Canada, and the Mount Keith Nickel Mine (MKM), Western Australia (circles) with annual GHG emissions at mine sites of various size and power sources (stars). Orange and black stars represent estimated point source and total CO₂-equivalent emissions, respectively. Total reactive capacity including Mg-silicate carbonation is indicated by the green vertical dashed-dot line. The reactive capacity per tonne tailings based on brucite carbonation alone at various brucite contents is indicated by the purple vertical dashed lines at 2 wt.% brucite intervals (modified after Harrison et al., 2013; Chapter 2).

will not only exploit the sequestration potential of brucite, but may also help carbonate the more abundant Mg-silicates. Due to the lower reactivity of Mg-silicates in comparison to brucite, more aggressive methods are often employed in mineral carbonation processes to accelerate dissolution, such as the use of strong acids (e.g., Alexander et al., 2007). Hence, it is unlikely that injection of CO₂-rich gas alone will allow sufficient acceleration of Mg-silicate carbonation to take full advantage of the CO₂ sequestration potential. As research to enhance Mg-silicate carbonation continues, deployment of accelerated brucite carbonation strategies in the interim will help guide the development of Mg-silicate carbonation techniques for mine tailings, while providing an immediate and significant GHG benefit.

3.4 Conclusions

Experimental results indicate that passive rates of carbonation could theoretically be accelerated to offset ~20-60% of total CO₂ emissions at the Mount Keith Nickel Mine in Australia. This could be achieved via injection of CO₂-rich gas into tailings, such as flue gas from mine site power plants, to completely carbonate brucite and partially carbonate Mg-silicates. Mines that contain >6.5 wt.% brucite in their tailings may have the potential to completely offset point source CO₂ emissions via brucite carbonation alone. Carbonation of the more abundant Mg-silicates could capture >10-fold the scale of mine emissions at a large mine such as MKM. Deployment of accelerated brucite carbonation strategies would offer a first step towards the development of methods that take advantage of the total CO₂ sequestration capacity of mine tailings, while providing an immediate GHG benefit.

4. Enhanced mineral reactivity driven by pore fluid mobility in partially wetted porous media³

4.1 Introduction

Mineral-fluid reactions in Earth's shallow subsurface regulate element transport in nature, disturbed environments, and man-made materials such as industrial wastes. They are vital for nutrient availability, water quality, and carbon cycling (Blowes and Jambor, 1990; McKinley et al., 2006; Manning, 2008; Maher et al., 2009; Brantley and White, 2009). Despite the importance of mineral-fluid reactions in controlling element cycling, predictions of large-scale mass transport are hindered by the scale-dependence of mineral dissolution-precipitation rates and the use of the continuum approach in numerical models that represents porous media with continuous domains of volume-averaged properties (Molins et al., 2012). This approach can lead to significant error in the prediction of geochemical reaction rates (Li et al., 2006; Li et al., 2008; Molins et al., 2012). Global patterns in rainfall and soil moisture content will be altered in response to climate change (IPCC, 2013), therefore the impact of wetting and drying on mineral-fluid reactions is likely to be of increased significance and concern. In particular, partially wetted porous media exhibit highly heterogeneous pore microenvironments that are subject to significant change during gas and fluid mobility. Others have posited that particle entrainment by the mobile fluid meniscus during evaporation or water recharge contributes to hardening of soils, and have shown indirect textural evidence of this process (Mullins et al., 1987; Bresson and Moran, 1995), but the more important chemical impacts of particle mobility have not been previously appreciated. We anticipate that pore scale reaction rates will be highly dynamic and variable in these environments.

Experiments using microfluidic reactors (i.e., micromodels) allow visualization of pore

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scale processes that can inform development of pore scale reactive transport models (Yoon et al., 2012; Boyd et al., 2014). To date, most of these experiments have focused on flow dynamics; only recently have mineral precipitation reactions been studied in water filled micromodels (Zhang et al., 2010; Yoon et al., 2012; Boyd et al., 2014) and few have investigated precipitation in mixed fluid-gas conditions representative of the shallow subsurface (Kim et al., 2013). Here, we consider the reactivity of magnesium hydroxide in the form of the mineral brucite, of interest because of its fast reaction rate at ambient laboratory conditions and because it actively reacts with the atmosphere in mine wastes to immobilize carbon (Harrison et al., 2013a; Chapter 2). We investigated coupled brucite dissolution-carbonate mineral precipitation in a variably water-filled silica glass micromodel under evaporative conditions to elucidate controls on mineral-fluid reactions and highlight the importance of pore scale processes on reactivity at conditions representative of the shallow subsurface.

4.2 Methods

As an example of mineral dissolution-precipitation reactions in the shallow subsurface, duplicate microfluidic brucite carbonation experiments were conducted using an unsaturated silica glass microfluidic chip. The microfluidic chip (micromodel) had a pore network that was 5.0 cm long by 1.5 cm wide with cylindrical glass pillars representative of quartz [SiO_2] grains (Appendix 2 (A2) Fig. A2.1). The network consisted of regularly spaced pillars of two sizes: $\sim 180\ \mu\text{m}$ and $\sim 70\ \mu\text{m}$. Pore throats were between ~ 215 and $260\ \mu\text{m}$, the depth was $\sim 130\ \mu\text{m}$, and the porosity was approximately 0.87. The micromodel was fabricated using standard photolithography techniques and wet etching with hydrofluoric acid (Kim et al., 2013). Prior to experimentation and between experiments, the micromodel was thoroughly flushed with toluene, isopropyl alcohol, 12 M hydrochloric acid, deionized water, and then the experimental slurry. Experimental slurries consisted of 0.5 M MgCl_2 prepared using deionized water and reagent grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 5 wt.% pulverized brucite. The brucite was sieved to < 53

μm in diameter with a mean particle diameter of $23\ \mu\text{m}$, and surface area of $5.2\ \text{m}^2\ \text{g}^{-1}$. The brucite was $\sim 79\ \text{wt.}\%$ pure, with the remainder consisting primarily of dolomite [$\text{CaMg}(\text{CO}_3)_2$] and magnesite [MgCO_3]. Slurries were sonicated to minimize particle aggregation prior to injection into the micromodel with a syringe. Refer to Appendix 2 for details regarding the analytical methods used to characterize the initial brucite.

After the slurry was injected, multiple pore volumes of research grade gaseous CO_2 (99.99% purity; Praxair) were flushed through the chip to displace the slurry, leaving the pore network with variable water content (i.e., not all pores were filled with water). The micromodel was then immediately connected to a stream of CO_2 supplied at a constant flow rate of $0.5\ \text{mL}\ \text{min}^{-1}$ using a Teledyne ISCO model D-260 pump. A high CO_2 supply rate compared to the micromodel pore volume ($\sim 85\ \mu\text{L}$) was utilized to ensure that the carbonation reaction was not limited by a lack of CO_2 . The first experiment was conducted for 18 h, and the second for 8 h.

Time lapse greyscale brightfield images were taken at 5 minute intervals during the experiment using an inverted Olympus CKX41 transmitted light microscope and an Orca-ER (1344×1024 pixels) Hamamatsu camera. These images comprised a field of view of $3.5\ \text{mm}$ wide $\times$ $2.6\ \text{mm}$ long. Additional images were collected in color to characterize the entire pore network following the second experiment using a Nikon eclipse E600 POL microscope and Canon EOS Rebel T2i camera at various fields of view. Raman spectra of the reaction products were collected following the second experiment using a Renishaw inVia microscope with $785\ \text{nm}$ excitation. Mineral identifications were conducted with reference to the RRUFFTM database of Raman spectra.

4.3 Results and discussion

Injection of pure CO_2 gas into micromodels induced evaporation of water, dissolution of brucite, and precipitation of prismatic nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] crystals and other Mg-carbonate minerals (Fig. 4.1A; A2 Figs. A2.2 and A2.3). Brucite particles dissolved

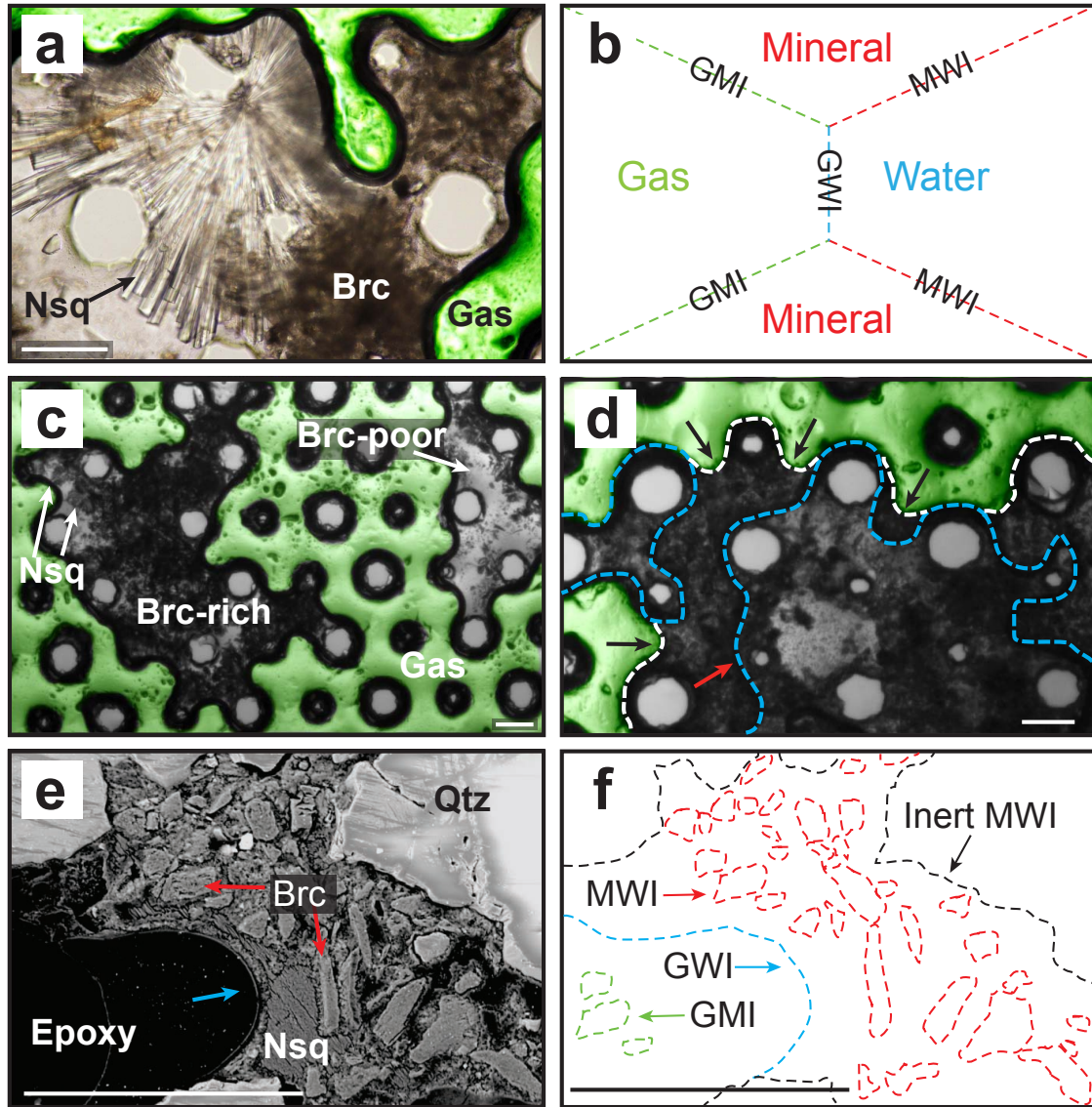


Figure 4.1. Conceptual schematic and transmitted light and backscattered electron micrographs of brucite carbonation (see following page for caption).

Figure 4.1 (continued). Conceptual schematic and transmitted light and backscattered electron micrographs of brucite carbonation. Gas-filled areas are false colored in green. A) Prismatic nesquehonite. B) Conceptual model of key interfaces. The mineral-water interfacial area (MWI) is defined as the reactive mineral surface area per unit volume of water (red dashed line), the gas-mineral interfacial area (GMI) is the mineral surface area in effectively dry pores (green dashed line) and the gas-water interfacial area (GWI) is the surface area of the gas-water interface (blue dashed line). C) Nesquehonite precipitation in a brucite-rich, water filled zone (left-hand side) compared to lack of carbonation in a brucite-poor, water filled zone (right-hand side) and gas-filled, dry area (middle). D) Evidence of brucite entrainment by water menisci during evaporation (indicated by black arrows). The former GWI is indicated by the white dashed line and black arrows, whereas the present GWI is indicated by a red arrow and the blue dashed line. E) Backscattered electron micrograph of reaction products from a bench scale brucite carbonation experiment (Harrison et al., 2015; Chapter 5) exhibiting textures consistent with particle entrainment by the mobile fluid meniscus. The epoxy-mineral interface, indicated by the blue arrow, is an approximate representation of the location of the GWI at the end of the experiment. F) Schematic representation of the key interfaces in (E). Dashed lines are color coded according to the scheme in (B), except the black dashed line, which represents the effectively inert quartz [SiO_2]-water interface. All scale bars are 200 μm .

(Accompanying Materials (AM) Video AM.1) and drove pore fluid to chemical saturation with carbonate minerals. This is consistent with the replacement of brucite by carbonate minerals as has been documented in bench scale experiments and inferred from weathering of industrial wastes under similar geochemical conditions (Harrison et al., 2013a; Chapter 2). In the micromodel, and by inference in the shallow subsurface of Earth, interfaces between gas, liquid, and solid are mobile and exert a first order control on reactivity and hence element transport. We differentiate between the gas-water interfacial area (GWI), gas-mineral interfacial area (GMI), and mineral-water interfacial area (MWI) in Figure 4.1B. Light microscopy revealed that evaporative water loss drove changes to the GWI and GMI, and that the mobility of solid particles by moving water menisci resulted in order-of-magnitude changes to the local volume-specific MWI (AM Videos AM.1-2).

Many mineral reactions proceed via dissolution and precipitation mechanisms in which aqueous solutions play a critical role. This is evident in our experiments wherein brucite in

dry pores remained visibly unreacted, whereas hydrated carbonate precipitates were abundant in water filled pores (Fig. 4.1C; AM Video AM.1), demonstrating that the GMI is effectively unreactive. The experiments revealed that in nearly all occurrences of nesquehonite, the size, lateral extent, and morphology of crystals was limited by the location of the GWI (Fig. 4.2). Only in large, connected, water-filled zones was nesquehonite precipitation not interface-limited (Fig. 4.2D). The micromodel experiments also revealed a propensity for formation of carbonate reaction products in areas of higher brucite abundance, i.e., “mineral buffered” zones (Fig. 4.1C; AM Video AM.1). Time-lapse images clearly demonstrate the absence of carbonation in a brucite-poor water-filled zone in contrast to abundant nesquehonite precipitation in an adjacent, comparatively brucite-rich water-filled zone (Fig. 4.1C; AM Video

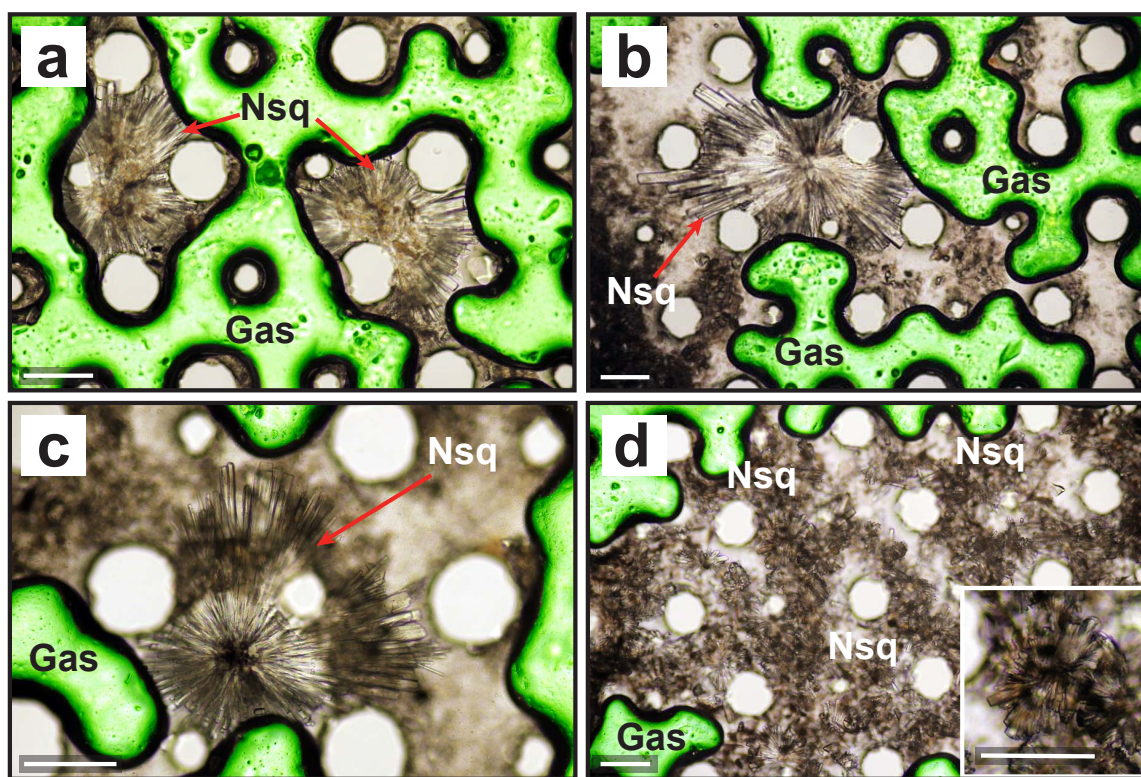


Figure 4.2. Transmitted light micrographs of nesquehonite precipitates. Gas-filled areas are false colored in green. A-C) Nesquehonite precipitates in water-filled areas, with lateral growth limited by the gas-water interface. D) Abundant nesquehonite precipitates in a large, connected, water-filled zone. Inset showing a close-up of a nesquehonite crystal in this zone. All scale bars are 200 μm .

AM.1). This is attributed to the higher MWI, which allows rapid dissolution due the higher mineral surface area, contributes a higher density of nucleation sites, and provides greater pH buffering capacity that promotes both increased CO₂ uptake into solution and carbonate precipitation. Geochemical models predict that at low MWI, even complete dissolution of the available brucite may not be sufficient to stabilize carbonate precipitates, a likely explanation for the lack of carbonation in the brucite-poor, “fluid buffered” zone (A2 Fig. A2.4).

Particle entrainment by moving water menisci during evaporation may enhance coupled mineral dissolution-precipitation reactions by increasing the MWI by a factor of 100 or more (Fig. 4.3). During evaporation, brucite particles were entrained behind the retreating fluid menisci, rather than being left behind in dry pores where they would be effectively inert (Fig. 4.1D, AM Video AM.1), similar to the coffee-ring effect in unconstrained droplet evaporation (Yunker et al., 2011). Particle movement is attributed to capillary and surface tension forces and advective water movement within water-filled pores (Maenosono et al., 1999; Xu et al., 2008). Particle entrainment by mobile fluid menisci has been posited as an explanation for changes in physical structure and strength of agricultural soils upon wetting/drying, and is

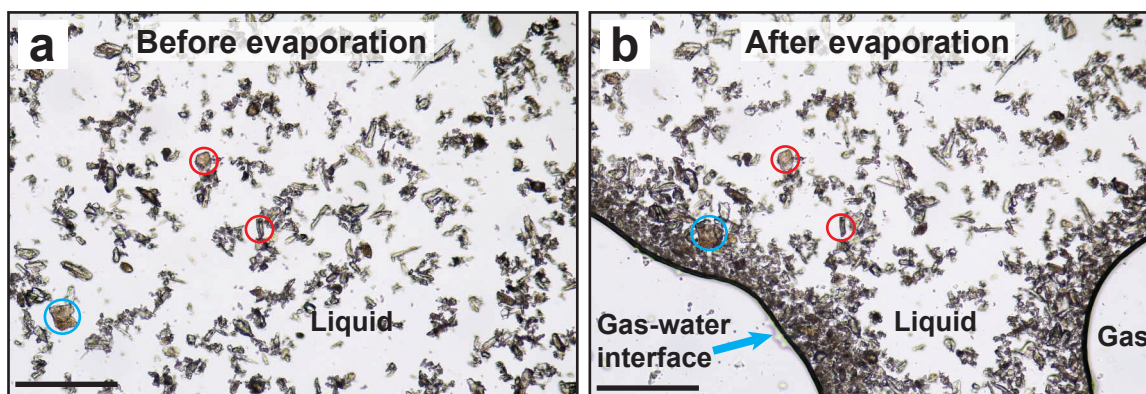


Figure 4.3. Entrainment of brucite particles by the retreating water meniscus during evaporation. Initial brucite slurry (5 wt.%) (A) and brucite slurry following 10 minutes of evaporation (B) at room temperature between two glass slides, as observed using transmitted light microscopy. Circles indicate identical brucite particles before and after evaporation for spatial reference. Red circles show particles that remained stationary and the blue circle shows a particle that has been moved and rotated. Scale bars are 200 μm .

consistent with textures in soils (Fig. 4.1E) (Kemper and Rosenau, 1984; Mullins et al., 1987; Bresson and Moran, 1995) and bench-scale experiments (Fig. 4.1F) (Harrison et al., 2015; Chapter 5). Soils in arid and semi-arid environments are particularly vulnerable, and tend to form hard surface crusts that may decrease infiltration of water, enhance erosion, and inhibit root growth (Mullins et al., 1987; Bresson and Moran, 1995). Although substantial research has been devoted to understanding the physical dynamics of drying in porous media, the more complex impacts, such as the advective transport of solutes and particle migration remain open questions (Prat, 2011). To our knowledge, the relevance of these processes to larger scale mineral weathering in the natural environment, and their potential impact on local fluid chemistry and reaction rate has not previously been recognized.

Recent advances in pore scale numerical modeling reveal that heterogeneity in physical pore structure can alter mineral dissolution rates (Molins et al., 2012). Physically, both the bulk pore structure and the local GWI are changed. Porosity is augmented in areas that dry out, increasing the relative permeability for gas flow, while the collection of fine particles in the water-filled zones could decrease permeability to water upon rewetting. Water recharge may remobilize particles in some circumstances (Lazouskaya et al., 2013), although the formation of mineral cement between grains would limit their remobilization (Harrison et al., 2015; Chapter 5) (Fig. 4.1E). In addition, a significant increase in solid material at the gas-water interface, as exhibited during evaporation of a brucite slurry between two glass slides (Fig. 4.3), could alter the rate of gas uptake into solution by providing a CO₂ sink near the interface.

Particle entrainment also results in a dynamic evolution of the chemical environment due to changes in mineral distribution, partitioning the system into fluid buffered and mineral buffered environments. These pore scale heterogeneities can lead to the development of water chemistry microenvironments different than the bulk solution (Li et al., 2007), not unlike the effect of microbes that change localized reaction rates by orders of magnitude (Mielke et al., 2003). During evaporation of a 5 wt.% brucite slurry, the MWI was estimated to increase by approximately two orders of magnitude (Fig. 4.3). Simple batch geochemical modeling of

$[\text{HCO}_3^-]$ -dependent kinetic brucite dissolution suggests that carbonation rates may be increased by a similar magnitude (Fig. 4.4A). The increase in MWI triggered by particle movement may drive “brucite-poor,” fluid buffered zones into the more reactive “brucite-rich,” mineral buffered field (Fig. 4.4A), enhancing overall reactivity of the system as evaporation progresses. Of particular consequence is that an increased MWI in fluid buffered microenvironments could stimulate carbonation in previously unreactive pores (Fig. 4.4A). Thus particle mobility may initiate reaction in otherwise unreactive microenvironments. For example, Assima et al. (2012) observed that carbonation reaction in periodically wetted brucite-rich mine wastes was double that of experiments in which the same volume of water was introduced in a single wetting event. Manipulation of these processes could lead to enhanced control of mineral reactivity in agriculture and industrial processes such as carbon sequestration. Rates of fertilizer and mineral dissolution could be optimized by tailoring wetting/drying cycles to increase the MWI.

The dynamic evolution of the MWI in soils in a changing climate may likewise lead to changes in chemical weathering rates in the vadose zone through solute release to river catchment areas. The effect of the changing MWI on mineral reaction rate will depend on the relative rate of attachment/detachment of ions at the mineral surface during dissolution/precipitation (“reaction controlled” if rate limiting) and the timescale of reactant/product transport towards and away from the mineral surface (“transport controlled”). The dimensionless Damköhler number (Da), can be used to distinguish between these regimes, and is defined as the ratio of the timescale of transport to the timescale of reaction (Steefel and Maher, 2009). The Da is related to the MWI as follows (Eq. 4.1):

$$Da = \frac{t_{res} k MWI}{C_{eq}} \quad (\text{Eq. 4.1})$$

where t_{res} is the residence time of the fluid (s), k is the kinetic dissolution rate constant ($\text{mol m}^{-2} \text{ mineral s}^{-1}$), C_{eq} is the solubility of the mineral phase ($\text{mol m}^{-3} \text{ fluid}$), and MWI is in units of $\text{m}^2 \text{ mineral m}^{-3} \text{ fluid}$. As Da is proportional to MWI, particle movement could shift

the overall control of the reaction (Fig. 4.4B). Although our experiments were specifically designed to remain reaction controlled, a three order of magnitude increase in Da indicates that a transition from reaction to transport control could be achieved, for example, via adjustment of CO_2 supply rate (Fig. 4.4B).

At the transport timescale typical of soil moisture in the unsaturated zone ($\sim 10^6$ s) (Stewart and McDonnell, 1991), reaction of the common silicate minerals quartz and anorthite [$CaAl_2Si_2O_8$] may change from reaction to transport controlled as a function of the MWI (Fig. 4.4B). In contrast, calcite [$CaCO_3$] remains transport controlled over a large range of MWI.

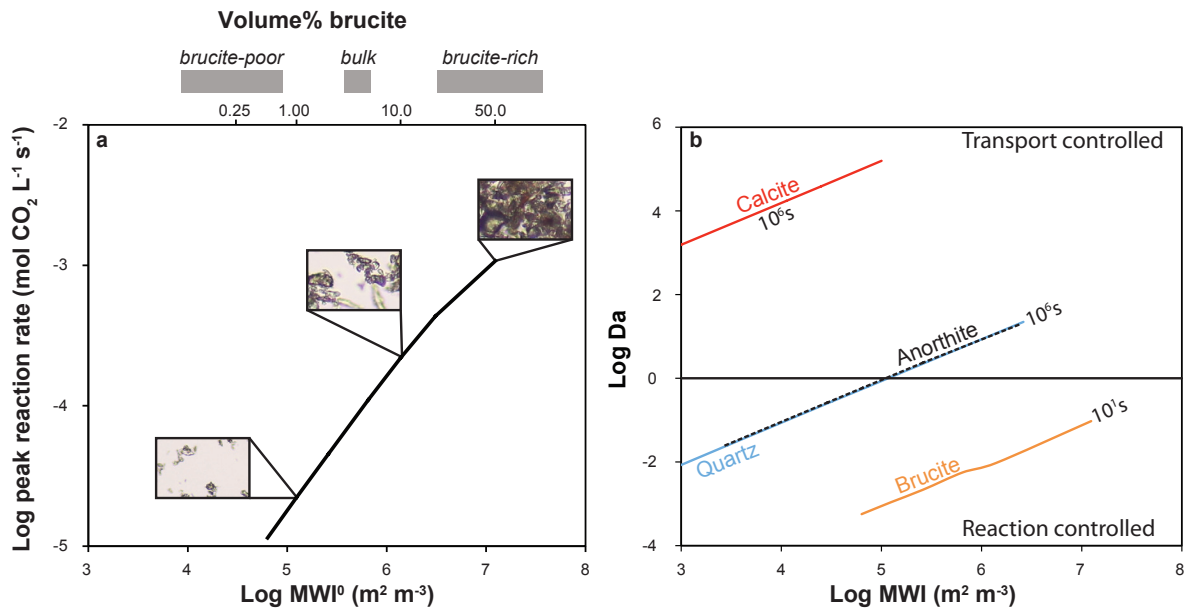


Figure 4.4. Modeled carbonation rate versus initial mineral-water interfacial area (MWI⁰) and volume percent brucite (A) and Damköhler number (Da) versus MWI (B). Grey bars in (A) illustrate the approximate range of ‘brucite-poor’, bulk (initial slurry), and ‘brucite-rich’ zones observed in the micromodels. Inset photomicrographs in (A) display examples of brucite-poor, initial (bulk), and brucite-rich slurry from the evaporation experiment pictured in Figure 4.3. Lines in (B) were calculated using a transport timescale equal to the approximate residence time of soil moisture ($\sim 10^6$ s; Stewart and McDonnell, 1991), save for brucite, which was calculated based on the CO_2 velocity in the experimental systems. The residence time of CO_2 in the micromodels was ~ 10 s. The timescale of reaction was defined as the time to reach 80% equilibrium (i.e., a saturation index of -0.1), and was determined using geochemical modeling of kinetic dissolution of each mineral (refer to Appendix 2 for details regarding modeling).

The net solute flux derived from a catchment depends on the reaction regime (Maher, 2011): solute flux will be increased disproportionately for transport controlled regimes (Tipper et al., 2006). For example, Tipper et al. (2006) attribute seasonal variation in dissolved load of river systems to the combined influence of transport controlled carbonate dissolution, which will vary strongly between high and low runoff periods, and reaction controlled silicate dissolution, which is more strongly influenced by the fluid residence time. Figure 4.4 implies that under the influence of extreme wetting and drying cycles, as might be induced by climate change, some silicate minerals may switch from reaction controlled to transport controlled, which in turn will affect solute fluxes and seasonal variations thereof. If the net effect of extreme wetting/drying cycles is to increase MWI, catchments may be driven towards ‘chemostatic’ behavior, as defined by Maher (2011), which maximizes solute fluxes derived from chemical weathering and thus the capture of atmospheric CO₂. Alternatively, if wetting during extreme precipitation events redistributes particles and lowers the MWI, the net impact will be negligible compared to current estimates of weathering fluxes.

5. Influence of surface passivation and water content on mineral reactions in unsaturated porous media: Implications for brucite carbonation and CO₂ sequestration⁴

5.1 Introduction

The evolution of mineral reactive surface area during dissolution-precipitation reactions is an important control on long-term reaction rates in both natural and anthropogenic environments (White and Brantley, 2003). Mineral dissolution reactions require that mineral surfaces be exposed to a reactive fluid, a criterion that is not always met in porous media. Dry conditions in unsaturated media may leave mineral surfaces insufficiently wetted for dissolution-precipitation reactions to occur, and precipitation of secondary phases at the surface of dissolving phases and within pores may occlude and passivate reactive surfaces. Understanding the effects of water scarcity and secondary precipitates on reactive surface areas of dissolving minerals is important for many areas of research in the Earth sciences, such as nutrient and element cycling, water quality, and CO₂ sequestration. The reaction of silicate and hydroxide minerals, such as brucite [Mg(OH)₂], with CO₂ to form carbonate minerals represents a model system to study these effects due to the coupled nature of the reactions and the extensive reaction progress that can be achieved on an experimental time scale (e.g., Daval et al., 2009a; Assima et al., 2013a; Power et al., 2013b and references therein). Such carbon mineralization reactions are currently under investigation due to their potential application as CO₂ sequestration technologies to help offset anthropogenic greenhouse gas emissions (Seifritz, 1990; Lackner et al., 1995; Lackner et al., 1997; Lackner, 2003). These technologies

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involve injection of CO₂-rich fluids or gases into subsurface mafic and ultramafic formations (McGrail et al., 2006; Kelemen and Matter, 2008; Gislason et al., 2010; Van Pham et al., 2012; Gislason and Oelkers, 2014), *ex situ* acceleration in industrial reactors (Gerdemann et al., 2007; Power et al., 2013b), and reaction of Mg and Ca-rich industrial wastes (Pronost et al., 2011; Bobicki et al., 2012; Pronost et al., 2012; Oskierski et al., 2013; Power et al., 2013b; Power et al., 2014a; Assima et al., 2014b; Wilson et al., 2014; Chapter 7). Similar reactions occur in natural environments during weathering and carbonation of ultramafic rock (e.g., Kelemen and Matter, 2008; Boschi et al., 2009; Power et al., 2014b). Prediction of reaction progress and the fate of CO₂ in these and other environments requires accurate representation of the evolution of reactive surface area.

Numerous studies have endeavored to determine the effect of surface coatings on mineral dissolution rates, with conflicting results (c.f., Hodson, 2003; Park and Fan, 2004; Cubillas et al., 2005; Béarat et al., 2006; Lekakh et al., 2008; Andreani et al., 2009; Huntzinger et al., 2009; Daval et al., 2009a; Daval et al., 2009b; Daval et al., 2011; Stockmann et al., 2011; Stockmann et al., 2013). For example, Stockmann et al. (2011; 2013) report no inhibitory effects of calcite precipitation on the dissolution of basaltic glass or diopside. Yet, several studies report inhibited dissolution of serpentine and olivine due to formation of a silica-rich layer at the mineral surface (Park and Fan, 2004; Béarat et al., 2006; Andreani et al., 2009; Daval et al., 2011; Sissmann et al., 2014; Johnson et al., 2014), and Daval et al. (2009a) documented passivation of wollastonite via calcite precipitation. Similarly, Hövelmann et al. (2012a) suggest that precipitation of magnesite during olivine carbonation clogs pores and limits reaction progress. Yet, the passivating effect of Mg-carbonates alone may be difficult to assess during silicate carbonation due to the concomitant formation of potentially passivating Si-bearing phases (King et al., 2010). Moreover, a multitude of metastable Mg-carbonate minerals are known to form during carbon mineralization reactions (Hänchen et al., 2008; Power et al., 2009; Wilson et al., 2009a; Beinlich and Austrheim, 2012; Power et al., 2013b). Differences in structure amongst these Mg-carbonates and between Mg- and Ca-carbonates

means that their passivating effects are likely highly variable, and may differ from the Ca-carbonates studied previously. The formation of hydrous Mg-carbonates is favored over precipitation of the anhydrous Mg-carbonate, magnesite [MgCO_3] at low temperature (e.g., Hänchen et al., 2008); hence the precipitation of secondary carbonates is accompanied by a loss of pore water due to its incorporation in the mineral structure. The initial volume of water available may restrict the mass of CO_2 that can be stored (i.e., the reaction progress) based on the stoichiometry of the hydrated phase (e.g., Schaef et al., 2011). For example, the extent of carbonation of chrysotile mining residues at ambient conditions as well as reaction of brucite and several silicates with wet supercritical CO_2 is limited under low water conditions (Loring et al., 2011; Schaef et al., 2011; Schaef et al., 2013a; Assima et al., 2013a; Miller et al., 2013). Evaluation of the passivating effects of hydrated Mg-carbonates is therefore complicated by the concurrent loss of pore water.

In this study, we investigate the controls on brucite [$\text{Mg}(\text{OH})_2$] carbonation in unsaturated column experiments supplied with 10% CO_2 gas, that provide simplified representations of carbon mineralization reactions in partially water saturated porous media. The objective of this study was to evaluate the effect of water saturation and precipitation of hydrous Mg-carbonates at the brucite surface on reaction progress. Because our experiments investigated carbonation of a silica-free mineral, we can assess the effect of Mg-carbonate precipitates and their different morphologies on the extent of passivation, without the complication of silica layer formation. In addition, experiments of varying water saturation were conducted in order to distinguish between surface passivation-limited and water-limited reaction. The passivating effect of surface coatings has mainly been assessed in fluid dominated stirred reactors as opposed to mineral dominated column reactors as employed in this study. Passivating effects may differ in these environments due to the limited pore volumes in which secondary phases can form, the relative scarcity of water, and the lack of abrasion that could loosen precipitates in a stirred reactor. The reactive transport model, MIN3P-DUSTY (Mayer et al., 2002; Molins and Mayer, 2007) is applied to help elucidate the processes governing carbonation and to aid in

the development of improved modeling capabilities to capture the evolution of reactive surface area during coupled dissolution-precipitation reactions, with implications for predicting the fate of CO₂ in subsurface formations or alkaline waste piles.

5.2 Methods

5.2.1 Experimental design

Two types of column experiments were used to investigate the effects of brucite grain size and water content on the carbonation reaction. The first consisted of three columns at 35% water saturation, with saturation defined as the ratio of water volume to pore volume. Each column contained a different size fraction of brucite, a ‘very fine’ fraction of <53 µm, a ‘fine’ fraction with particles between 53 and 180 µm, and a ‘medium’ fraction with particles ranging from 250 to 500 µm in diameter. The second set of experiments consisted of columns with different water saturations: 15%, 35%, and 50%, all of which contained ‘medium’ brucite. These saturation values correspond to the total bulk water saturations, while the actual saturations varied somewhat with depth. Duplicate 15%, 35% and 50% saturated medium brucite columns were set up to assess the reproducibility of carbonation rates, but no solids were sampled from these duplicate columns. In order to assess the effect of fine particulates coating larger brucite surfaces that were produced during the crushing process, a triplicate 35% saturated medium brucite column was conducted using brucite that had been repeatedly rinsed with deionized water to remove these fine particles. All experiments were conducted in 16.0 cm tall × 5.9 cm diameter polycarbonate columns manufactured by W.A. Hammond Drierite. These were filled with 10 wt.% pulverized brucite ore and 90 wt.% quartz sand to a height of 12.3-13.7 cm (Fig. 5.1). The brucite/quartz mixtures were prepared by mechanically mixing 45 g of brucite ore, and 405 g of quartz sand (total mass = 450 g). Solids were poured into columns and mechanically re-homogenized. The columns were tapped gently to allow solids to settle according to their intrinsic bulk density. The brucite ore was obtained from Premier Magnesia LLC, and was pulverized using a hammermill and sieved to separate into the appropriate size

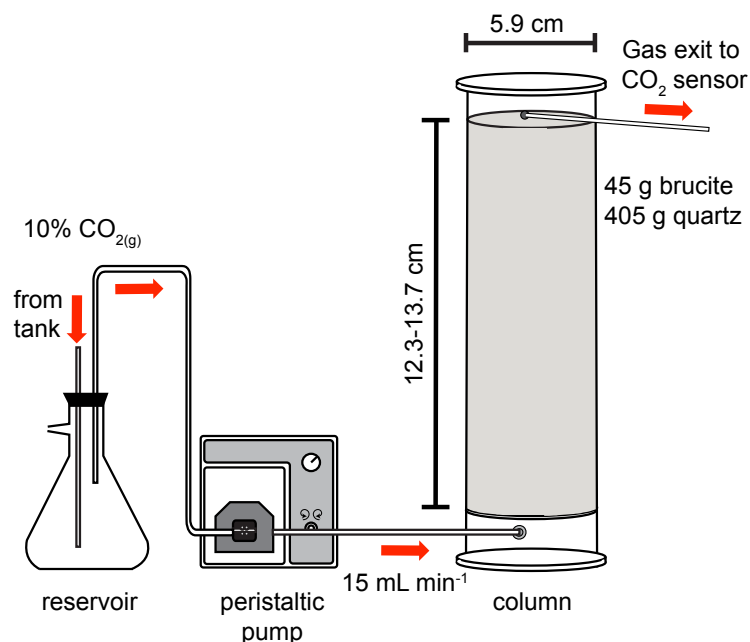


Figure 5.1. Schematic of experimental apparatus.

fractions. The quartz sand was a product of Lane Mountain Materials that had been sieved to $<600\ \mu\text{m}$ (median $\approx 210\ \mu\text{m}$). The initial major oxide composition of the brucite ore and quartz sand was determined using X-ray fluorescence spectroscopy (XRF; refer to Appendix 3 (A3) for details). XRF measurements of 5 duplicate samples indicated that the oxides present in the brucite ore at $\geq 1.00\% \pm 1\sigma$ abundance were: MgO ($60.16 \pm 0.43\%$), SiO₂ ($2.71 \pm 0.04\%$), CaO ($2.04 \pm 0.03\%$), with $34.29 \pm 0.43\%$ loss on ignition. Analysis of duplicate quartz sand samples indicated that it was $97.94 \pm 1.26\%$ SiO₂ and $\leq 2.49\%$ Al₂O₃. Rietveld refinement of X-ray diffraction (XRD) data from analysis of duplicate samples indicated that the quartz sand was nearly 100% pure with trace muscovite ($\leq 0.9\ \text{wt.}\%$). Analysis of triplicate samples of the medium brucite ore indicated it contained $78.8 \pm 3.8\ \text{wt.}\%$ brucite, $5.5 \pm 0.4\ \text{wt.}\%$ dolomite, $1.9 \pm 0.3\ \text{wt.}\%$ magnesite, $7.4 \pm 1.0\ \text{wt.}\%$ hydromagnesite, and $<0.5\ \text{wt.}\%$ lizardite and pyroaurite. The remainder was amorphous content. Analysis of single samples of the very fine and fine size fractions indicated there was no significant difference in mineral abundance between the different size fractions, save for magnesite which was equal to 2.7 wt.% and 4.0 wt.% in the very fine and fine size fractions, respectively. The surface area of the brucite ore

was determined on duplicate samples using BET with N_2 adsorption, and was equal to 5.2 ± 0.2 , 3.7 ± 0.3 , and $2.4 \pm 0.7 \text{ m}^2 \text{ g}^{-1}$ for the very fine, fine, and medium brucite, respectively (Table 5.1). The particle size distribution of the very fine and fine brucite was determined using a Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer (A3 Fig. A3.1). This indicated that the mean particle radius was $12 \text{ }\mu\text{m}$ and $39 \text{ }\mu\text{m}$ for the very fine and fine

Table 5.1. Summary of experimental conditions.

	Experiment	Brucite particle diameter (μm)	Mean particle radius (μm)	Brucite surface area ($\text{m}^2 \text{ g}^{-1}$)	Sediment height (cm)	Porosity	Volume water added (mL)	Saturation ^a (%)
Grain size trial	very fine	<53	12	5.2	12.3	0.49	58	35
	fine	53-180	39	3.7	12.3	0.49	58	35
	medium	250-500	188	2.4	13.7	0.54	71	35
Saturation trial	15%	250-500	188	2.4	13.2	0.53	29	15
	35%	250-500	188	2.4	13.7	0.54	71	35
	50%	250-500	188	2.4	13.4	0.53	97	50

^a Saturation = (volume water/volume pore space) $\times$ 100%

brucite, respectively. The medium brucite size fraction had a mean particle radius of $188 \text{ }\mu\text{m}$ as estimated based on sieving results (A3 Fig. A3.1). The porosity of the sediment in each column was calculated based on the density of the solids and the bulk volume of the porous media; it ranged from 0.49–0.53 (Table 5.1).

Initial solutions contained 0.1 M MgCl_2 added as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ from Fisher Scientific to deionized water, and $<4.0 \times 10^{-4} \text{ M}$ dissolved inorganic carbon (DIC) from the laboratory atmosphere. The solution was slowly applied across the sediment surface in the columns and allowed to infiltrate the column under the force of gravity. The volume of solution added was dependent on the desired water saturation for each experiment (Table 5.1). Once the wetting front was observed to reach the base of the column, the gas supply was initiated.

Columns were supplied with $10.0 \text{ vol.}\%$ gaseous CO_2 ($90.0 \text{ vol.}\%$ N_2), through a hose barb at their base (Fig. 5.1). The gas streams were not humidified, and therefore induced evaporation from the columns. Gas was introduced to the base of the sediment through a

stainless steel grate covered with fabric mesh (300 mesh). A Cole-Parmer Masterflex® L/S precision® standard pump system fitted with an L/S Easy-Load II® pump head was used to supply the gas stream at $\sim 15 \text{ mL min}^{-1}$ ($\sim 2.7 \times 10^{-3} \text{ g CO}_2 \text{ min}^{-1}$) to each column at atmospheric pressure and room temperature ($\sim 21^\circ\text{C}$). The gas stream exited through a port at the top of each column to maintain close to atmospheric pressure within the column (Fig. 5.1). The CO_2 concentration of the gas effluent from each column was recorded at five minute intervals using Vaisala® GMT221 CO_2 concentration sensors. The accuracy of the sensor measurements varied between $\pm 0.5\%$ to $\pm 2.0\%$ depending on the measurement apparatus, which at times became contaminated with ambient laboratory air. Gas composition data were unavailable for the 15% saturated columns due to atmospheric contamination of the measurement apparatus. The CO_2 breakthrough is expressed as ' C/C_0 ,' the ratio of the CO_2 concentration in the gas effluent at a given time to the measured CO_2 concentration of the gas effluent after the reaction was complete.

Experiments were conducted for time periods ranging from 160 to 261 h depending on the time required for the reaction to cease. Following completion of the experiments, solids were sampled by removing the entirety of the material in 2 cm intervals. The water saturation profile was estimated gravimetrically using the mass difference before and after samples were dried at room temperature. Solid samples were then analyzed for total inorganic carbon content using coulometry and mineral abundance using Rietveld refinement of XRD data (refer to A3). The solid samples were also prepared for characterization using scanning electron microscopy (SEM) both as disaggregated powders and as polished epoxy-embedded mounts to allow cross-sectional views of reacted grains. Experimental conditions including grain size, water content, and porosity are summarized in Table 5.1. For further detail regarding the experimental setup and analytical techniques, refer to Appendix 3.

5.2.2 Assessment of reaction progress

The mass of CO₂ sequestered was estimated using several lines of evidence, including (1) the total carbon content in the solid phase, (2) the mass gain of the columns during the course of the experiment, and (3) abundance of mineral phases. The measured carbon content for all experiments is expressed as %CO₂ by mass. The initial brucite/quartz mixtures had an average of $0.67 \pm 0.07\%$ CO₂ based on analysis of 6 samples that was contained in dolomite, hydromagnesite, and magnesite present in the initial brucite ore. This initial mass of CO₂ was subtracted from CO₂ content values measured for reacted samples to determine the mass of CO₂ gained. This was justified by the presence of approximately the same mass of dolomite in the reaction products as in the initial material, although the data were insufficient to resolve changes in hydromagnesite and magnesite abundances. To estimate the CO₂ gain gravimetrically, columns were placed on a scale with ± 0.01 g accuracy and their mass was recorded four times a day. At least one column in every experimental trial began to lose mass by the end of the experiment due to evaporation driven by the flux of dry CO₂/N₂ gas. Under the assumption that the evaporation rate remained relatively constant, this mass loss rate was applied to all experiments of a given trial to correct the gravimetric CO₂ measurements for evaporative loss (i.e., measured mass gain + evaporative loss = total CO₂ gain). Both total carbon and gravimetric measurements provided comparable estimates of the mass of CO₂ sequestered. The error on total carbon measurements was ± 0.22 g and was ± 0.04 g for gravimetric measurements. The error on gravimetric measurements is small compared to the uncertainty in evaporation rate calculations. However, the accuracy of reaction progress measurement is confirmed by good agreement between these two independent analyses.

The mass of CO₂ contained in crystalline carbonate phases was quantified using Rietveld refinement of XRD data. In order to determine whether CO₂ was also stored in non-crystalline phases, a known mass of a highly crystalline phase ([CaF₂] or [Al₂O₃]) was added to experimental samples. This allowed for quantification of poorly- or nano-crystalline phases (e.g., Gualtieri, 2000). For further detail regarding extent of carbonation measurement methods

and results, refer to Appendix 3.

Instantaneous carbonation rates ($r_{instant}$ in g CO₂ h⁻¹) were determined based on the mass gain between each measurement as follows (Eq. 5.1):

$$r_{instant} = \frac{[m_2 - m_1]}{[t_2 - t_1]} \quad (\text{Eq. 5.1})$$

where m_i is the column mass (g) at a given measurement time, and t_i is the time of measurement (h).

5.2.3 Reactive transport modeling

The experimental conditions were modeled using the multicomponent reactive transport code MIN3P-DUSTY (Molins and Mayer, 2007) to elucidate reaction mechanisms and allow for calibration of a model to capture reaction progress during carbonation of brucite. MIN3P-DUSTY comprises a suite of chemical reactions including mineral dissolution-precipitation, and can model flow and transport in both the gas and aqueous phases. Gas transport was modeled as an advective-diffusive process according to Darcy's law and the Dusty Gas model (Mason and Malinauskas, 1983; Molins and Mayer, 2007). For a complete description of the constitutive equations refer to Mayer et al. (2002) and Molins and Mayer (2007). Brucite dissolution kinetics were modeled using a far-from-equilibrium HCO₃⁻ concentration-dependent kinetic dissolution rate law based on data from Pokrovsky et al. (2005b) and Pokrovsky and Schott (2004) (Eqs. 5.2 and 5.3):

$$r_{brc} = k_{eff}^0 [\text{HCO}_3^-]^{0.56} (1 - \Omega^2) \quad (\text{Eq. 5.2})$$

$$k_{eff}^0 = k^0 SA \quad (\text{Eq. 5.3})$$

where k_{eff}^0 is the effective rate constant, k^0 is the initial reaction rate constant equal to 10^{-6.13} L s⁻¹ m⁻², SA is the brucite surface area (m²), and Ω is the saturation ratio. Saturation ratio is

defined as the ratio of the ion activity product to the equilibrium constant. Although the presence of multiple carbonate phases was evident in most experiments, thermodynamic data were only available for nesquehonite; therefore nesquehonite precipitation was used as a surrogate to represent precipitation of all secondary carbonate phases. Nesquehonite precipitation was effectively simulated as an equilibrium process. Porosity was set to a representative value of 0.53 for all simulations, and soil hydraulic function parameters were estimated based on results of Tempe cell tests of the solid materials (e.g., Fredlund and Rahardjo, 1993) and measured water saturation profiles. CO₂ breakthrough curves measured in the experiments were used as a fitting parameter to estimate effective reactive surface areas and interpret reaction mechanisms. For a complete list of transport parameters used in the simulations, refer to Appendix 3.

5.3 Results

5.3.1 Instantaneous carbonation rates and CO₂ breakthrough

The replacement of brucite by carbonate phases was evident in all experiments (Figs. 5.2 and 5.3). Four distinct stages in the carbonation reaction were identified, with each stage typified by a distinct trend in carbonation rate and CO₂ breakthrough (Figs. 5.4 and 5.5). Although all stages were reproducible in duplicate experiments, the presence of each stage was dependent on the experimental parameters (Figs. 5.4 and 5.5). Specifically, stage 1 was absent from the very fine and fine brucite column experiments, and stage 2 was absent from the 15% saturated medium brucite columns.

Stage 1 in the medium brucite columns was demarcated by rapid carbonation rates (up to ~0.16 g CO₂ h⁻¹) for the first ~1-2 h of the experiment, which corresponded to periods of negligible CO₂ in the outflow (Figs. 5.4C and 5.5C and D). Because conservative flushing of one pore volume in the columns would take approximately 0.1 h in these columns, the period with negligible CO₂ in the outflow is attributed to it being trapped in the column, in both the solid and aqueous phase.

Stage 2 was typified by periods of relatively constant reaction rates, and consequently,

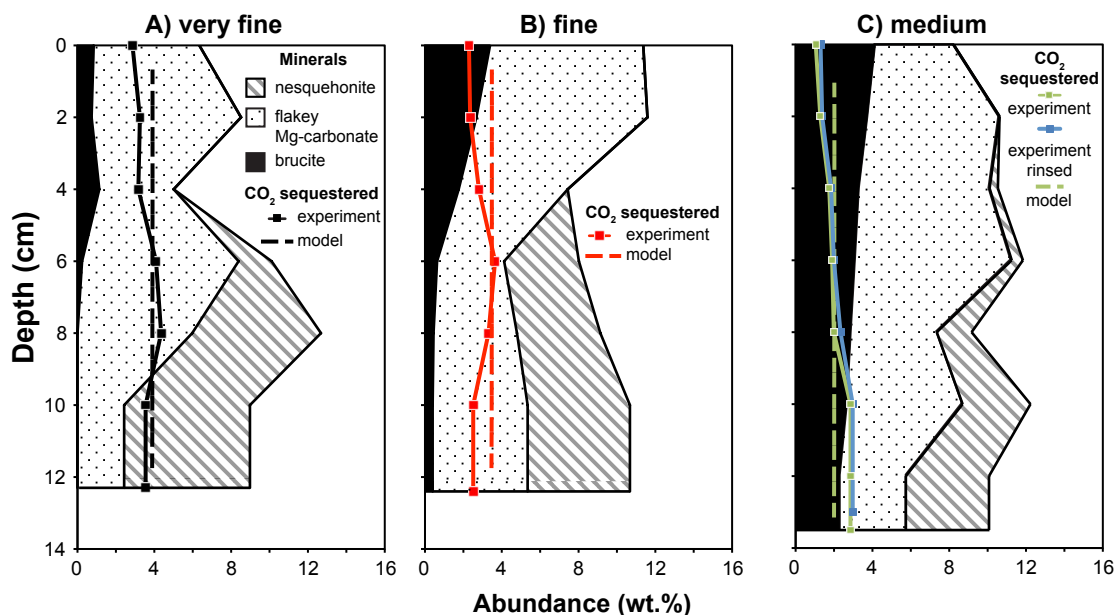


Figure 5.2. Mineral abundance profiles determined using Rietveld refinement of X-ray diffraction data for 35% saturated columns with very fine (A), fine (B), and medium (C) brucite. The black shaded, dotted, and diagonally striped areas represent the abundance of brucite, the poorly crystalline flakey Mg-carbonate phase, and nesquehonite, respectively. Lines with symbols represent the abundance of CO₂ by mass in the solid material with depth as determined using %CO₂ measurements. %CO₂ data from a 35% saturated column using brucite that was rinsed to remove the surface powder is plotted with a blue line and filled square data points in (C). Dashed lines represent MIN3P-DUSTY output for the abundance of CO₂ by mass in the solid phase for each grain size using the threshold function. CO₂ was supplied at the base.

relatively constant CO₂ concentrations in the gas effluent (Figs. 5.4B-C and 5.5). In both the very fine and fine brucite columns, stage 2 persisted for the first ~68 h, during which little to no CO₂ was measured at the column outlet (Figs. 5.4B and 5.5A-B). Carbonation rates during this period were on average 0.15 g CO₂ h⁻¹ in both columns (Table 5.2). Similarly, in the 35% and 50% saturated medium brucite columns, stage 2 was marked by relatively constant carbonation rates, and relatively constant, but elevated CO₂ concentrations in the gas effluent of 4.0-5.0% and 5.0-6.0% CO₂, respectively (Fig. 5.5C-D). Rates were between 0.08 and 0.11 g CO₂ h⁻¹ in the 35% saturated columns, and between 0.07 and 0.10 g CO₂ h⁻¹ in the 50% saturated columns. Carbonation rates in the finer grained brucite columns exceeded those in

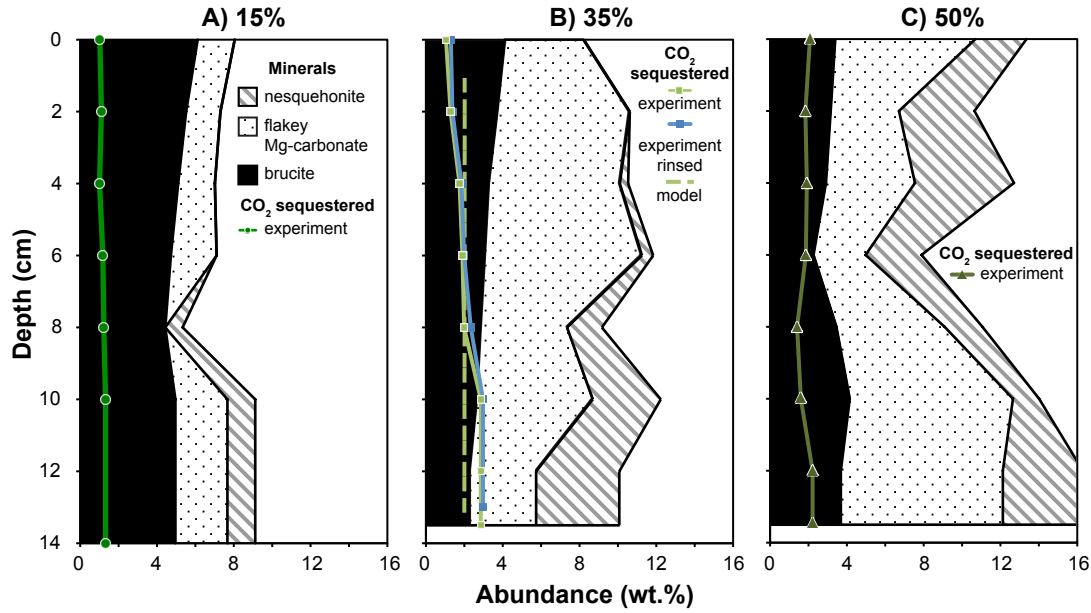


Figure 5.3. Mineral abundance profiles determined using Rietveld refinement of X-ray diffraction data for columns containing medium brucite at 15% (A), 35% (B), and 50% (C) water saturation. The black shaded, dotted, and diagonally striped areas represent the abundance of brucite, the poorly crystalline flakey Mg-carbonate phase, and nesquehonite, respectively. Lines with symbols represent the abundance of CO₂ by mass in the solid phase with depth as determined using %CO₂ measurements. %CO₂ data from a 35% saturated column using brucite that was rinsed to remove the surface powder is plotted with a blue line and filled square data points in (B). Dashed lines represent MIN3P-DUSTY output for the abundance of CO₂ by mass in the solid phase for each grain size using the threshold function. CO₂ was supplied at the base.

the medium brucite columns on average by 1.6-1.9 times during stage 2.

In stage 3, carbonation rates declined steadily in all experiments, with a concurrent increase in the CO₂ content of the gas effluent (Figs. 5.4B-C and 5.5). During stage 3, the CO₂ content increased to ~7.5% and 8.0% CO₂ in the very fine and fine brucite columns, respectively, and to ~9.5-10.0% in the 35% and 50% saturated medium brucite columns (Fig. 5.5). Transient sharp changes in CO₂ content over short durations (i.e. ~1 h) are attributed to disturbance of the CO₂ content measurement vials during column mass measurements (Fig. 5.5). Although gas composition data were unavailable, stage 3 was evident in the 15% saturated medium brucite column, with carbonation rates declining throughout the experiment and becoming negligible

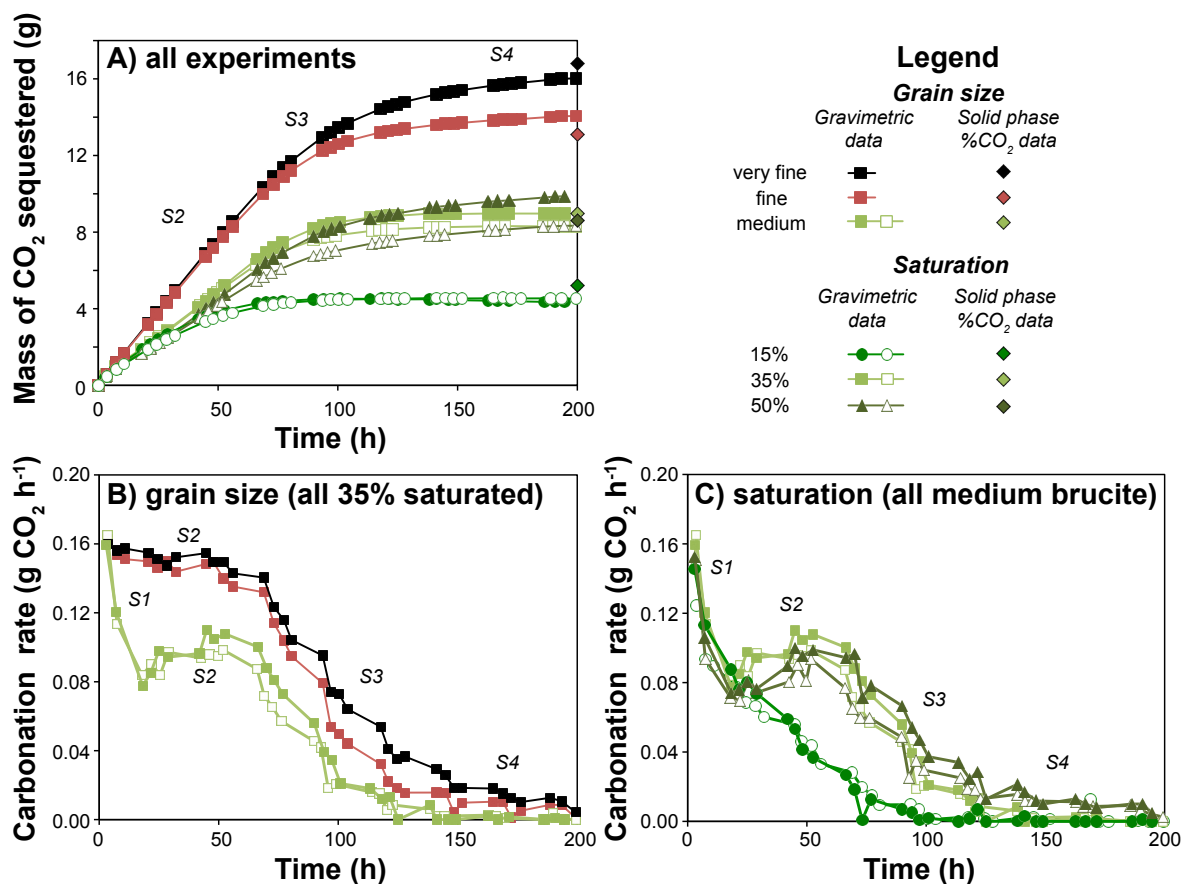


Figure 5.4. Mass of CO₂ sequestered versus time calculated based on the column mass gain over time (A). Instantaneous carbonation rate versus time in 35% saturated columns containing very fine, fine, and medium brucite (B). Instantaneous carbonation rate versus time in columns containing medium brucite at 15%, 35%, and 50% water saturation (C). Square symbols represent columns at 35% saturation, triangles are 50% saturation, and circles are 15% saturation. Grain size for columns of the same water saturation are distinguished by color, whereas all columns with medium brucite are represented by various shades of green. Open symbols represent duplicate experiments, and diamonds represent the mass of CO₂ sequestered calculated using %CO₂ measurements. ‘SX’ labels indicate reaction stages 1-4.

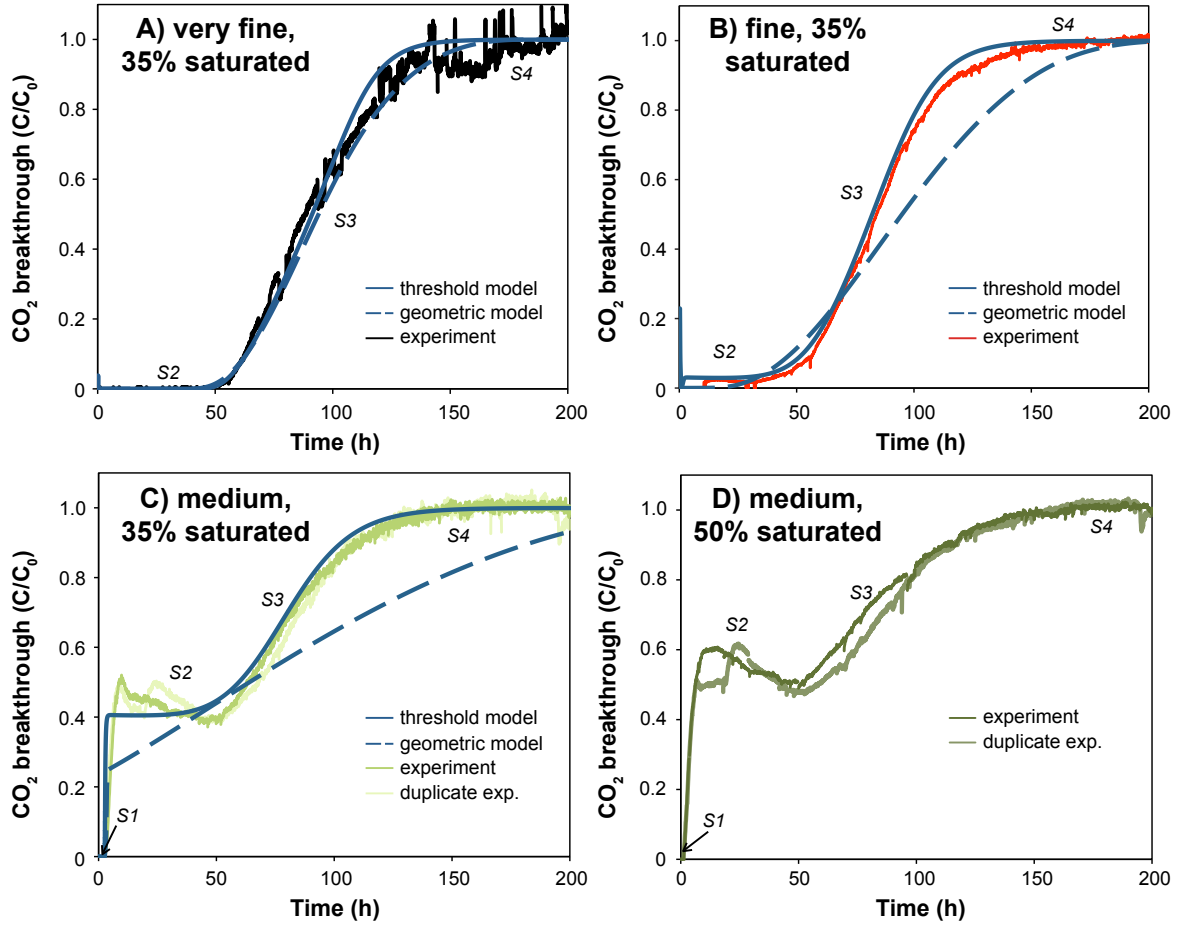


Figure 5.5. CO₂ breakthrough curves measured at column outlets versus time and MIN3P-DUSTY modeling results for 35% saturated columns containing very fine (A), fine (B), and medium brucite (C), and columns containing medium brucite with 50% water saturation (D). CO₂ breakthrough data were unavailable for 15% saturated medium brucite columns. CO₂ breakthrough curves are expressed as ‘C/C₀’, where C is the CO₂ concentration of the gas effluent at a given time, and C₀ is the CO₂ concentration of the effluent following the carbonation reaction. Solid black, red, and green lines represent experimental data from the very fine, fine, and medium 35% and 50% saturated columns, respectively. Dashed and solid blue lines represent MIN3P-DUSTY output from simulations employing the geometric and threshold models, respectively. ‘SX’ labels indicate reaction stages 1-4.

Table 5.2. Summary of mass of CO₂ sequestered, carbonation rate, reaction stoichiometry, and extent of carbonation in experiments for which solids were analyzed.

	Experiment	Total mass CO ₂ sequestered (g)		Experiment mass gain	Mass CO ₂ in flakey phase (g)	Extent of carbonation (%)	Bulk molar Mg:CO ₂ ratio	Carbonation rate ^a (g CO ₂ h ⁻¹)
		Mass CO ₂ in nsq (g)	%CO ₂ data					
Grain size trial	very fine	4.0	16.8	16.4	12.8	94	1.5	0.15
	fine	3.6	13.1	14.3	9.4	81	1.7	0.15
	medium	2.1	9.0(9.3) ^b	8.3(9.2) ^b	6.9	59	1.8	0.09
Saturation trial	15%	0.7	5.2	4.4	4.5	35	1.8	<0.08
	35%	2.1	9.0(9.3) ^b	8.3(9.2) ^b	6.9	59	1.8	0.09
	50%	4.7	8.6	8.4	3.9	58	1.8	0.08

^aAverage carbonation rate during stage 2.^bBracketed values are from the 35% saturated rinsed medium brucite column.

after ~97 h (Fig. 5.4C).

Stage 4 was evident in all columns, and was defined by a period of negligible carbonation rate and relatively constant CO₂ concentration in the gas effluent, approximately equal to the composition of the supplied gas within the estimated measurement error (Figs. 5.4B-C and 5.5). Although the final CO₂ content of the gas effluent did not exactly equal the inlet composition in the very fine and fine brucite columns, the lack of mass gain after ~115 hours (Fig. 5.4A), and the near complete depletion of brucite in these experiments (Fig. 5.2) clearly indicate that stage 4 is coincident with the effective cessation of the carbonation reaction.

5.3.2 Reaction progress

The total mass of CO₂ sequestered as determined using carbon content (%CO₂) measurements indicated that a total of 16.8 g, 13.1 g, and 9.0 g CO₂ were sequestered in the very fine, fine, and medium brucite columns at 35% saturation, respectively. A total of 5.2 g, 9.0 g, and 8.6 g CO₂ were sequestered in the 15%, 35%, and 50% saturated medium brucite columns, respectively. Similarly, 9.3 g CO₂ were sequestered in the 35% saturated column with rinsed medium brucite. These values are in very good agreement with those determined gravimetrically (Fig. 5.4A; Table 5.2).

In all experiments, brucite was replaced by a combination of the hydrated Mg-carbonate mineral, nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$], and an amorphous or nano-crystalline solid phase that could not be resolved using XRD (A3 Fig. A3.2). The abundance of this phase as determined using Rietveld refinement included any non-crystalline content in the initial materials. However, it is the relative trends in amorphous content that are important, rather than the absolute values. The total mass of CO_2 sequestered in each column was significantly greater than can be attributed to the measured abundance of nesquehonite (Table 5.2). This discrepancy implies that the unidentified phase quantified using the XRD data must be a carbonate phase.

The greatest extent of carbonation in terms of the mass of brucite converted to carbonate was achieved in the very fine brucite column at 94%, followed by the fine brucite column at 81%. A similar extent of carbonation was documented in the 35% and 50% saturated medium brucite columns, at 59% and 58%, respectively. The lowest extent of carbonation was attained in the 15% saturated medium brucite column at 35%.

The abundance and distribution of nesquehonite, the poorly crystalline carbonate phase, and total CO_2 sequestered varied significantly between experiments of different grain size (Fig. 5.2). Both the very fine and fine brucite columns exhibited similar % CO_2 trends, with the greatest CO_2 content near the column inlet (Fig. 5.2). Similarly, brucite abundance was lowest at the column inlet, where nesquehonite abundance tended to be highest (Fig. 5.2). Although a similar extent of carbonation was achieved in the 35% and 50% saturated columns, the distribution of brucite and carbonate precipitates differed (Fig. 5.3). In the 35% saturated column, total CO_2 content and nesquehonite abundance decreased along the flow-path, whereas nesquehonite, brucite, and total CO_2 were more evenly distributed throughout the 50% saturated column (Fig. 5.3). The poorly crystalline carbonate phase increased in abundance along the flow-path in all 35% saturated columns, but was more abundant with depth in the 50% saturated medium brucite column (Figs. 5.2 and 5.3). The total CO_2 content in the 15% saturated medium brucite column was effectively constant along the flow-path (Fig. 5.3A).

5.3.3 Qualitative characterization of solids

SEM micrographs of the initial material revealed that the brucite grains were coated by brucite powder, an artifact of the crushing process (Fig. 5.6A). Reaction products were comprised of elongated, narrow crystals, consistent with the morphology of nesquehonite (Ferrini et al., 2009; Harrison et al., 2013a; Chapter 2), and flakey material similar to that documented for other hydrated Mg-carbonate-hydroxide phases, such as dypingite (e.g., Power et al., 2007; Power et al., 2009; Power et al., 2013a; Fig. 5.6B-C). Energy dispersive spectroscopy confirmed that these phases consisted of Mg, C, and O (A3 Fig. A3.4). The observed abundance of flakey material was greater in the very fine and fine brucite columns than in the medium brucite columns, and generally increased along the flow path. We interpret the flakey material to represent the poorly crystalline carbonate-hydroxide phase, as the observed trend in abundance of this material along the flow path in the very fine and fine columns is consistent with the XRD data (Fig. 5.2A-B). The nanometer scale thickness of the carbonate flakes is consistent with its X-ray amorphous nature, as the crystals may be too small to exhibit long-range order that can be resolved using XRD. Cross-sectional views of reacted grains from the medium brucite columns showed that carbonate precipitates generally surrounded and coated unreacted brucite, whereas quartz surfaces typically remained uncoated (Fig. 5.6B). In some instances brucite grains had one or more sides lacking carbonate precipitates (Fig. 5.6B). Conversely, in the very fine brucite columns, carbonate precipitates formed interstitial cement that filled pore spaces between brucite and quartz grains (Fig. 5.6D). Nesquehonite rinds appeared non-porous at a submicron scale (Fig. 5.6E-F).

5.3.4 Water content

Final water content measurements are provided in terms of the ratio of water volume to bulk porous media volume (volumetric water content) rather than water saturation, owing to possible changes in pore volume due to carbonation. In the 35% saturated columns, a water loss of 28% (16.2 g), 28% (16.3 g), and 22% (15.9 g) was measured in the very

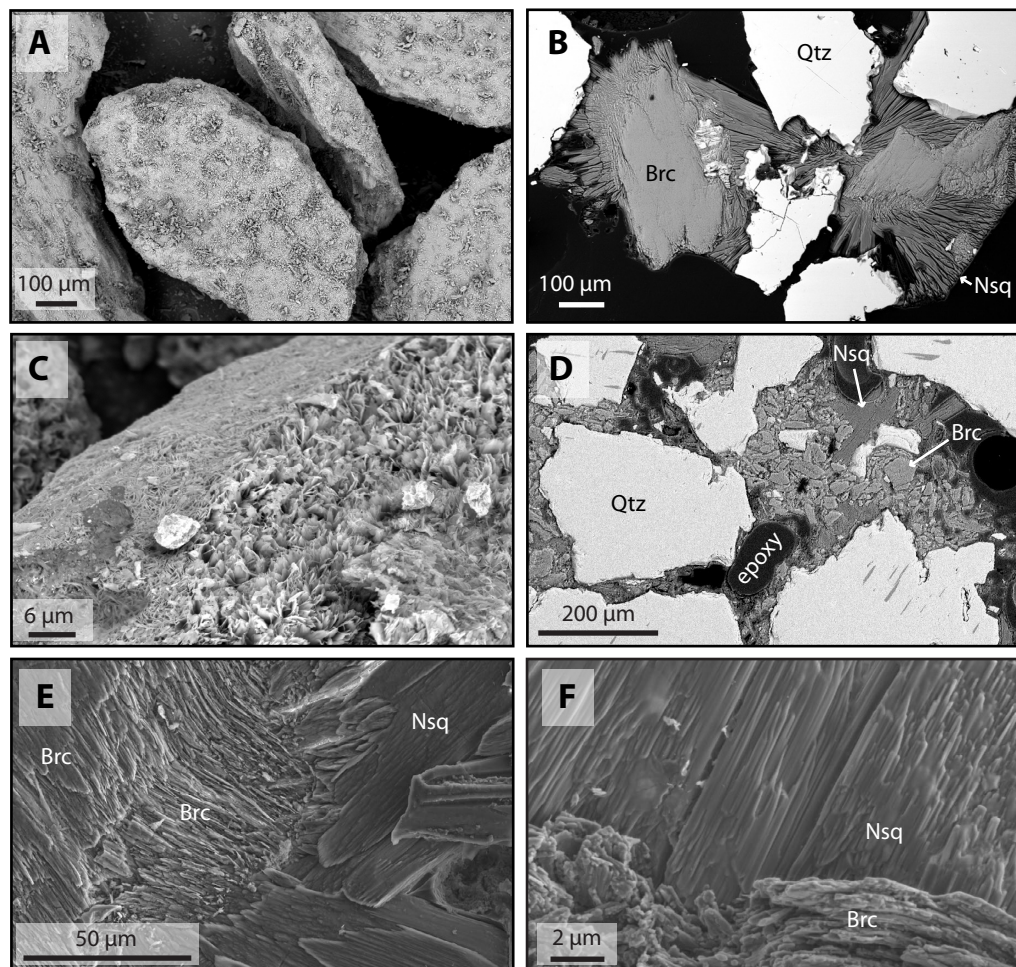


Figure 5.6. Scanning electron micrographs of initial and reacted material. Initial medium brucite (brc) showing brucite powder on the surface of large grains (A). Reaction products from the 35% saturated medium brucite column showing nesquehonite (nsq) surrounding unreacted brucite, a lesser extent of precipitates surrounding quartz (qtz), and some edges of brucite that are not coated by carbonate precipitates (B). Micrograph showing a coating of the flakey, poorly crystalline secondary Mg-carbonate phase covering a brucite grain in a sample from the fine brucite column (C). Micrograph of a sample from the very fine brucite column showing secondary carbonate infilling the space between quartz and remaining brucite grains, and cementing grains together (D). Micrographs of non-porous nesquehonite coating a ‘medium’ brucite grain from the 35% saturated column (E-F).

fine, fine, and medium brucite columns, respectively. In the 15%, 35%, and 50% saturated medium brucite columns, a water loss of 37% (10.6 g), 22% (15.9 g), and 17% (16.5 g) was recorded, respectively. Initial water volumes are provided in Table 5.1. Water loss occurred via evaporation and incorporation into precipitates. The very fine and fine brucite columns had final volumetric water contents (VWC) ranging between 0.09-0.17, compared to an initial bulk VWC of 0.17 (35% saturation) (A3 Fig. A3.3). VWC increased with depth and ranged from 0.08-0.24 and 0.17-0.30 in the 35% and 50% saturated medium brucite columns, respectively (A3. Fig. A3.3). In the 15% saturated medium brucite column the VWC remained relatively constant with depth, at values between 0.04 and 0.06 compared to an initial bulk VWC of 0.08 (A3 Fig. A3.3). Water movement during reaction likely led to its redistribution as the reaction progressed.

The mass of water lost in all experiments is much greater than expected due to evaporation alone. Evaporative losses were estimated by bulk column mass loss rates after cessation of reaction where applicable, and were between 1.8 and 3.3 g water in all experiments. Between 69% and 89% of water lost from the pore space in the columns is therefore attributed to incorporation into hydrated carbonate phases. The mass of water in nesquehonite is insufficient to account for the total water mass incorporated into the solid phase. Based on the ideal stoichiometry of nesquehonite (3 moles water per mole nesquehonite) it contained only ~8-35% of the water attributed to the solid phase. This implies that the poorly crystalline carbonate was also a hydrated phase, as is expected under the experimental conditions (Hänchen et al., 2008).

5.3.5 Reaction stoichiometry

In order to model the carbonation reaction, it is important to quantify the reaction stoichiometry to accurately represent the mass of CO₂ that can be sequestered for a given mass of brucite reacted. The reaction stoichiometry for conversion of brucite to nesquehonite is 1 mole brucite per mole CO₂. However, the presence of the poorly crystalline hydrated

carbonate phase complicates the overall reaction stoichiometry for the brucite carbonation reaction. Mass balance calculations based on XRD and %CO₂ data reveal that if the unidentified carbonate is a single phase, the Mg:CO₂ ratio in this phase is ~2. In order to maintain charge balance, this implies that the unidentified phase is likely a hydroxy-carbonate with a formula of Mg₂CO₃(OH)₂·xH₂O, similar to that of the Mg-carbonate, artinite [Mg₂CO₃(OH)₂·3H₂O]. Based on the water mass balance in each experiment, it is estimated that 'x' is between 1 and 3 (average ≈ 2).

No thermodynamic data are available to model precipitation of the poorly crystalline carbonate phase. Thus, the reactive transport models were simplified such that nesquehonite precipitation represented formation of all carbonate precipitates. This maintains the experimental CO₂, OH⁻, and Mg balance. Because the formation of the poorly crystalline carbonate reduced the ratio of CO₂ stored per mole of Mg, the initial brucite content in the models was treated as a fitting parameter to match the measured overall reaction stoichiometry. This was done rather than changing the stoichiometry of nesquehonite to avoid alteration of its solubility product and equilibrium constant.

The overall reaction stoichiometry was also calculated using the experimental data. The reduction in brucite mass and the total CO₂ mass gain in each column were determined with XRD and solid phase CO₂ measurements, respectively. The stoichiometric ratio was then calculated according to the following equation (Eq. 5.4):

$$\frac{Mg}{C} = \frac{[n_{brc_i} - n_{brc_f}]}{[n_{CO_2_f} - n_{CO_2_i}]} \quad (\text{Eq. 5.4})$$

where $\frac{Mg}{C}$ is the ratio of moles Mg consumed to moles CO₂ sequestered, n_{brc_i} is number of moles of brucite initially in the column, which was determined to be 0.61 ± 0.02 moles (1 σ), n_{brc_f} is the moles of brucite at the end of the experiment, and $n_{CO_2_i}$ and $n_{CO_2_f}$ are the moles of CO₂ in the solid phase at the beginning and end of the experiment, respectively. The values of $\frac{Mg}{C}$ for the 35% saturated very fine, fine, and medium brucite columns were 1.5, 1.7, and

1.8, respectively, compared to 1.0 for conversion to pure nesquehonite. The medium brucite columns at 15%, 35%, and 50% saturation all had $\frac{Mg}{C}$ values of 1.8, and the average $\frac{Mg}{C}$ from all experiments was 1.7. Due to the inherent measurement error in the brucite and CO₂ contents, and the variation of brucite content in the initial brucite ore, these values were not directly input in the models. However, the model-fitted values were in good agreement with the calculated values, and are provided in Appendix 3. The reaction stoichiometry, along with reaction rates and extent of carbonation are summarized in Table 5.2.

5.4 Discussion

5.4.1 Reaction stages

Both the absolute carbonation rate and the reaction stages were strongly influenced by brucite grain size, but were relatively insensitive to water content when above 15% initial saturation (Fig. 5.4). In general, higher reaction rates were achieved with finer grain size due to the greater specific surface area of the finer particles (Tables 5.1 and 5.2). Another key difference between the grain sizes was the absence of stage 1 in the very fine and fine brucite columns. Stage 1 is distinguished from the similarly high stage 2 reaction rates in the very fine and fine brucite columns due to its comparatively short duration (Fig. 5.4B-C). This transient rapid reaction rate is attributed to the carbonation of the brucite powder that was observed at the surface of larger brucite grains (Fig. 5.6A). It is expected that these finer particles reacted rapidly and were consumed in the first ~1-2 hours of the experiment owing to their higher surface area (Fig. 5.7; Helgeson et al., 1984; Andreani et al., 2009; Assima et al., 2013a). Although stage 1 may occur in the very fine and fine brucite columns, it remains unresolved due to the similarly high reaction rate of the bulk material.

Stage 2 is demarcated by a period of relatively constant carbonation rates in all experiments, and near constant CO₂ concentration in the effluent gas (Figs. 5.4 and 5.5). This represents carbonation of the bulk of the brucite (Fig. 5.7). The non-zero (~4-6%) outlet CO₂

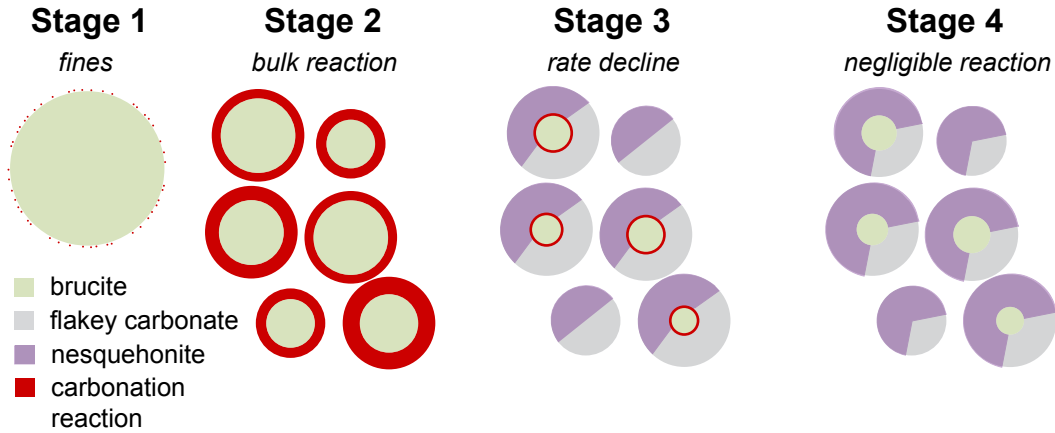


Figure 5.7. Conceptual diagram of the four reaction stages: stage 1) carbonation of fines, stage 2) reaction of the bulk of the brucite, stage 3) the majority of brucite is no longer available for reaction such that the reaction rate approaches zero, and stage 4) negligible reaction. Areas shaded green represent brucite grains, grey represents flakey poorly crystalline Mg-carbonate, purple represents nesquehonite, and red indicates where the carbonation reaction is predominantly occurring during each stage.

concentration during stage 2 is unique to the medium brucite columns (Fig. 5.5). Slight declines in CO_2 concentration during this period may be due to an increase in carbonate precipitation rate after initial nucleation has occurred.

In all experiments, the final decline in reaction rate and increase in outlet CO_2 concentration during stage 3 (Figs. 5.4 and 5.5) is attributed to a decrease in the abundance of reactive brucite along the column length. Finally, stage 4 is reached when the reaction rate has declined sufficiently such that CO_2 flow through the column is effectively conserved (Fig. 5.7).

5.4.2 Controls on reaction

Over this range of experimental conditions, several controls on reaction were realized, including: CO_2 supply, brucite dissolution, and water content. During stage 2 in the very fine brucite column, negligible CO_2 was vented (Fig. 5.5A), and the rate of CO_2 supply to the column was approximately balanced by the rate of brucite carbonation (Fig. 5.8). This implies that the overall carbonation rate was limited by the rate of CO_2 supply to the column (Fig.

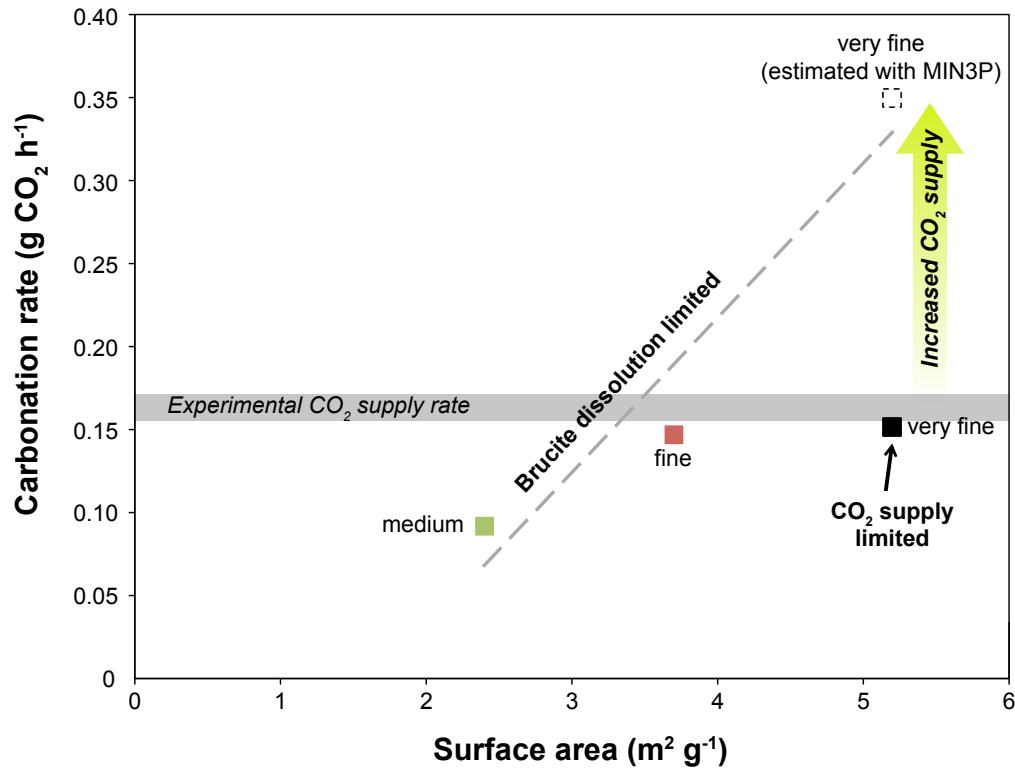


Figure 5.8. Absolute carbonation rate ($\text{g CO}_2 \text{ h}^{-1}$) for all 35% saturated columns of different grain size versus BET measured initial brucite surface area ($\text{m}^2 \text{ g}^{-1}$) for each grain size. The medium brucite is indicated by the green square, the fine by the red square, and the very fine by the black square. The white square with the dashed line indicates the approximate carbonation rate that would be achieved for very fine brucite with a 5-fold greater CO_2 supply rate, as estimated using MIN3P-DUSTY. The grey dashed line indicates the approximate trend in carbonation rate with BET surface area if CO_2 supply were not limiting. The grey shaded region indicates the rate of CO_2 supply to the columns as estimated using the measured gas flow rate out of the very fine column with laboratory air flow only, and at the end of the experiment once the column ceased gaining mass.

5.8); an increase in the CO_2 flux would therefore accelerate carbonation. Conversely, in the medium brucite columns, only ~40-60% of the supplied CO_2 is captured before reaching the column outlet, indicating that the rate of CO_2 supply outpaced the rate of carbonation. Thus, the carbonation rate of medium brucite was limited either by the rate of brucite dissolution, carbonate precipitation (Fig. 5.8), or lack of available water (e.g., Schaef et al., 2011; Assima et al., 2013a). Under similar experimental conditions, it has been documented that carbonate

precipitation occurs relatively rapidly, and is therefore unlikely to be rate limiting (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2).

The fine brucite experiment represents the transition between these two “endmembers” of rate limitation. The low but measureable amount of CO₂ vented during stage 2 (Fig. 5.5B), and the slightly lower rate of reaction compared to the very fine brucite (Fig. 5.4B) suggests that the rate of CO₂ supply slightly exceeded the carbonation rate. Thus, the moderate decrease in reactive surface area between the very fine and fine brucite sufficiently lowered the rate of brucite dissolution to shift the overall reaction from being CO₂ supply to mineral dissolution limited (Fig. 5.8). However, in both the fine and medium brucite columns, a significant portion of brucite was not carbonated despite the effective cessation of the reaction before the end of the experiment (Fig. 5.4C). This implies that brucite carbonation became inhibited at some point during the reaction.

The extent of carbonation was strongly dependent on the initial grain size; the amount of brucite consumed in the 35% water saturated columns declined from 94% to 81% to 59% in very fine, fine, and medium brucite columns, respectively (Table 5.2). As is consistent with results of Assima et al. (2013a) for carbonation of chrysotile mining residues, reaction progress was restricted at low water content. Only 41% of the brucite was reacted in the column with the lowest water saturation (15% saturated). It is possible that the incomplete reaction of brucite within the timeframe of the experiments can be attributed to a reduction in total brucite surface area as it is consumed, leading to a decline in the bulk brucite dissolution rate. In reactive transport models, the decrease in total surface area with dissolution is commonly updated assuming particles can be represented by a uniform population of perfect spheres or cubes that shrink as they dissolve (e.g., Lichtner, 1996; Mayer et al., 2002; Appelo and Postma, 2005; Wanner et al., 2011). This is described by the following equation, henceforth designated the ‘geometric model’ (Eq. 5.5; Mayer et al., 2002):

$$k_{eff}^g = (k^0 SA) \left(\frac{\phi^t}{\phi^0} \right)^{2/3} \quad (\text{Eq. 5.5})$$

where φ^0 is the initial mineral volume fraction, and k_{eff}^g and φ^t are the effective geometric reaction rate constant and mineral volume fraction at a given time greater than zero, respectively. Here, k_{eff}^g replaces k_{eff}^0 in Equation 5.2. This function calculates the decline in reactive surface area that is geometrically related to the consumption of the initial material (i.e., when φ^t shrinks), where the ‘2/3’ exponent represents the ratio of the surface area of a sphere to its volume. This function was applied in MIN3P-DUSTY to model the experimental conditions and was compared against experimental data. Owing to the similarity in the CO₂ breakthrough curves of the 50% and 35% saturated columns, and the lack of data for the 15% saturated column, the 35% saturated columns were the only medium brucite columns that were modeled. The presence of the powder coating the bulk brucite (Fig. 5.6A) was included in the model by incorporating a small mass of brucite with a significantly higher surface area than the bulk material (stage 1). The removal of this surface powder corresponds to the sharp increase in CO₂ concentration in the gas effluent after ~2 h of reaction (Fig. 5.5C-D). The very similar extent of carbonation achieved in the rinsed medium brucite column confirms that reaction of the powder comprised only a small fraction of the total brucite consumed (Fig. 5.3B). Due to the lack of a mechanistic model to simulate movement of brucite particles, as documented in microfluidic experiments (Chapter 4), this process was neglected in all models. Because the reaction rate of the finer material was controlled primarily by the rate of CO₂ supply rather than brucite dissolution, and the coarser grains likely bore the skeletal load of overlying material, this is not expected to significantly alter the results.

Application of the geometric model to simulate the very fine brucite column reproduced the CO₂ breakthrough curve and extent of reaction in the very fine brucite column very well with an adjustment of the initial reactive surface to ~20% of the BET measured surface area (Fig. 5.5A). The BET surface area is often an overestimate of the true reactive surface area, due to variability in the reactivity of surface features and the inclusion of “internal” surface area in BET measurements, which may be less reactive than the actual “external” surface area

(Brantley and Mellot, 2000; Gautier et al., 2001; Luttge and Arvidson, 2008). The reduction of the initial brucite surface area in the model is justified to account for these effects. The same reduction in reactive surface area was thus employed to model the fine and medium brucite columns.

The geometric model predicts a gradual decrease in reaction rate during stage 2 due to consumption of the bulk material and the reduction in total surface area. Yet, it cannot reproduce the precipitous shut down of reaction prior to complete consumption of the brucite in the fine and medium brucite columns, as evidenced by the poor fit between the modeled and experimental data ('geometric model' in Fig. 5.5). There are several hypotheses that could explain this incomplete reaction and precipitous decline in reaction rate: 1) water-limited reaction, 2) a disproportionate decline in reactive surface area over time due to preferential consumption of highly reactive surface sites and finer grains during the early stages of the reaction, and 3) a loss of effective reactive surface area due to passivation of the brucite surface via carbonate precipitation. The two latter hypotheses are mechanisms by which brucite dissolution may be limiting, whereas water-limited reaction affects both brucite dissolution and carbonate precipitation. We evaluate these hypotheses in light of the available data to discern the primary cause for the lack of reactivity in each column, and to allow reaction progress to be better modeled.

5.4.2.1 Water-limited reaction

Water is required not only as a reaction medium to solubilize and transport ions, but also as a reactant to form hydrated Mg-carbonate phases that incorporate water in their crystal structures. The distribution of water may therefore be a strong control on the extent of carbonation at the grain scale. At low water contents, water is held primarily around grains and in pore throats as opposed to larger pore spaces. Thus, the wetted pore volume available for precipitation is limited, and precipitation of carbonate phases may largely be restricted to the area immediately surrounding brucite grains (Fig. 5.6B). Although pH was

not directly measured, previous experimental results suggest it would drop from ~ 9.3 to ~ 7.6 during brucite carbonation (Harrison et al., 2013a; Chapter 2). However, gradients in pH and solute concentrations at the pore scale may lead to variation in saturation state within pores. In the medium brucite columns for instance, the quartz grains were generally not coated with carbonate (Fig. 5.6B), suggesting that the interfacial fluid in contact with quartz may have been undersaturated with respect to carbonate phases. Alternatively, the carbonates may favor nucleation on brucite grains compared to quartz. For example, Stockmann et al. (2014) demonstrate that carbonate precipitates preferentially nucleate on certain mineral substrates over others. In any case, without nucleation on quartz, the volume in which carbonate precipitates may form is further restricted.

The incorporation of water in the crystal structure of hydrated Mg-carbonate phases means that there is a stoichiometric limit to the mass of CO_2 that can be stored based on the amount of water available. For example, Schaef et al. (2011) demonstrate that the volume of water available to incorporate into nesquehonite dictates the extent of brucite carbonation in wet supercritical CO_2 . If all the brucite in the columns were converted to nesquehonite, two moles of water would be required per mole of brucite consumed (Eq. 5.6). Thus, 22 g (1.22 moles) of water are required to convert the initial 0.61 moles of brucite to nesquehonite. The initial volume of water added to the columns exceeded this limit for all experiments (Table 5.1). Moreover, in all but the 15% saturated medium brucite column, even the final water saturation is in excess of this value for the entire depth of the column (A3 Fig. A3.3).



Thus, an insufficient supply of water can explain the lack of carbonation in the 15% saturated column, but cannot account for incomplete carbonation in the other columns. The distribution of water at the pore scale is likely heterogeneous and leaves some grains relatively dry, suggesting that the true reactive capacity may be lower than the theoretical stoichiometric

limit. Still, the near complete consumption of brucite in the very fine brucite column with the same water content as the fine and medium brucite 35% saturated columns confirms that the lower extent of reaction cannot be attributed to insufficient water. The similar extent of reaction achieved in both the 35% and 50% saturated medium brucite columns, despite the difference in water volume is consistent with this conclusion.

5.4.2.2 Consumption of highly reactive sites and fine grains

An alternative hypothesis to explain the incomplete reaction in these columns is that the net surface area of the brucite is progressively reduced due to the preferential consumption of the finest grains in each size fraction during the early stages of the reaction. Neglecting the powder coating, the geometric specific surface area of the finest particles within the medium brucite size fraction is within a factor of three of the coarsest grains, assuming spherical particles. This difference is too small to explain the effective shutdown of the reaction. It is also possible that the pulverization of the initial brucite induced defects at the mineral surface with higher reactivity than the underlying material (White and Brantley, 2003). As these highly reactive sites were consumed, the reaction rate would decline. For example, Petrovich (1981) shows that dissolution rates of ground quartz are higher during removal of a ~3 nm surface layer altered by grinding. However, more than 50% of the brucite is consumed prior to the stage 3 rate decline for brucite of all grain sizes; it is unlikely that reaction at these grinding induced reactive sites alone could consume such a large proportion of the brucite. Moreover, the >80% consumption of brucite in the very fine and fine columns implies that a significant proportion of coarser grained material in each size fraction is reacting along with the fines. Thus the preferential consumption of highly reactive sites and finer grains cannot explain the rapid shut off of the reaction prior to completion.

5.4.2.3 *Surface passivation*

The surface passivation hypothesis is most consistent with the experimental data, for all but the 15% saturated, water-limited columns. Scanning electron micrographs clearly depict carbonate precipitates forming a rind (10s-100s of microns) surrounding an unreacted brucite core, and as pervasive coatings on mineral surfaces (Fig. 5.6B-F). However, the presence of a surface coating does not necessarily imply that the surface is passivated. Reports in the literature on the effect of surface coatings are highly variable. For example, experimental studies using stirred or agitated reactors found that precipitation of calcite did not inhibit dissolution of basaltic glass or diopside (Stockmann et al., 2011; Stockmann et al., 2013), and amorphous Fe-rich coatings did not affect anorthite dissolution (Hodson, 2003). On the other hand, the rate of pyrite oxidation is slowed by precipitation of oxide coatings (Nicholson et al., 1990), and the reaction of Ca-rich steel making slags and cement kiln dust with CO₂ is inhibited by precipitation of calcium carbonate coatings (Lekakh et al., 2008; Huntzinger et al., 2009). Similarly, silica rich layers have been found to passivate the surfaces of olivine and serpentine, although the effect is lessened for basalt (Park and Fan, 2004; Béarat et al., 2006; Andreani et al., 2009; Daval et al., 2011; Sissmann et al., 2014; Johnson et al., 2014). Daval et al. (2009a) and Hövelmann et al. (2012a) show that precipitation of calcium carbonate and magnesite can inhibit reaction of wollastonite and olivine, respectively.

Despite the disagreement in the literature as to the effect of secondary phases on dissolution, the extent of passivation is typically a function of the degree of coverage of the primary phase surface and the density and permeability of the secondary phases (e.g., Cubillas et al., 2005; Daval et al., 2009a; Daval et al., 2009b). For example, Daval et al. (2009b) show that porous silica layers are not passivating for wollastonite carbonation until the porosity of this layer becomes clogged with calcite precipitates. The degree of passivation was also dependent on the microstructure of the secondary calcite (Daval et al., 2009a). At circum-neutral pH, the precipitation of many small calcite crystals formed denser, more impermeable layers and greater passivation than at acidic pH. Similarly, Cubillas et al. (2005) found that

epitaxial growth of otavite [CdCO_3] coating a calcite surface inhibited dissolution, but its formation as islands rather than layers on aragonite [CaCO_3] surfaces did not slow dissolution. In the case of brucite, hydrated carbonates tend to favour upward growth of islands, but these islands may form a continuous layer over time (Hövelmann et al., 2012b), consistent with our observation of carbonate coatings. In our experiments, the degree to which these coatings are passivating may depend on which carbonate phase is dominant (i.e., the flakey poorly crystalline phase or crystalline nesquehonite). Velbel (1993) highlights the importance of the molar volume ratio of product to reactant for the extent of passivation, indicating that it must exceed 1 in order to completely passivate the surface. In any case, hydrated Mg-carbonates tend to have higher molar volume than brucite (e.g., brucite = $24 \text{ cm}^3 \text{ mol}^{-1}$, nesquehonite = $75 \text{ cm}^3 \text{ mol}^{-1}$), increasing the chances of passivation and pore clogging. SEM images of the flakey Mg-carbonate phase indicate that although it can completely coat brucite grains, it has a relatively porous structure that may not significantly inhibit transport (Fig. 5.6C). Nesquehonite, on the other hand, forms thick rinds that exceed $100 \mu\text{m}$ in places, with a low porosity, bladed microstructure (Fig. 5.6B, E-F). This low porosity coating is likely to substantially inhibit reaction.

The geometric surface area update model does not account for these effects, resulting in the poor fit with the experimental data (Fig. 5.5). We instead develop an empirical function that successfully reproduces the instantaneous carbonation rate through time (as represented by the CO_2 breakthrough curves; Fig. 5.5). The proposed model relates the reactive surface area at a given time to the extent of conversion of brucite, allowing a relatively constant rate of reaction up to a threshold degree of conversion (A3 Fig. A3.5). At this threshold, the reaction rapidly shuts down with increasing brucite consumption. This function is henceforth referred to as the ‘threshold model’ (Eq. 5.7):

$$k_{eff}^t = (k^0 SA) \left[1 - \left(\frac{\varphi^0 - \varphi^t}{\varphi^0 - \varphi^p} \right)^5 \right] \quad (\text{Eq. 5.7})$$

the equation is valid for $\varphi^t \leq \varphi^p$, where k_{eff}^t is the effective threshold rate constant and φ^p is a threshold brucite volume fraction (i.e., conversion threshold) at which the reaction rate becomes negligible (stage 4). Here, k_{eff}^t replaces k_{eff}^0 in Equation 5.2. The value of φ^p was equal to the amount of brucite remaining in the lower half of each column, and the exponent was adjusted to provide the best fit with the experimental CO₂ breakthrough curves. In order to fit the experimental data from all grain sizes, a value of 5 was required. The requirement of such a large exponent implies that the reaction shuts down rapidly when the conversion threshold is reached. The threshold model produces excellent agreement with the experimental CO₂ breakthrough curves for all of the brucite grain sizes (Fig. 5.5A-C). A modest decrease in initial specific surface area equal to ~15% of the measured BET surface area for each grain size was employed.

Although the threshold model is empirically derived, its form provides information as to the mechanism of reaction. Similar behavior has been documented for diffusivity in weathering rinds on basalt clasts: upon reaching a threshold porosity, the pore space becomes interconnected, and diffusivity increases considerably (Navarre-Sitchler et al., 2011). During brucite carbonation, the threshold may represent a sudden decrease in permeability of both the bulk porous media and the carbonate surface coatings due to the transformation from the poorly crystalline flakey Mg-carbonate phase to crystalline nesquehonite. The decrease in nesquehonite abundance along the flow path despite only moderate, if any, declines in total CO₂ sequestered, indicates it may be forming via replacement of a metastable phase (Figs. 5.2-5.3). Such a reaction path is not uncommon in the Mg-carbonate system (e.g., Hänchen et al., 2008; Schaef et al., 2011; Felmy et al., 2012; Schaef et al., 2013a). Poorly crystalline phases are often precursors to more crystalline phases due to a lower mineral-solution interfacial energy (Steefel and Van Cappellen, 1990; Hellevang et al., 2013); the flakey Mg-carbonate may represent such a precursor. Thus, the shutdown of the reaction may relate to the conversion of the porous, poorly crystalline phase to low porosity nesquehonite. This is consistent with the lack of passivation in the very fine-grained column, as the rapid brucite dissolution rate may

facilitate complete conversion to carbonate prior to the nesquehonite phase transformation. In the medium brucite columns, on the other hand, the slower brucite dissolution rate may cause simultaneous brucite dissolution and carbonate transformation, inhibiting dissolution prior to complete consumption. If this were the case, the overall reaction rate in the latter stages of carbonation would depend on the kinetics of the transition between the flakey phase and nesquehonite. It has recently been noted that the kinetics of carbonate precipitation may be an important control on the overall carbonation reaction (Pham et al., 2011; Gautier et al., 2014), but the effect of Mg-carbonate phase transitions on surface passivation have not previously been considered to our knowledge. Because the rate of transition between the carbonate phases is unknown, we cannot directly model this effect, and thus rely on the empirical function. However, the empirical formulation is able to describe the evolution of reactivity at the macroscale as a function of reaction progress and surface passivation, consistent with mineralogical observations. Detailed studies of the brucite-carbonate interface are required to further evaluate the effect of the phase transformation on the porosity of the surface coating and to develop a mechanistic model of surface passivation. Similar to the model of Navarre-Sitchler et al. (2011), an alternative explanation for the rapid shutdown in reaction, is that at a threshold brucite conversion, a sufficient volume of carbonate has formed, such that the porosity in the surface coating becomes disconnected and effectively shuts off access to the brucite surface. In either case, the effective cessation of reaction prior to complete conversion of the brucite is attributed to surface passivation, although the exact mechanism of passivation cannot be directly assessed based on the current results.

5.5 Implications

5.5.1 Reactive transport modeling

Recent studies have highlighted the need for improved reactive transport models to predict the fate of CO₂ during subsurface geologic storage. In particular, better constraints on secondary phase nucleation and precipitation kinetics are necessary (Pham et al., 2011;

Paukert et al., 2012; Hellevang et al., 2013; Galeczka et al., 2014; Gautier et al., 2014). Our experiments have highlighted the importance of phase transitions in the Mg-carbonate system for surface passivation and pore space clogging, a potentially important effect during subsurface injection of CO₂ into Mg-bearing rock, and formation of natural, serpentinite-hosted magnesite deposits (Boschi et al., 2009). These same mechanisms may inhibit carbon sequestration in alkaline industrial wastes. While a mechanistic model for passivation remains elusive, the excellent agreement between modeled and experimental results indicates that thresholding processes represent real constraints on carbon sequestration efficiency. The mechanism behind the passivating effects requires further study in order to develop a more generally applicable mechanistic model. Conventional geometric models alone do not adequately reproduce reaction progress during brucite carbonation, hindering the ability to predict the fate of CO₂ injected in the subsurface or alkaline waste storage facilities. This also has implications for modeling of reaction progress in natural systems that involve coupled dissolution-precipitation reactions, as the reactive surface area may not evolve in a straightforward manner. For example, the porosity and morphology changes associated with phase transformations may be relevant for other mineral systems. In particular, Mg-sulfate, zeolite, and smectite minerals may undergo transitions between different hydration states at low temperatures, with relevance for bioavailability of water and nutrients in dry environments (e.g., Bish et al., 2003; Wilson and Bish, 2012). In unsaturated porous media, the effective reactive surface area may be reduced due to the decreased exposure to the reactive fluid (White and Brantley, 2003 and references therein). Experimental evidence indicates that inclusion of water-limited reaction in terms of its effect on the reactive capacity, rather than just the rate, may also be required for modeling reactions in unsaturated porous media involving hydrated mineral phases.

5.5.2 CO₂ sequestration

Surface passivation and water limitations are potentially important constraints for carbonation efficiency of mafic and ultramafic materials, although physical and chemical

heterogeneities and more complex chemistry limit direct extrapolation from the experiments to field scale. Injection of supercritical CO₂ in the subsurface displaces formation water, resulting in a potentially water-limited reaction zone, and phase transitions between Mg-carbonates are common under these conditions (Loring et al., 2011; Schaef et al., 2011; Van Pham et al., 2012; Schaef et al., 2013a; Miller et al., 2013). Phase transformations in the Mg-carbonate systems may also have implications for formation of natural Mg-carbonate deposits. For example, Boschi et al. (2009) postulate that hydrous carbonate may have formed as a precursor to magnesite in serpentinite-hosted veins in Tuscany, Italy. Surface passivation may be less significant during carbonation of alkaline industrial wastes, however, which tend to be fine-grained. The grain size of mine tailings, for example, typically falls in the size range of the very fine and fine brucite employed in the experiments (e.g., Power et al., 2011b). The passivating effects of other Mg-carbonates than formed in this study (e.g., hydromagnesite, dypingite) may differ, and requires further investigation. The availability and distribution of water will play an important role controlling both the rate and extent of carbonation of mine tailings (Assima et al., 2013a), and other near surface carbon mineralization strategies that involve reaction in porous media such as engineered urban soils (Renforth et al., 2009; Washbourne et al., 2012). Low water contents will inhibit dissolution-precipitation processes, while high water content may effectively block gas transport (e.g., Collin and Rasmuson, 1988), promoting the development of preferential flow paths and reducing efficiency. If gaseous CO₂ were supplied to variably saturated porous media to enhance carbonation (Harrison et al., 2013b; Chapter 3; Harrison et al., 2013a; Chapter 2; Wilson et al., 2014; Chapter 7), higher water contents would require greater pressure to maintain gas flow, increasing energy costs (Fig. 5.9). The consumption of water as reaction progresses may also provide an interesting feedback on the relative permeability of the porous media; an area that requires further study.

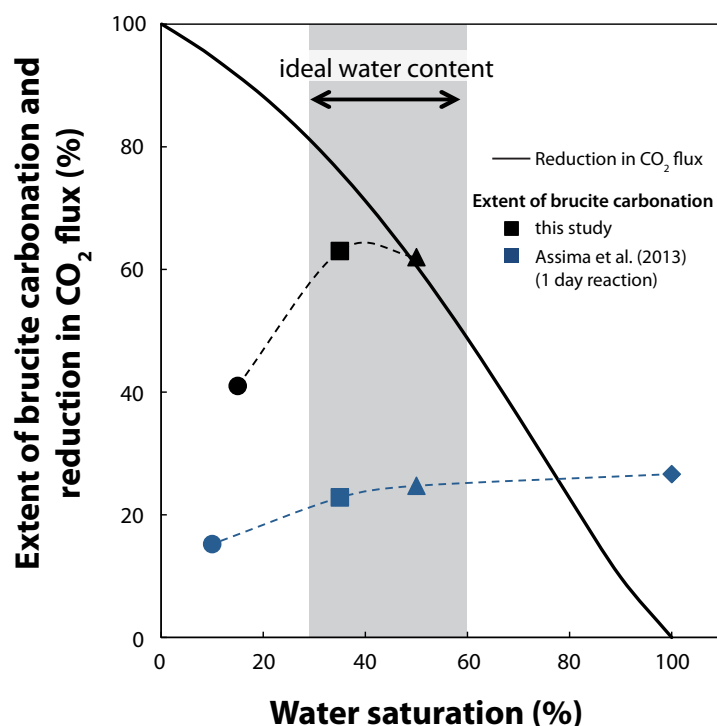


Figure 5.9. The extent of brucite carbonation measured in this study and by Assima et al. (2013a) and the calculated percent reduction in gaseous CO₂ flux through a porous medium at a fixed pressure as a function of various degrees of water saturation. Circles represent data from 10-15% saturated experiments, squares represent 35% saturated experiments, triangles represent 50% saturated experiments, and diamonds represent 100% saturated experiments. The shaded region represents the approximate range of water saturation that may both optimize the extent of carbonation and minimize energy costs associated with increased CO₂ injection pressure were gaseous CO₂ supplied to a porous medium as part of an industrial CO₂ sequestration project (e.g., Wilson et al., 2014; Chapter 7). The experiments conducted by Assima et al. (2013a) investigated carbonation of chrysotile mining residues that contained brucite using 14 vol.% CO₂ with an experimental duration of 1 day. The carbonation extent of brucite was estimated assuming that 93% of the CO₂ sequestration recorded was due to brucite carbonation (after Assima et al., 2013a). The CO₂ flux was calculated using Darcy's law for a 10 vol.% CO₂ gas mixture (balance N₂) at a constant pressure of 1 atm, assuming transport is dominated by advection (refer to A3 for details regarding the calculation).

6. Physical and chemical influences of water on mineral carbonation in variably saturated porous media: Implications for CO₂ sequestration⁵

6.1 Introduction

Mineral weathering in the unsaturated zone is an important control on nutrient availability, contaminant transport, and the carbon cycle (e.g., McKinley et al., 2006; Manning, 2008; Maher et al., 2009). The rate at which these reactions occur depends on the available surface area in contact with a reactive fluid (e.g., Helgeson et al., 1984; Brantley and Mellot, 2000). The available surface area is dependent on both the physical and chemical properties of the mineral, and environmental conditions such as water saturation (White and Brantley, 2003). In the unsaturated zone, quantification of reactive surface area is complicated by several factors, including the occurrence of dry pores and poorly connected water pathways, and secondary mineral precipitation that can dictate solution chemistry and passivate reactive surfaces (Pačes, 1983; White and Brantley, 2003; Brantley, 2008; Maher et al., 2009; Scislawski and Zuddas, 2010). Moreover, the effective reactive surface area may change over time due to consumption of the reactive phase, preferential dissolution of defects and highly reactive sites, changes in surface morphology, and formation of surface coatings (Chapter 5; Daval et al., 2009a; Helgeson et al., 1984; Maher et al., 2006; Petrovich, 1981; Scislawski and Zuddas, 2010; White and Brantley, 2003). Environmental factors are also highly variable over time in natural systems; water saturation in the shallow subsurface is altered in response to short-term weather events and longer-term climate forcings that may change the amount of surface area in contact with water, and the development of preferential flow paths may decrease exposure to reactants. Low water saturation may also reduce the reactive capacity of a porous medium, defined as the

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maximum extent of reaction possible (e.g., Dipple, 1995), due to a lack of water available to facilitate dissolution-precipitation reactions and incorporate into secondary hydrous minerals (Chapter 5; Assima et al., 2013a; Felmy et al., 2012; Loring et al., 2011; Miller et al., 2013; Schaef et al., 2013a, 2011; Thompson et al., 2013). Here, we aim to ascertain the impact of water saturation on the availability of reactive surface area and total reactive capacity. Experiments demonstrate that reactive surface area is not influenced by water saturation alone, therefore we use reactive transport modeling to elucidate the evolution of reactive surface area due also to changes in physical properties during carbonation of brucite $[\text{Mg}(\text{OH})_2]$ in partially water saturated meter-scale column reactors.

The reaction of brucite and other alkaline earth metal-bearing hydroxide and silicate minerals with CO_2 to form carbonate minerals is known as mineral carbonation (e.g., Lackner et al., 1995). Mineral carbonation reactions are model systems with which to study reactive surface area evolution and water limited reaction, due to the coupled nature of the reaction and relatively high extent of reaction that can be achieved on experimental time scales (Chapter 5). As a natural weathering reaction, mineral carbonation is an important part of the global carbon cycle and regulates atmospheric CO_2 concentrations over geologic time (Berner et al., 1983). These reactions may also be harnessed as engineered CO_2 sequestration strategies, for instance by injection of CO_2 -rich gases or fluids in the subsurface or alkaline waste stockpiles (McGrail et al., 2006; Kelemen and Matter, 2008; Gislason et al., 2010; Bobicki et al., 2012; Power et al., 2013b), or direct air capture via enhanced weathering of pulverized rock or wastes (Wilson et al., 2006; Renforth et al., 2009; Schuiling and Boer, 2010; Pronost et al., 2011; Renforth et al., 2011; Assima et al., 2012; Washbourne et al., 2012; Assima et al., 2013a; Assima et al., 2013b; Wilson et al., 2014; Chapter 7). Brucite carbonation is of specific interest for CO_2 sequestration (e.g., Zhao et al., 2010; Hövelmann et al., 2012b; Nduagu et al., 2013; Fricker and Park, 2013), particularly as a component of ultramafic mine wastes that can be exploited for its high reactivity (Chapter 5; Pronost et al., 2011; Assima et al., 2012; Bea et al., 2012; Beinlich and Austrheim, 2012; Assima et al., 2013a; Assima et al. 2013b, Harrison et al., 2013a; Chapter

2; Harrison et al., 2013b; Chapter 3; Wilson et al., 2014; Chapter 7) . The study of brucite carbonation therefore allows assessment of fundamental controls on reactivity during coupled dissolution-precipitation reactions in the unsaturated zone, with important implications for offsetting anthropogenic greenhouse gas emissions responsible for global climate change.

6.2 Methods

6.2.1 Experimental design

Column experiments were used to investigate reactive surface area evolution during dissolution-precipitation reactions in the unsaturated zone. In order to examine the impacts of water saturation on rates, extent, and distribution of reaction, experiments with heterogeneous water content and different initial water saturation profiles were performed. A total of three experiments were conducted in 25 cm diameter $\times$ 90 cm tall acrylic columns that contained 10 wt.% pulverized brucite ore and 90 wt.% quartz sand (Fig. 6.1). Of these, two were duplicates with 35% bulk water saturation and one had 60% bulk water saturation. The duplicate experiments are henceforth referred to as “35% 1 and 2.” The brucite ore was obtained from Premier Magnesia LLC and was pulverized using a hammer mill to between 250 and 500 μm in diameter (mass weighted median $\approx$ 188 μm as estimated based on sieving; Appendix 4 (A4) Fig. A4.1). The quartz sand was a product of Lane Mountain Materials (“LM 50”) that had been sieved to between 53 and 425 μm .

The initial major oxide composition of the brucite ore and quartz sand was determined using X-ray fluorescence spectroscopy (XRF; refer to Appendix 4 for details). XRF measurements indicated that the oxides present in the brucite ore at $\geq 1.00\% \pm 1\sigma$ abundance were: MgO ($60.16 \pm 0.43\%$), SiO₂ ($2.71 \pm 0.04\%$), and CaO ($2.04 \pm 0.03\%$), with $34.29 \pm 0.43\%$ loss on ignition. The quartz sand was $99.10 \pm 0.28\%$ SiO₂, with the remainder consisting primarily of Al₂O₃. Rietveld refinement of X-ray diffraction (XRD) data from analysis of the quartz sand indicated it was nearly 100% pure with trace mica (biotite or muscovite at ≤ 1.0 wt.% abundance). Analysis of triplicate samples of the brucite ore indicated it contained 78.8 ± 3.8 wt.% brucite,

5.5 ± 0.4 wt.% dolomite, 1.9 ± 0.3 wt.% magnesite, 7.4 ± 1.0 wt.% hydromagnesite, and <0.5 wt.% lizardite and pyroaurite. The remainder was amorphous content. The surface area of the brucite ore was determined on duplicate samples using BET with N₂ adsorption, and was equal to 2.4 ± 0.7 m² g⁻¹.

Mixtures of 10 wt.% brucite ore and 90 wt.% quartz were prepared by mechanically mixing 4.5 kg of brucite ore, and 40.5 kg of quartz sand (total mass = 45.0 kg). The mixtures were wetted with approximately half of the total desired water volume prior to being loaded into the column. The added water had 0.1 M MgCl₂ and <9.0 × 10⁻⁹ M dissolved inorganic carbon (DIC). The partially wetted mixtures were loaded into the columns and compacted by manual compression under a flat surface (height of porous medium = 72 cm). After loading, additional MgCl₂ solution was added to the surface to reach the desired saturation using a watering can to minimize surface disturbance. The water was allowed to infiltrate under the force of gravity. The porosity was approximately 0.52-0.54 for all columns, as estimated based on the bulk density of the solids and the volume of the porous medium.

The columns were continuously flushed with N₂ gas at 220 ± 25 mL min⁻¹ overnight to remove air with atmospheric composition from the pore space prior to initiating the supply of CO₂, and to allow time for the water distribution to equilibrate. The CO₂ supply was begun without interrupting the flow of N₂, such that the total gas flow rate was 250 ± 25 mL min⁻¹ and the supplied gas was 10 vol.% CO₂. The gas entered through a hose barb into a 4 cm tall gas filled chamber at the base of the column. The chamber was capped with a porous ceramic plate overlain by a 2 cm thick gravel layer and a sheet of fabric mesh (300 mesh) to promote homogeneous distribution of the gas into the brucite/quartz medium (Fig. 6.1). The flow rate of the gas effluent was measured at least twice a day using a Cole-Parmer® direct reading acrylic flow meter to ensure the gas supply rate was consistent. The top of the column was sealed with a gas-tight acrylic lid, and the gas effluent exited through a single 6.35 mm outer diameter tube (Fig. 6.1).

Sensors and sampling ports were installed at three points along the column length at

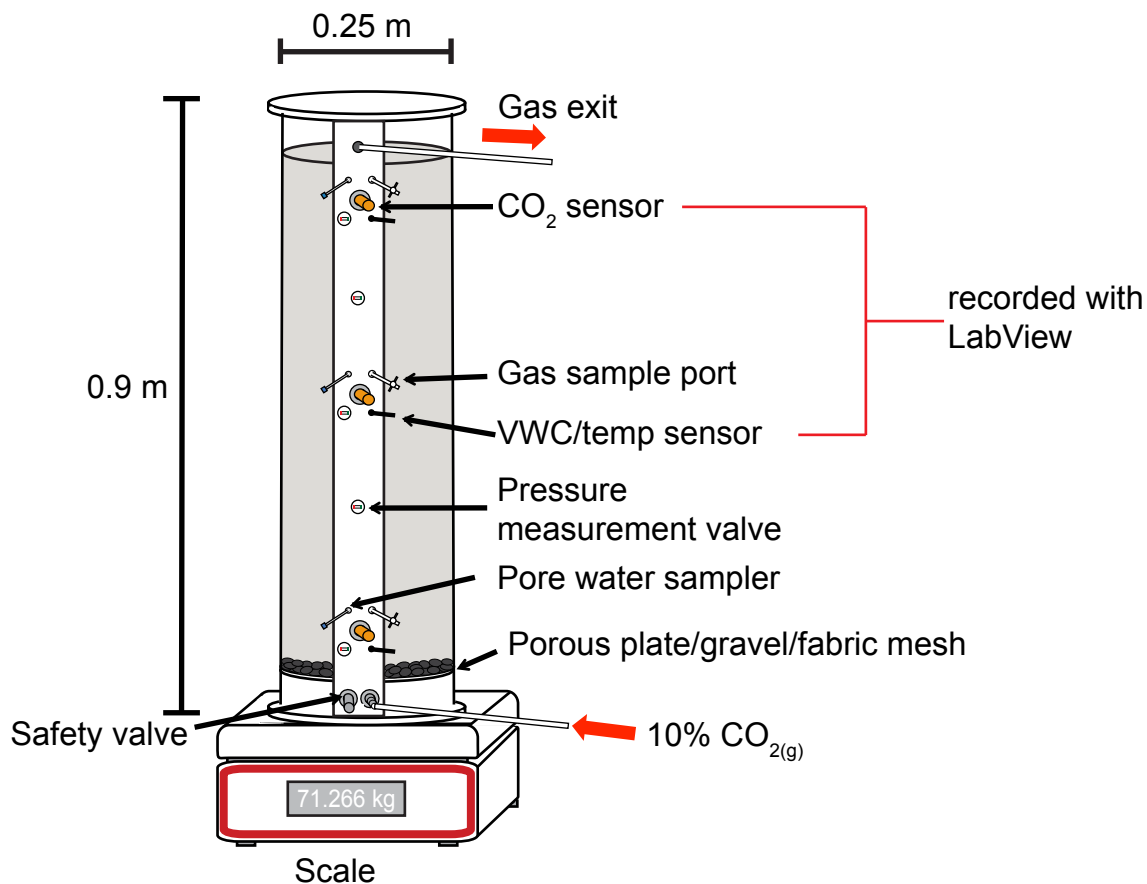


Figure 6.1. Schematic of experimental apparatus.

1) the base (5 cm above the gravel), 2) the middle (35.5 cm above the gravel), and 3) the top (65.5 cm above the gravel). Each port consisted of a Vaisala[®] GMT221 CO₂ concentration sensor (measurement error $\pm 0.5\%$ CO₂), a Decagon 5TM soil moisture and temperature probe (measurement error $\pm 1^{\circ}\text{C}$, $\pm 2\%$ volumetric water content), tubing from which to extract gas samples, a SoilMoisture micro pore water sampler, and a Mininert[®] valve to allow pressure measurements (Fig. 6.1). A Mininert[®] valve was also located between each sampling port, for a total of five measurement points. The data from the CO₂ and soil moisture and temperature probes was recorded every 5 or 10 minutes using National Instruments[®] LabVIEW[™] 8.6 software (National Instruments, 2008).

Water and gas samples were removed every 2-8 hours for at least the first 24 hours, after which the sampling interval was lowered to once a day or once every two days as the reaction

slowed. Pressure was measured manually before each sampling time using a Dwyer Mark® II plastic manometer (measurement error $\pm 2.290 \times 10^{-4}$ atm). Gas samples were collected for measurement of the stable carbon isotopic composition ($\delta^{13}\text{C}$) of the CO_2 using a Los Gatos Research instrument for laser spectroscopy (Barker et al., 2011). All $\delta^{13}\text{C}$ values are reported in δ -notation relative to Vienna Pee Dee Belemnite (VPDB) in units of per mil (‰). Water samples were collected for determination of pH, Mg and DIC concentration, and the $\delta^{13}\text{C}_{\text{DIC}}$. All water samples were filtered through 0.22 μm syringe filters, and cation samples were acidified to 2% ultrapure HNO_3 . The solution pH was measured immediately after sampling using a portable Thermo Scientific® Orion 4-Star pH/ISE meter. DIC and $\delta^{13}\text{C}_{\text{DIC}}$ data were unavailable from 35% 1 due to the formation of precipitates while in storage. To avoid this issue for 35% 2 and the 60% saturated column experiments, DIC and $\delta^{13}\text{C}_{\text{DIC}}$ samples were diluted by 10-20 times with deionized water ($<9.0 \times 10^{-9}$ M DIC) immediately following sampling to prevent precipitation of carbonate minerals prior to analysis. All water samples were stored in vials with no headspace to prevent gas exchange and were kept at $\sim 4^\circ\text{C}$ prior to analysis.

The duration of the experiments varied between 430 and 504 h depending on reaction progress. Following completion of each experiment the entirety of the solid material was removed in 10 cm intervals for analysis of the mineralogical composition, the total solid phase CO_2 content, and the $\delta^{13}\text{C}$ of the carbonate minerals. The major oxide composition and volatile content of the solids was also determined for 35% 1 and the 60% saturated experiment using XRF spectroscopy. For at least three of the depth intervals in each column, triplicate discrete samples were taken to assess heterogeneity in reaction extent and mineralogy. The remaining intervals were mechanically homogenized and an aliquot of the bulk material was removed for analysis. Experimental products were examined using scanning electron microscopy (SEM) in thin section and as disaggregated particles on conventional aluminum SEM stubs. To estimate the water saturation with depth, aliquots of known volume from each depth interval were weighed immediately after sampling. The aliquots were then reweighed following drying at 70°C , and the difference in mass was equated to the mass of water present in the wet samples.

Total water content at the end of the experiments was estimated for 35% 2 and the 60% saturated column experiments by collection, drying, and weighing of all reaction products.

6.2.2 Assessment of the rate and extent of carbonation

The extent of reaction was estimated using several lines of evidence, including (1) the total carbon content in the solid phase (%CO₂), (2) the mass gain of the columns during the course of the experiment, (3) the abundance of mineral phases, and (4) the reduction of CO₂ content in the gas phase. The %CO₂ and mineral abundance data provided information as to heterogeneity in reaction extent and mineralogical distribution, whereas the gravimetric and gas phase CO₂ measurements were used to estimate the total CO₂ sequestered, and the latter to determine the rate of carbonation. The total carbon content for all experiments is expressed as %CO₂ by mass and was measured using coulometry (refer to A4). The initial brucite/quartz mixtures had an average of 0.65% CO₂ that was contained in dolomite, hydromagnesite, and magnesite present in the initial brucite ore. This initial mass of CO₂ was subtracted from CO₂ content values measured for reacted samples to determine the mass of CO₂ gained. This was justified by the presence of approximately the same mass of dolomite in the reaction products as in the initial material as determined using XRD, although the data were insufficient to resolve changes in hydromagnesite and magnesite abundances. In order to estimate the CO₂ gain gravimetrically, the columns were placed on a scale with ± 20 g accuracy and their mass was recorded three to four times a day. The abundance of secondary carbonate phases and reduction in brucite content was determined using Rietveld refinement of XRD data. A known mass of highly crystalline fluorite [CaF₂] was added to solid aliquots to assess whether CO₂ was also stored in X-ray amorphous carbonate phases (e.g., Gualtieri, 2000). Finally, because the flux of CO₂ into the column was known, the mass of CO₂ sequestered and carbonation rate were also determined based on the reduction in this flux along the column length as measured using the CO₂ concentration sensors. The CO₂ breakthrough curves measured with the sensors are expressed as 'C/C₀,' the ratio of the CO₂ concentration in the gas effluent at a given time to

the concentration of CO₂ in the supplied gas. The instantaneous rate of carbonation ($r_{instant}$ in g CO₂ h⁻¹) was determined as follows (Eq. 6.1):

$$r_{instant} = [n_{in} - n_{out}] M_{CO_2} = \left[q_{in} \times \frac{\%CO_{2in}}{100} \times \frac{P}{RT} \right] - \left[\left(q_{in} \times \frac{\left(1 - \frac{\%CO_{2in}}{100} \right)}{\left(1 - \frac{\%CO_{2out}}{100} \right)} \right) \times \frac{\%CO_{2out}}{100} \times \frac{P}{RT} \right] \quad (\text{Eq. 6.1})$$

where M_{CO_2} is the molar mass of CO₂ (g mol⁻¹), n_{in} and n_{out} are the molar rate of entrance and exit of CO₂ (mol s⁻¹), respectively, $\%CO_{2in}$ and $\%CO_{2out}$ are the CO₂ concentration of the supplied gas and gas effluent, respectively (%), q_{in} is the total rate of supply of gas to the column (L s⁻¹), P is the gas phase pressure (atm), R is the ideal gas constant (L atm mol⁻¹ K⁻¹), and T is the temperature (K). The total CO₂ sequestered is the integration of the instantaneous rates throughout the experimental duration. For further detail regarding the experimental setup and analytical techniques, refer to Appendix 4.

6.2.3 Geochemical and reactive transport modeling

The variation in mineral saturation indices with reaction progress was calculated based on the measured aqueous chemistry data using PHREEQC V.3 (Parkhurst and Appelo, 2013) with the Pitzer database and mineral solubility data from the Minteq database. Reaction progress under the experimental conditions was simulated using the multicomponent reactive transport code MIN3P-DUSTY (Mayer et al., 2002; Molins and Mayer, 2007) to elucidate reaction mechanisms and evaluate conceptual models for water-limited reaction and surface area updates. MIN3P-DUSTY comprises a suite of chemical reactions including mineral dissolution-precipitation, and can model flow and transport in both the gaseous and aqueous phases. Gas transport was modeled as an advective-diffusive process according to Darcy's law and the Dusty Gas model (Mason and Malinauskas, 1983; Molins and Mayer, 2007). For a complete description of the constitutive equations refer to Mayer et al. (2002) and Molins

and Mayer (2007). Brucite dissolution kinetics were modeled using a far-from-equilibrium HCO_3^- concentration-dependent kinetic dissolution rate law based on data from Pokrovsky et al. (2005b) and Pokrovsky and Schott (2004) (Eqs. 6.2 and 6.3):

$$r_{brc} = k_{eff}^0 [\text{HCO}_3^-]^{0.56} (1 - \Omega^2) \quad (\text{Eq. 6.2})$$

$$k_{eff}^0 = k^0 SA \quad (\text{Eq. 6.3})$$

where r_{brc} is the brucite dissolution rate (mol s^{-1}), k_{eff}^0 is the effective rate constant, k^0 is the initial reaction rate constant equal to $10^{-6.13} \text{ L s}^{-1} \text{ m}^{-2}$, SA is the brucite surface area (m^2), and Ω is the saturation ratio. Saturation ratio is defined as the ratio of the ion activity product to the equilibrium constant.

The identity and rate of formation of secondary phases were selected based on experimental results. The two precipitates were an X-ray amorphous phase and nesquehonite $[\text{MgCO}_3 \cdot 3\text{H}_2\text{O}]$, the former having stoichiometry and solubility similar to artinite (refer to Results). Precipitation of artinite $[\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}]$ was modeled effectively as an equilibrium process, but nesquehonite precipitation was slowed such that precipitation occurred at supersaturated conditions, as was consistent with experimental data. Porosity was set to a representative value of 0.52 for all simulations, and soil hydraulic function parameters were estimated based on results of Tempe cell tests of the solid materials (e.g., Fredlund and Rahardjo, 1993) and measured water saturation profiles. Model output was calibrated against both the measured CO_2 breakthrough curves and mineralogy profiles. For a complete list of transport parameters used in the simulations and results of Tempe cell tests, refer to Appendix 4 (A4 Fig. A4.2; A4 Tables A4.2 and A4.3).

6.3 Results

6.3.1 Rate and extent of carbonation

The CO₂ concentration in the gas phase (CO₂ breakthrough curves) varied significantly with depth in all experiments (Fig. 6.2). Similar trends were documented in the duplicate experiments, although a slightly higher CO₂ concentration was measured by the middle sensor in 35% 2 during the first ~100 hours (Fig. 6.2), which may indicate the presence of preferential flow paths. Consistent with our previous work for carbonation of brucite in smaller scale columns (Chapter 5), four distinct carbonation stages were evident in the breakthrough curves (Fig. 6.2). Stage 1 represents rapid reaction of brucite powder coating the brucite grains that was an artifact of the pulverization process (A4 Fig. A4.3). Stage 2 is the reaction of the bulk of the brucite. Stage 3 comprises a rapid decline in reaction rate due to loss of reactive brucite. Finally, stage 4 is when the reaction rate becomes negligible because any remaining brucite is effectively inaccessible for reaction. However, during stage 4 the CO₂ concentration did not return to its initial value ($C/C_0 < 1$), implying that minor sequestration was still occurring. Diurnal fluctuations in $p\text{CO}_2$ measured at the top of the columns during stage 4 were coincident with temperature variations in the laboratory (A4 Fig. A4.4A). The experimental apparatus was not insulated, thus the pore water temperature experienced diurnal fluctuations in response to variations in the laboratory air temperature (A4 Fig. A4.4A). This suggests that exothermic effects from the carbonation reaction were insignificant in comparison to changes in ambient laboratory temperature.

Substantial differences were evident between the breakthrough curves of the 35% and 60% saturated columns (Fig. 6.2). In the 60% saturated column, the CO₂ concentration measured at the middle sensor was virtually identical to that measured at the base. This early breakthrough is indicative of transport of CO₂ along preferential flow paths. Similarly, CO₂ reached the top of the column at measurable concentrations earlier in the 60% saturated column, at ~16 h compared to ~80 h in the 35% saturated columns.

The CO₂ breakthrough at the top of the columns was used to calculate the bulk rate of

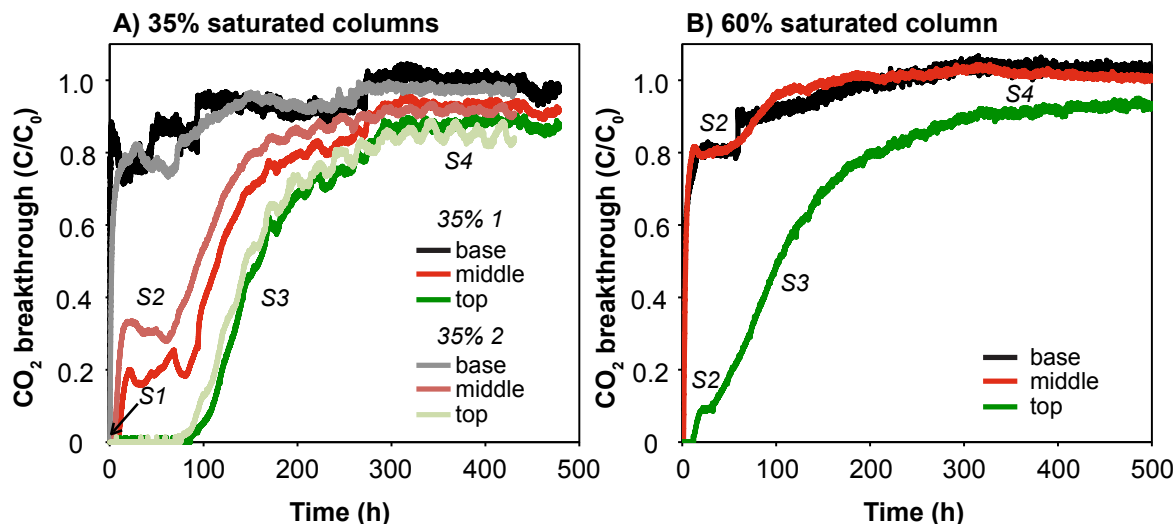


Figure 6.2. CO₂ breakthrough curves at three positions along the flow path plotted as C/C_0 (ratio of the measured CO₂ concentration at the measurement port to the CO₂ concentration in the supplied gas) versus time. Black, red, and green lines show the CO₂ breakthrough curves measured at the base, middle, and top of the 35% saturated columns (A) and the 60% saturated column (B). “SX” labels denote reaction stages 1 through 4.

carbonation over time. Carbonation rates in Figure 6.3 are normalized to the CO₂ supply rate for ease of comparison, as slight differences (10% relative) in gas flow rate were documented between experiments. These calculations revealed that the rate of carbonation was comparable between the duplicate 35% saturated columns, and these rates exceeded that in the 60% saturated column for the majority of the experimental duration (Fig. 6.3).

The extent of carbonation in each experiment as calculated using the reduction of CO₂ content in the gas phase and the total mass gain during the course of the experiments agreed fairly well (Fig. 6.3), except for 35% 1, for which the gravimetric estimate was ~17% lower than indicated by the gas phase measurements. As the gravimetric measurements were not corrected for evaporation due to difficulty controlling and measuring evaporation rates between experiments, these values represent the minimum mass of CO₂ gained. This could account for the discrepancy between the two types of measurements, and would imply that the evaporation was highest for 35% 1. Gravimetric measurements indicated that 528 g, 566 g, and 476 g

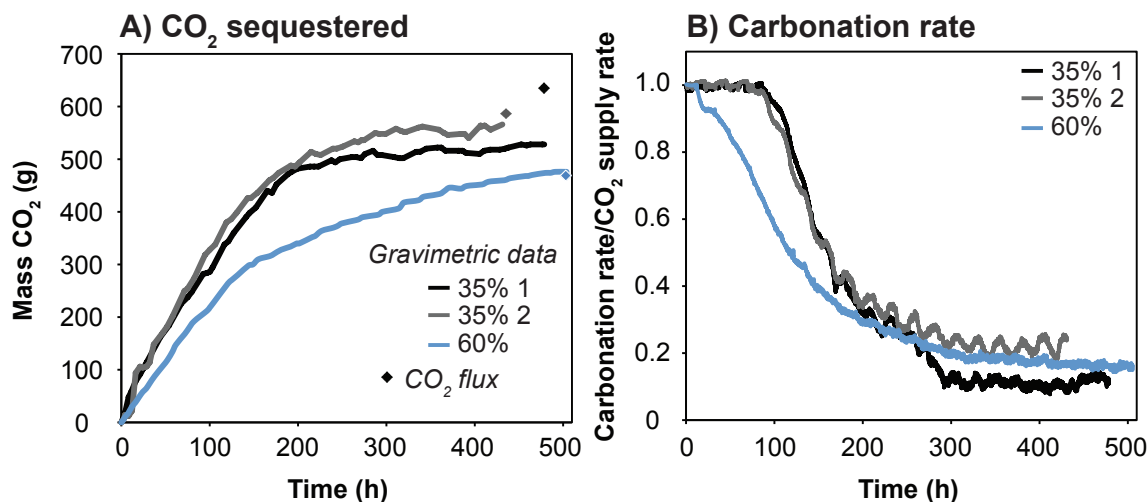


Figure 6.3. Mass of CO₂ sequestered (A) and instantaneous carbonation rate (B) versus time. Black, grey, and blue lines represent gravimetric measurements of 35% 1, 2, and the 60% saturated columns, respectively. Diamonds in (A) show cumulative CO₂ mass sequestered based on CO₂ flux analysis.

were gained in 35% 1 and 2, and the 60% saturated experiments, respectively. Gas phase CO₂ calculations indicated that 635 g, 587 g, and 469 g of CO₂ were gained in 35% 1 and 2, and the 60% saturated experiment, respectively. Both datasets indicated that a lower amount of CO₂ was sequestered in the 60% saturated column.

6.3.2 Characterization of precipitates

6.3.2.1 Composition and distribution of precipitates

In all experiments, brucite was replaced by nesquehonite and an X-ray amorphous Mg-carbonate phase (Fig. 6.4; A4 Fig. A4.5). A minor amount of lansfordite [MgCO₃·5H₂O] was also documented in 35% 1 (Fig. 6.4C). Only total amorphous content can be calculated using Rietveld refinement, therefore quantified abundances of the X-ray amorphous Mg-carbonate include any amorphous content as other phases. The XRD quantified abundance is not used to calculate the mass of this phase but allows assessment of the general trends in abundance. Nesquehonite was not resolved above ~35 cm depth, but %CO₂ measurements indicate that CO₂ was still sequestered (Fig. 6.4C and D). This confirms that the X-ray amorphous phase is

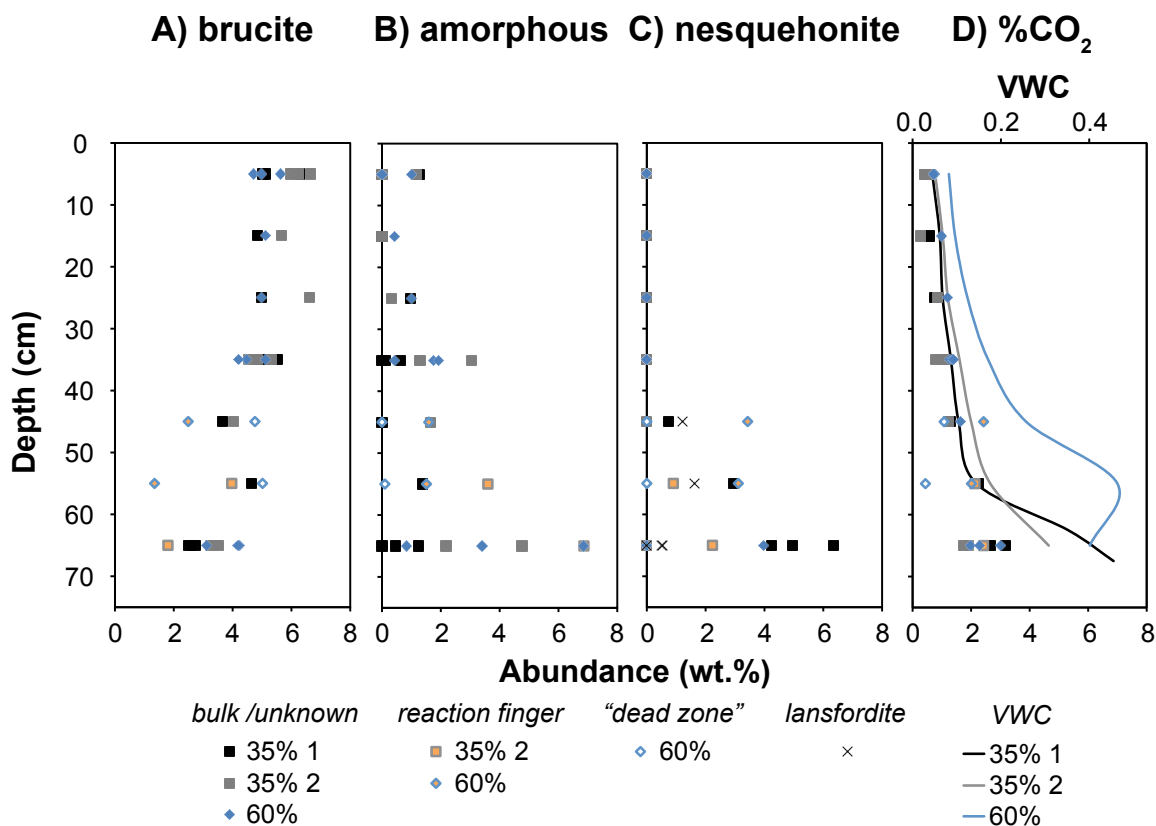


Figure 6.4. Mineral and solid phase CO₂ abundance profiles. A) Brucite abundance versus depth. B) Amorphous content versus depth. C) Nesquehonite abundance versus depth from all columns, and lansfordite abundance versus depth in 35% 1. D) Total solid phase CO₂ content in the experimental products that is contained in secondary carbonate phases and final volumetric water content (VWC) versus depth. Black and grey squares represent 35% 1 and 2, respectively. Blue diamonds represent the 60% saturated column experiment. Black, grey, and blue lines represent the VWC of 35% 1, 2, and the 60% saturated experiment, respectively. Black 'Xs' in (C) represent lansfordite abundance in 35% 1; lansfordite was not documented in the other experiments. Orange filled symbols represent samples taken from reaction fingers, and white filled symbols represent samples taken from "dead zones" outside fingers. All others represent bulk samples or samples for which it was not possible to ascertain visually whether they were part of a reaction finger.

also a carbonate, in agreement with previous experimental results (Chapter 5). The abundance of both Mg-carbonates tended to decrease with distance along the flow path in all experiments, although significant heterogeneity in the extent of carbonate precipitation was documented in triplicate samples from the same depth intervals (Fig. 6.4B and C). The greatest extent of heterogeneity for both the carbonate minerals and total %CO₂ was documented in the 60% saturated column (Fig. 6.4). Due to the high degree of heterogeneity in the extent of carbonation, these data were not used to calculate the total mass of CO₂ sequestered. Nowhere was brucite completely consumed, but the abundance typically increased along the flow path in parallel to the decreased %CO₂ sequestered (Fig. 6.4A). An orange coloration in reaction products was found to correlate with a greater extent of carbonation (A4 Fig. A4.6).

Precipitation of hydrated Mg-carbonates is expected under the experimental conditions (e.g., Hänchen et al., 2008). The stoichiometry of the X-ray amorphous phase was estimated by mass balance with XRF, XRD, and %CO₂ data for samples from 35% 1 and the 60% saturated columns (refer to Appendix 4). Only samples without measurable nesquehonite were used for the calculations, as the stoichiometry of precipitated nesquehonite may not be ideal, thereby introducing additional error into the stoichiometry calculation. The average Mg:C and H₂O:Mg ratios calculated for the X-ray amorphous phase in 35% 1 were 2.2 and 1.4, respectively. The average Mg:C and H₂O:Mg ratios calculated for this phase in the 60% saturated column were 1.9 and 1.6, respectively. The estimated chemical formula of the X-ray amorphous phase is thus postulated to be Mg₂CO₃(OH)₂·~2H₂O. This is similar to the composition of the known hydrated Mg-carbonate phase, artinite [Mg₂CO₃(OH)₂·3H₂O], and is consistent with the stoichiometry estimated for a phase formed under comparable conditions in smaller scale brucite carbonation column experiments (Chapter 5). We refer to this precipitate as pseudo-artinite.

6.3.2.2 Qualitative characterization of precipitates

Brucite ore was coated with a fine brucite powder that was an artifact of the crushing process (A4 Fig. A4.3). Precipitates of two morphologies were observed in all columns; long, narrow crystals with morphology typical of nesquehonite (e.g., Chapter 5; Power et al., 2007; Schaef et al., 2011; Assima et al., 2013a), and a fine, flakey material coating surfaces (Fig. 6.5A). Energy dispersive spectroscopy confirmed that both of these phases consisted of Mg, C, and O (A4 Fig. A4.7). The morphology of the flakey material is similar to that observed for an X-ray amorphous carbonate precipitated under similar experimental conditions (Chapter 5). The flakey material is abundant in samples known to be rich in pseudo-artinite, to which we attribute this morphology. Nesquehonite needles were observed to rim pseudo-artinite (Fig. 6.5A). The distribution of these two reaction products changed significantly with distance along the flow path. Near the base of the column, where water contents were high, large crystals of nesquehonite or lansfordite were observed to form 10-100s μm thick rinds surrounding partially reacted brucite grains (Fig. 6.5E and F). Precipitates were also documented to form pervasive cements that extended across several pore bodies even where brucite grains were lacking (Fig. 6.5E). Brucite surfaces are rough, with pieces lifted off the surface in some cases and thin pieces of brucite isolated between carbonate precipitates (Fig. 6.5G and H). Cracks filled with carbonate precipitates were also observed to extend towards the center of some brucite grains (Fig. 6.5B). Further along the flow path in the relatively dry upper portion of the columns, precipitates instead formed as thin ($\sim 5 \mu\text{m}$) coatings of pseudo-artinite surrounding both brucite and quartz grains (Fig. 6.5C and D). Consistent with pore scale observations of brucite carbonation (Chapter 4), carbonate precipitates in thin section mimicked the curvature of the water meniscus at the gas-water interface, as approximated by visible curvatures in the epoxy-mineral interface (Fig. 6.5C). The local water saturation can therefore be estimated based on the location of these interfaces. At low water saturation, carbonate precipitates are restricted to narrow regions where water films were present (Fig. 6.5C and D). The flakey carbonates were also observed to line the “gas-water interfaces,” but were typically not present

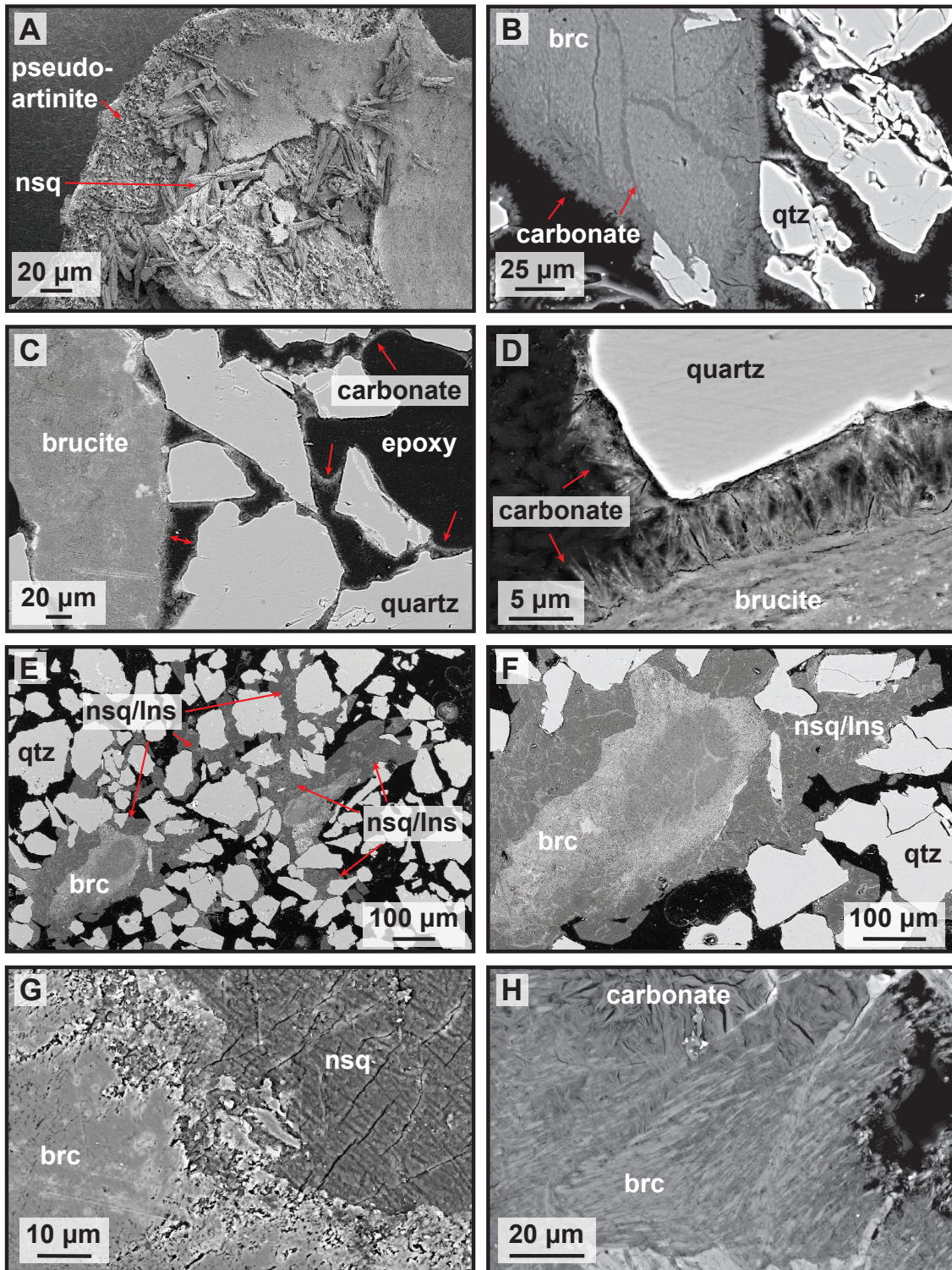


Figure 6.5. Representative scanning electron micrographs of experimental products (see following page for caption).

Figure 6.5 (continued). Representative scanning electron micrographs of experimental products. A) Secondary electron micrograph showing flakey pseudo-artinite with nesquehonite (nsq) needles on top from 30-40 cm depth in the 60% saturated column (~30% saturation). Images B through H are backscattered electron micrographs. B) A brucite grain with carbonate coating and channels infilled with carbonate that extend into the interior of the grain from 60-70 cm depth in the 60% saturated column (>80% saturation). C) Flakey carbonate coating (~5 μm thick; red arrows) surrounding brucite and quartz particles and lining the location of the gas-water interface (right half of micrograph) in an area with locally low water content (~10% saturation) from 20-30 cm depth in 35% 1. D) Close up image of ~5 μm thick flakey carbonate coating on brucite and quartz particles from 20-30 cm depth in 35% 1. E) Thick, dense carbonate rind (>100 μm) extending from a partially carbonated brucite particle in an area with locally high water content (~90% saturation) from 65-70 cm depth in 35% 1. F) Close up image of (E). G) The edge of a brucite grain with pieces “lifted” from the surface and encrusted in precipitated carbonate from 65-70 cm depth in 35% 1 (~90% saturation). H) Thin remnants of brucite interspersed with carbonate precipitates in an extensively carbonated area from 60-70 cm depth in the 60% saturated column (>80% saturation). Lighter grey areas are brucite, darker grey is secondary carbonate, and black is epoxy.

in the middle of larger pore bodies (Fig. 6.5C), in contrast to the wetter areas of the column wherein carbonate precipitates were present throughout the pore space (Fig. 6.5E).

6.3.3 Trends in aqueous chemistry and mineral saturation states

Rapid uptake of CO_2 into solution caused a spike in DIC concentration in the base of 35% 2, and the base and middle of the 60% saturated column (Fig. 6.6A) early in the experiments. Within 50 h these peak concentrations declined (stage 2), and approached 0.15-0.16 M in 35% 2 (Fig. 6.6A). In the middle of 35% 2, the DIC did not exhibit a peak at early time, but reached 0.16 M within 16 h after which it remained relatively constant (stages 2-4; Fig. 6.6A). In the 60% saturated column, on the other hand, DIC concentrations were highest in the middle of the column, fluctuating between 0.19 and 0.28 M (Fig. 6.6A). At the base of the column, after the transient peak at early time, the DIC slowly increased throughout the experiment, and did not reach a stable value (stage 2; Fig. 6.6A). This indicates that the middle of the column was receiving an anomalously high CO_2 flux, as is consistent with the

early CO₂ breakthrough measured in the gas phase. Uptake of CO₂ into solution drives brucite dissolution (e.g., Pokrovsky et al., 2005b; Zhao et al., 2010; Hövelmann et al., 2012b; Harrison et al., 2013a; Chapter 2), and not surprisingly, Mg concentrations were observed to follow a similar trend as DIC concentrations (Fig. 6.6C). Rapid initial increases within 24 h were followed by a gradual reduction (stage 1-3). Mg concentrations stabilized at ~0.2 M within 120 h at both sampling locations in 35% 2, and in the middle of the 60% saturated column (stage 4; Fig. 6.6C). At the base, an early transient peak was followed by a slow increase in Mg concentration for the remainder of the experiment (Fig. 6.6C).

The pH in the system is controlled by the balance between CO₂ dissolution, which decreases pH, and brucite dissolution, which increases pH. As such, the rapid DIC uptake was accompanied by a decline in pH in all columns (Fig. 6.6B; stages 1-2). The pH values declined from an initial value of 9.1 in all columns to ~8.0 within 12 h at the base of the 35% saturated columns. In the middle of these columns, the pH dropped rapidly to ~8.3 within 24 h, after which the rate of decline slowed considerably (stage 3; Fig. 6.6B). Final pH values were fairly stable at 7.6-7.8 at both locations (stage 4). The 60% saturated column exhibited a unique trend; the pH at the middle of the column followed a similar development as the base of the other columns, whereas the base sustained a higher pH throughout (~8.0-8.3; Fig. 6.6B). This is consistent with CO₂ largely bypassing this sampling zone due to preferential flow along a different pathway.

Mineral saturation indices were calculated from the aqueous chemistry data using PHREEQC (Parkhurst and Appelo, 2013). Prior to initiation of the CO₂ supply, the solutions were moderately undersaturated with respect to brucite (-0.5 to -0.7). DIC uptake rapidly drove the solutions to be increasingly undersaturated with respect to brucite (-1.5 to -3.4), and supersaturated with respect to both nesquehonite and artinite (Fig. 6.6D). Nesquehonite remained slightly supersaturated (0.1 to 1.2) throughout the experimental duration, whereas artinite became moderately undersaturated after 100 h (-0.1 to -1.1; Fig. 6.6D).

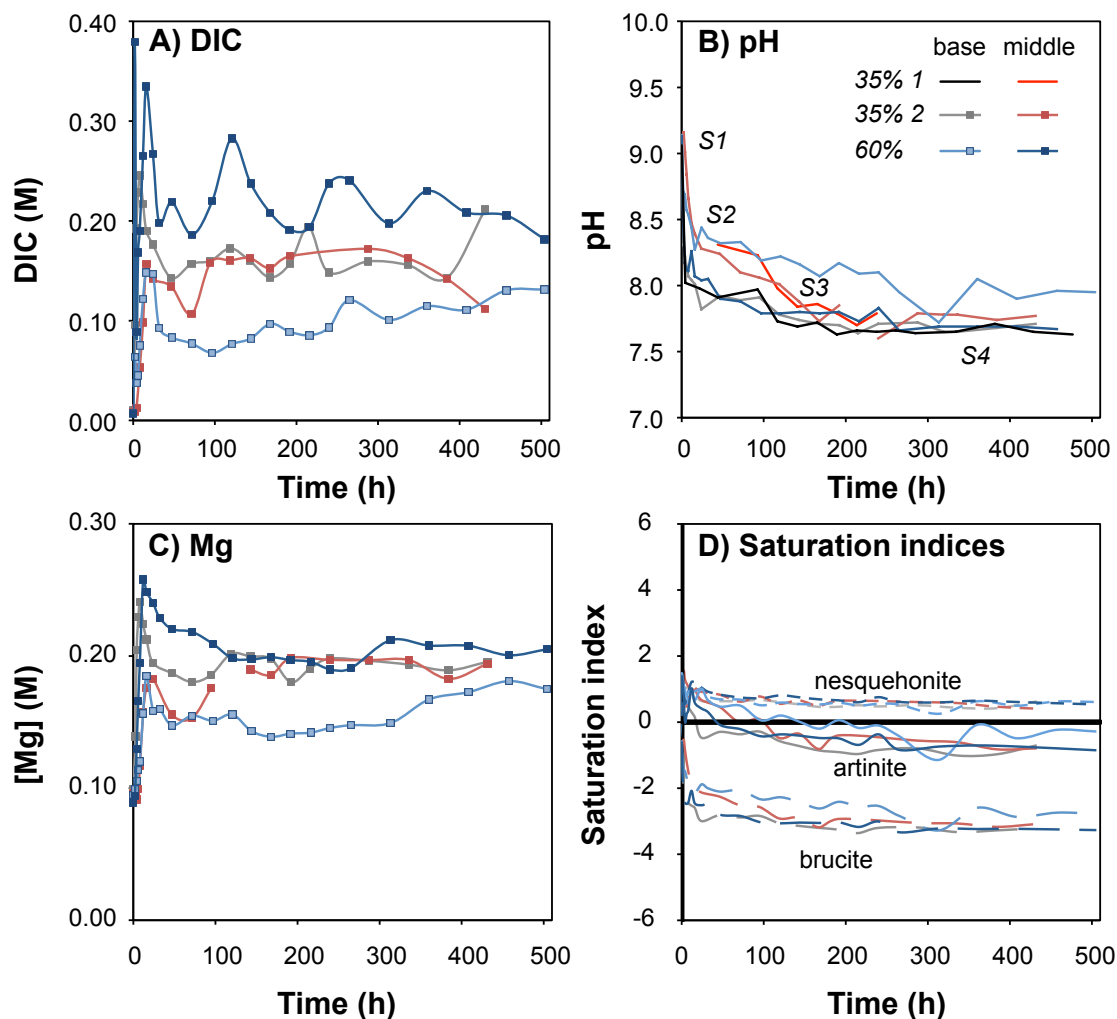


Figure 6.6. Aqueous chemistry data versus time. A) Dissolved inorganic carbon (DIC) concentrations, B) pH, and C) Mg concentrations versus time. D) Mineral saturation indices versus time as calculated using PHREEQC with the Pitzer database and mineral solubility data from the minteq database. Light red and grey lines and squares represent data from the middle and base of 35% 2, respectively. Dark blue and light blue lines and squares represent data from the middle and base of the 60% saturated column, respectively. The black and bright red lines in (B) represent the base and middle of 35% 1, respectively. In (D), the long and short dashed lines represent the saturation indices of brucite and nesquehonite, respectively, and the solid lines represent the saturation index of artinite.

6.3.4 Water and gas flow

Although a gradient in gas phase pressure must have existed to drive the gas flux through the columns, differences in gas phase pressure were too low to be resolved within measurement error ($\pm 2.290 \times 10^{-4}$ atm), and remained circum-atmospheric (1.000 atm). In all columns the water content was lowest at the top of the column (~15% saturated) and highest at the base (close to 100% saturated; Fig. 6.4). Because the supplied gas was not humidified, it is expected that water was lost due both to evaporation and precipitation of hydrated Mg-carbonates. However, the volumetric water content sensors did not resolve significant changes in water saturation at any of the three measurement depths (A4 Fig. A4.4B). Conversely, estimates of the total water mass in the columns calculated by mass difference before and after the solid materials were dried at the end of the experiments indicated that up to ~30% of the initial water was lost. As some solid material and pore water was lost during deconstruction of the experimental apparatus some of the final pore water was not accounted for; thus these estimates likely represent the lower limit for the final water content. The discrepancy between these two measurements suggests either that hydraulic redistribution between measurement points resulted in little change in saturation at the sensor measurement points, or that reaction induced water loss was localized and did not significantly change the water saturation measured in the vicinity of each sensor.

6.3.5 Stable carbon isotopic compositions

The supplied gas had $\delta^{13}\text{C}$ values between -37.5‰ and -36.5‰; variations between experiments were due to the use of different CO_2 gas tanks. The $\delta^{13}\text{C}_{\text{DIC}}$ plummeted rapidly in the first ~12 h of the experiments as the gaseous CO_2 dissolved into solution. Gas could not be sampled from the base of the experiments owing to the high water content, but its composition can be assumed nearly equal to that at the inlet (i.e., directly from the gas tank). In addition, samples collected from the middle and top of the columns for at least the first 47 h of the experiment had insufficient CO_2 content to analyze. Nevertheless, progressive depletion of ^{13}C

in the supplied gas along the flow path is evident in both datasets (Fig. 6.7A). Consequently, the $\delta^{13}\text{C}_{\text{DIC}}$ in the middle of the column was also depleted with respect to that at the base during stage 2 in 35% 2 (Fig. 6.7A). Within 200 h, the isotopic composition of the gas phase throughout the column returned to the composition of the supplied gas, coincident with the cessation of the carbonation reaction (stage 4, Fig. 6.7A). The $\delta^{13}\text{C}_{\text{DIC}}$ values also stabilized after this time at values between -28.8‰ and -25.6‰ in all experiments. These $\delta^{13}\text{C}_{\text{DIC}}$ values fall within the expected range for equilibrium fractionation calculated using the fractionation factor of Mook et al. (1974) for fractionation between gaseous CO_2 and HCO_3^- , the dominant aqueous DIC species at the experimental pH. The range of equilibrium values was calculated considering the temperature fluctuations of the experimental apparatus and the total range of composition of the initial gas. Temperatures varied between 16.9°C and 24.5°C for both experiments for which $\delta^{13}\text{C}_{\text{DIC}}$ data were available (A4 Fig. A4.4A).

Solid samples could only be collected at the end of the experiment; therefore the $\delta^{13}\text{C}$ values of solid phases represent a cumulative signature developed over the entire experiment. The $\delta^{13}\text{C}$ values of the secondary phases were calculated from measured bulk values by correcting for the contribution from the dolomite present in the initial brucite ore as quantified with XRD data. The $\delta^{13}\text{C}$ value of the initial carbonates was $-6.5 \pm 0.3\text{‰}$ as measured in triplicate unreacted samples. Although magnesite and hydromagnesite were also documented in the initial brucite ore, they are not present at sufficient abundance to be quantified in the reaction products; therefore all initial CO_2 is attributed to dolomite. The fractionation factor between HCO_3^- and nesquehonite or pseudo-artinite is unknown. However, the equilibrium fractionation factor of Wilson et al. (2010) between dypingite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$ and HCO_3^- was found to be relatively consistent with fractionation observed during precipitation of nesquehonite under similar experimental conditions (Harrison et al., 2013a; Chapter 2), and is therefore employed here. A wide range in ^{13}C composition of the final solids was measured, but the majority was within the range of expected values based on equilibrium fractionation with the range of $\delta^{13}\text{C}_{\text{DIC}}$ measured during brucite carbonation (Fig. 6.7B). Due to the error

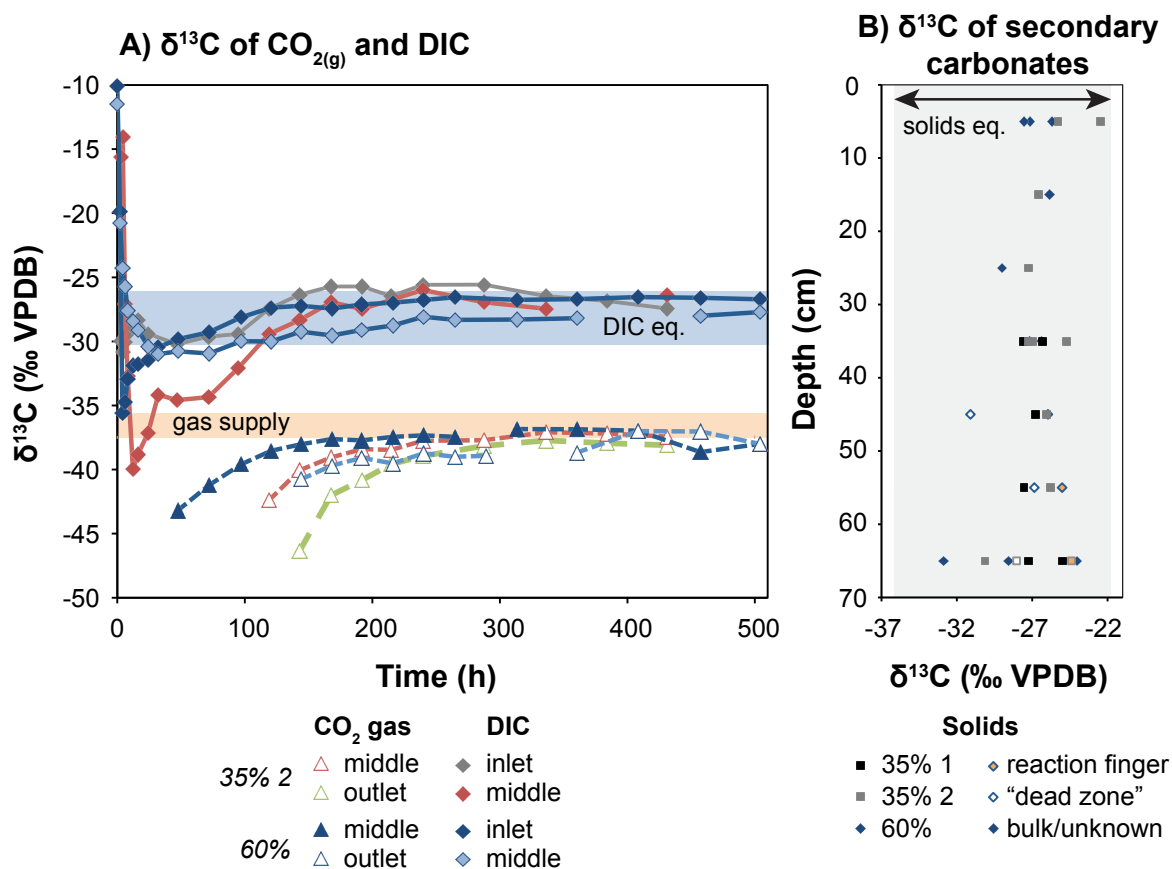


Figure 6.7. Stable carbon isotopic composition of gaseous CO_2 , dissolved inorganic carbon (DIC), and secondary carbonate solid phases. A) $\delta^{13}\text{C}$ values of gaseous CO_2 and DIC versus time. The blue shaded region represents the range of $\delta^{13}\text{C}_{\text{DIC}}$ expected for equilibrium fractionation with the supplied gas based on the fractionation factor of Mook et al. (1974) for gaseous CO_2 and HCO_3^- and the measured experimental temperature range. The orange shaded region represents the range of initial $\delta^{13}\text{C}$ values of the supplied gas. B) $\delta^{13}\text{C}$ values of the secondary carbonate solid phases versus depth in the columns. Orange filled symbols represent samples taken from reaction fingers, and white filled symbols represent samples taken from "dead zones" outside fingers. All others represent bulk samples or samples for which it was not possible to ascertain visually whether they were part of a reaction finger. The grey shaded region shows the range of $\delta^{13}\text{C}$ values of the secondary carbonate solid phases predicted for equilibrium fractionation with the DIC at any point during the experiment. The fractionation factor of Wilson et al. (2010) for HCO_3^- and dypingite was utilized.

associated with the corrections for the initial carbonate, and the lack of a specific fractionation factor, the uncertainty in these values is considerable. Nevertheless, they are broadly consistent with equilibrium fractionation between DIC and hydrated Mg-carbonates (Fig. 6.7B).

6.4 Reaction processes

The observed trends in CO₂ breakthrough curves are manifestations of reaction rate and progress along the length of the columns. Importantly, the reasonably constant $p\text{CO}_2$ measured during stage 2 reveals that reaction rates remained relatively constant at all column depths for ~85 h in the 35% saturated experiments and ~50 h in the 60% saturated experiments (Fig. 6.8A-C). The plateau occurs at similar timing and for similar durations at all three sensor locations within any single experiment (Fig. 6.8B and C). A precipitous cessation of carbonation following stage 2 is evidenced by the broader range in CO₂ sequestration rate and CO₂ concentration during stage 3 at each measurement depth within the columns (Fig. 6.8B and C), and the consistent approach towards the CO₂ concentration of the supplied gas ($C/C_0 \rightarrow 1$; Fig. 6.8A). Finally, in the 60% saturated column, the CO₂ breakthrough curves measured at the middle and outlet of the column are remarkably similar, implying that no significant reaction is occurring between these two points for most of the experimental duration. These features of the breakthrough curves are important indicators of the reaction processes governing carbonation during the different stages of reaction.

6.4.1 Reaction rate

It is typically expected that bulk mineral dissolution rates decline over time as the reactive phase is consumed, due to the geometric decline in particle size and consumption of reactive surface area (Levenspiel, 1999; Appelo and Postma, 2005). This decline in surface area is often approximated with the following relationship representative of a uniform population of shrinking spheres or cubes (Eq. 6.4; Lichtner, 1996; Mayer et al., 2002; Colón et al., 2004;

Appelo and Postma, 2005; Jeon et al., 2007; Wilson et al., 2014; Chapter 7):

$$k_{eff}^g = k^0 SA \left(\frac{\varphi^t}{\varphi^0} \right)^{2/3} \quad (\text{Eq. 6.4})$$

where k_{eff}^g (L s^{-1}) is the effective ‘geometric’ rate constant, k^0 is the initial reaction rate constant equal to $10^{-6.13} \text{ L s}^{-1} \text{ m}^{-2}$ (after Pokrovsky et al., 2005b), SA is the surface area (m^2), and φ^0 and φ^t are the volume fraction of the reactive phase initially and a given time greater than zero. Here, k_{eff}^g replaces k_{eff}^0 in Equation 6.2. Such a relationship results in a gradual decline in reaction rate associated with the shrinking geometric surface area of the particles, and is in poor agreement with the experimental observations (Fig. 6.8D). Rather, a period of constant reaction rate (stage 2; Fig. 6.8B) suggests either that the effective surface area of brucite remains relatively constant despite its consumption, or that the overall sequestration rate is not controlled by brucite dissolution kinetics. The latter implies that either the supply of CO_2 or the rate of carbonate precipitation was limiting the overall reaction rate. The advancement of a sharp reaction front through the columns could also produce a constant bulk rate of reaction, but the presence of contemporaneous gas composition plateaus throughout the column disqualifies this as an explanation (Fig. 6.8A-C).

A constant reaction rate would be achieved if the rate-limiting step for carbonation were the supply of CO_2 , as the sequestration rate would approximately balance the supply rate. However, the elevated CO_2 concentration throughout most of the column depth (Fig. 6.8A and B) implies that CO_2 gas is supplied to the column faster than it is locally removed. Other studies have shown that the gas-solution transfer and subsequent hydration of aqueous CO_2 to a form that can be mineralized may be relatively slow compared to the flux of CO_2 gas (Harrison et al., 2013a; Chapter 2; Power et al., 2013a; Wilson et al., 2010). This would result in CO_2 -limited brucite carbonation despite the non-zero CO_2 concentration in the gas phase. CO_2 uptake into solution has been demonstrated to be rate limiting under similar experimental conditions (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2; Power et al., 2013a), and is

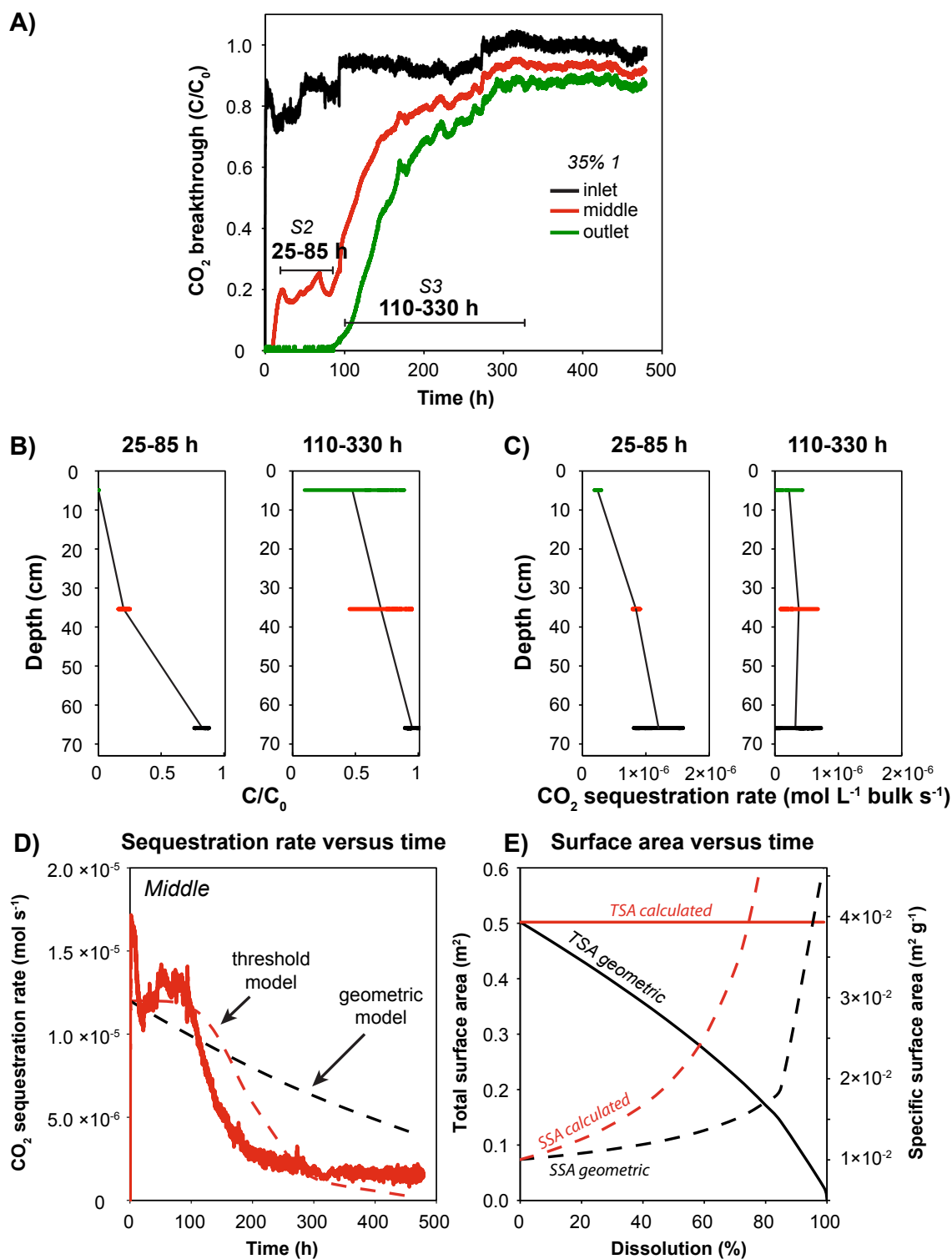


Figure 6.8. Analysis of CO₂ breakthrough curve features (see following page for caption).

Figure 6.8 (continued). Analysis of CO₂ breakthrough curve features. A) CO₂ breakthrough curves from 35% 1. Black, red, and green lines represent CO₂ concentration measurements at the base, middle, and top of the column. CO₂ breakthrough is expressed as C/C_0 , the ratio of the measured CO₂ concentration at a given time to the CO₂ concentration of the supplied gas. B) C/C_0 versus depth in 35% 1 during reaction stage 2 (35-85 h) and reaction stage 3 (110-330 h). C) CO₂ sequestration rate versus depth in 35% 1 during reaction stage 2 (35-85 h) and reaction stage 3 (110-330 h). Rates were calculated using the CO₂ flux data at each sensor and are expressed as mol CO₂ L bulk⁻¹ s⁻¹. For both (B) and (C), horizontal bars represent the range in value of C/C_0 or CO₂ sequestration rate at a given depth for the entire time range plotted. Data are averaged over 2 h intervals (25 measurements) to reduce measurement noise. D) Comparison of the experimental instantaneous reaction rate (solid red line) versus time in the middle of the column and the reaction rates predicted by the geometric (dashed black line) and threshold (dashed red line) models. E) Calculated evolution of total surface area and specific surface area versus extent of brucite dissolution. Solid and dashed black lines show the evolution of total and specific reactive surface area, respectively, as calculated using the geometric model. The solid red line shows the total surface area evolution required to maintain a constant reaction rate, and the dashed red line shows the evolution of specific surface area required to achieve this constant total surface area.

typified by anomalously depleted ¹³C compositions of both DIC and precipitated carbonates due to kinetic fractionation of stable carbon isotopes during uptake of CO₂ into solution (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2; Wilson et al., 2014; Chapter 7). However, the δ¹³C values of the DIC and the secondary carbonates are consistent with equilibrium rather than kinetic fractionation in the columns (Fig. 6.7), suggesting that CO₂ uptake into solution was not rate limiting. The discrepancy between these and previous experimental results (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2) is attributed to the use of different experimental apparatus. Previous studies that identified CO₂ uptake as the rate-limiting step were conducted in batch reactors; the increased gas-water interface provided in the column experiments likely facilitated more rapid uptake of CO₂ into solution. Thus it appears unlikely that reaction rate was limited by the rate of CO₂ supply.

Changes in total brucite surface area would also have less of an impact on the bulk rate of CO₂ sequestration if carbonate precipitation were to limit the overall carbonation rate, a limitation which has recently been recognized for certain carbonation reactions (e.g., Pham

et al., 2011; Saldi et al., 2012; Hövelmann et al., 2012a; Kampman et al., 2013; Gautier et al., 2014). A relatively slow rate of secondary phase precipitation may in some cases allow the solution to approach equilibrium with respect to the dissolving phase, retarding its dissolution (Maher et al., 2009). The moderate supersaturation with respect to nesquehonite documented in the columns (Fig. 6.6) implies that its precipitation was moderately kinetically inhibited. Nevertheless, brucite remained undersaturated (saturation index ≈ -0.5 to -3.4 ; Fig. 6.6), implying that reaction affinity effects due to relatively slow carbonate precipitation were unlikely to have limited the CO₂ sequestration rate. Furthermore, pH values tended to plateau contemporaneously with CO₂ concentrations, implying that a steady-state is achieved between brucite dissolution and carbonate precipitation. Because the reactions are sequential, the observed steady-state implies that brucite dissolution controls the overall reaction rate during stage 2 of the reaction.

It is therefore concluded that the overall reaction rate during stage 2 was primarily controlled by the rate of brucite dissolution, as is consistent with the observation that an increase in brucite surface area accelerated the carbonation reaction under similar experimental conditions (Chapter 5). This implies that the total reactive surface area remained relatively constant during stage 2 in order to maintain the relatively constant rate of reaction, invalidating the assumption that reactive surface area declines geometrically (Fig. 6.8D). It is recognized that the reactive surface area of a mineral is not always equal to the geometric surface area, and therefore may not evolve geometrically. Surface roughness and mesoporosity provide additional surface area that is not accounted for by simple geometric models (e.g., Brantley and Mellot, 2000), and not all surface area is equally reactive. For example, the crystal edges of several sheet silicate minerals dissolve much more rapidly than basal sheets (Bosbach et al., 2000; Bickmore et al., 2001; Hodson, 2006), as do edge dislocations associated with exsolution lamellae (Lee et al., 1998) and defects induced by grinding (Petrovich, 1981; White and Brantley, 2003; Maher et al., 2006). Yet, walls of etch pits formed during quartz dissolution do not contribute to the reactive surface area (Gautier et al., 2001). In the case of brucite, the relatively constant

reaction rate recorded during stage 2 implies that the specific surface area (i.e., surface area per unit mass) must be increasing to account for the loss of brucite mass to a greater extent than is predicted geometrically (Fig. 6.8E). This could be explained if reaction occurred primarily via the stepwise removal of $\text{Mg}(\text{OH})_2$ sheets. Hövelmann et al. (2012b) observed this process during brucite dissolution at the nano-scale using atomic force microscopy. If the majority of reaction occurs in this manner, the total reactive surface area may not change substantially until a particle is completely dissolved, as the surface area of each newly exposed sheet would be similar throughout the reaction. In addition, the formation of secondary phases of higher volume than the primary phase can induce fracturing and generate surface area as reaction progresses (Kelemen et al., 2011 and references therein). For example, Beinlich and Austrheim (2012) documented that precipitation of lansfordite fractured serpentinite clasts during weathering. Intragranular dissolution along planes can also lead to physical weakening of the mineral grain, which induces flaking and exposure of fresh surface area (Lee et al., 1998). This is consistent with the observed brucite pieces separated from the surface and isolated between extensive carbonate precipitates (Fig. 6.5G and H). Moreover, the presence of carbonate-filled cracks extending into the interior of brucite grains reveals that the reactive fluid accessed additional surface area (Fig. 6.5B). The roughened and fractured appearance of brucite particles following carbonation may be due to a combination of reaction induced cracking and preferential dissolution along weaknesses in the particles, causing continuous exposure of fresh surface area within the first ~100 h of reaction. This would counteract the reduction in brucite mass as the reaction progressed, allowing the relatively constant rate of reaction to persist (Fig. 6.8E).

6.4.2 Reaction shutdown

6.4.2.1 Surface passivation

Our previous experimental results from smaller scale brucite carbonation columns revealed that the transformation from a flakey, poorly or nano-crystalline carbonate phase to

low porosity, bladed nesquehonite resulted in abrupt passivation of brucite and arrested the reaction (Chapter 5). The morphology and stoichiometry of the poorly crystalline phase was similar to that of the pseudo-artinite in the present study. Due to the stoichiometric similarity between artinite and the pseudo-artinite formed in the experiments, and the good agreement between predicted artinite-buffered aqueous chemistry and measured aqueous chemistry in the experiments (Fig. 6.6D), artinite solubility data are used as a proxy for pseudo-artinite in all models. Aqueous chemistry data, which were not available from the smaller scale experiments, reveal that although nesquehonite quickly becomes supersaturated and remains so throughout the experiment, artinite becomes undersaturated within 100 h (Fig. 6.6D). The change in saturation state of artinite with time and the constant supersaturation with respect to nesquehonite are consistent with initially rapid precipitation of pseudo-artinite, coupled with relatively slow precipitation of nesquehonite replacing the earlier-formed carbonate. The observation of bladed crystals rimming pseudo-artinite is consistent with this process (Fig. 6.5A). The transformation from porous pseudo-artinite to low porosity nesquehonite as the chemical environment evolves results in abrupt passivation of the brucite surface, as is consistent with previous experiments using brucite of the same grain size and BET surface area (Chapter 5). In these experiments, surface passivation was found to limit the mass of CO₂ sequestered to ~2.5-3.0 wt.% CO₂ (Fig. 6.9; Chapter 5). Yet, above 35 cm depth in the 35% saturated columns, and at many locations throughout the 60% saturated column, a lower extent of reaction than this was achieved (Fig. 6.9), suggesting that there were additional processes limiting the extent of reaction.

6.4.2.2 Water-limited carbonation

Water is required both as a medium to transport and solubilize ions and as a reactant that is consumed during precipitation of hydrated Mg-carbonates. Due to the formation of hydrated phases, there is a fundamental stoichiometric limit to the amount of carbonate that can form based on the mass of water available. The solid black line in Figure 6.9 shows the

stoichiometric limit for conversion of brucite to nesquehonite, which consumes more water than pseudo-artinite. If the stoichiometric limit were the only restriction on the extent of reaction, the experimental data would fall on this line when water saturation was below 17%. Above 17% saturation, the reaction is no longer restricted by the stoichiometric limit, yet a large proportion of samples still exhibited a lower extent of reaction than is expected due to surface passivation or stoichiometry (Fig. 6.9). Nevertheless, the positive correlation between water saturation and the extent of carbonation (Fig. 6.9) implies that the decreased extent of reaction is likely a consequence of water content. Furthermore, SEM micrographs of the reaction products reveal that the thickness and location of carbonate surface coatings depended on the local water content (Fig. 6.5). At low water saturation, carbonate precipitates were restricted to narrow regions where water films were present (Fig. 6.5C and D), whereas at high water saturation, precipitates were observed throughout the pore space (Fig. 6.5E and F). The strikingly different textures observed between the water-poor and water-rich areas of the columns imply that the overall reaction progress fundamentally differs in low water conditions.

The decreased extent of reaction above the stoichiometric limit may relate to the requirement of water as a reaction medium rather than its role as a reactant. Heterogeneous water distribution at the pore scale may leave some mineral surfaces unexposed to reactive fluids, reducing the surface area available for reaction. This is consistent with pore scale observations of brucite carbonation, which revealed a lack of reaction of particles in dry pores, whereas particles in wet pores reacted with CO_2 to form nesquehonite (Chapter 4). Although water is the wetting fluid in this situation, poor connectivity between water films may leave some grains effectively unexposed to reactive fluid. In reactive transport models, effective reactive surface areas are often reduced to account for the combined effects of incomplete exposure of mineral surfaces to reactive fluid, surface aging, and surface passivation effects (Xu et al., 2007; Bea et al., 2012). Similarly, Pačes (1983) defines the mineral surface area available for reaction in natural catchments to be equal to the surface area in the saturated zone only. If mineral grains in “dry” pores were assumed to be unreactive, both the reactive

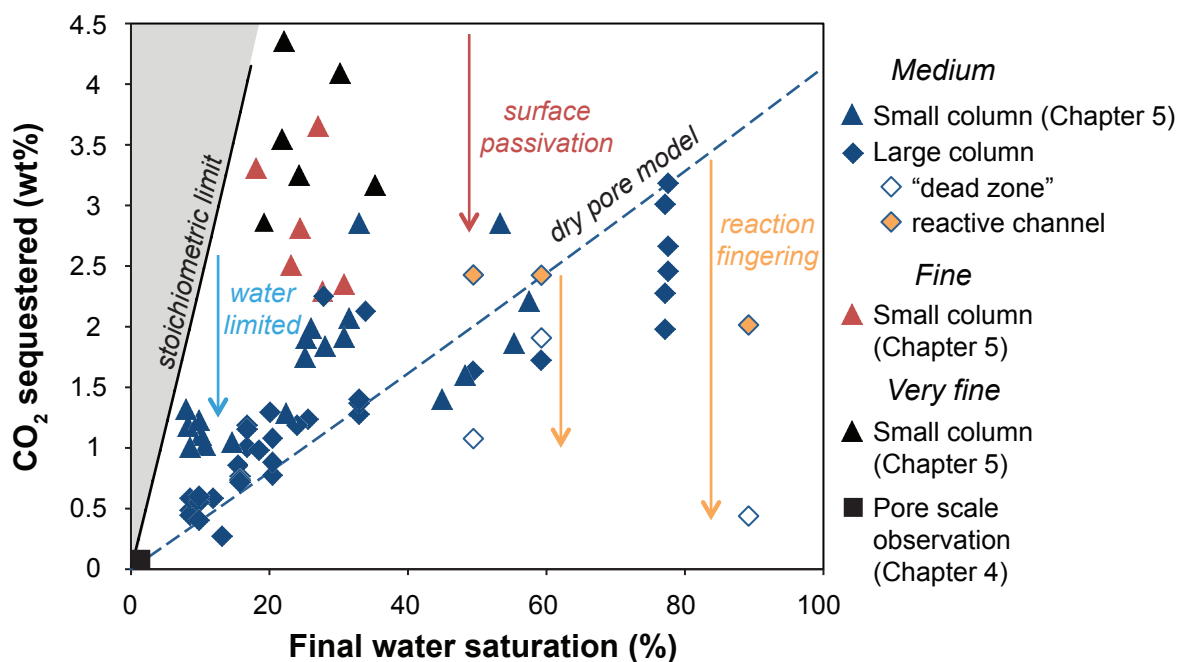


Figure 6.9. CO₂ sequestered versus final water saturation. The mass of CO₂ sequestered is from the total carbon measurements, as corrected for the initial carbon content. Diamonds represent data from the present study (large columns), whereas triangles represent data from our previous, smaller scale brucite carbonation columns (small columns; Chapter 5), and the square represents an observation from our previous pore scale experiments (pore scale observation; Chapter 4). Blue, red, and black data represent data from experiments that employed “medium brucite” that was 250-500 μm in diameter, the same as used in the present study, “fine” brucite that was 53-180 μm in diameter, and “very fine” brucite that was <53 μm in diameter, respectively. White and orange triangles with blue outlines show samples from obvious reaction fingers and “dead zones” that are bypassed by CO₂, respectively. The solid black line represents the stoichiometric limit for reaction based on the water available for reaction of brucite to form nesquehonite. The grey-shaded area to the left of this line represents a zone with no reaction due to the lack of water available to form hydrated carbonates. The dashed blue line shows a “dry pore” calculation, wherein the volume of brucite available for reaction (i.e., the extent of reaction) is proportional to the fraction of pore space occupied by water.

surface area and reactive capacity of the porous medium would decrease as a function of water saturation.

On the other hand, Nishiyama and Yokoyama (2013) documented that the effective surface area of quartz in a sandstone was unaffected by water saturation because the quartz grains were coated with sufficiently connected water films that maintained a high available surface area. The efficacy of these water films to support reaction may vary over time in our experimental systems compared to those of Nishiyama and Yokoyama (2013), because water saturation evolves with reaction progress and the reaction involves precipitation of minerals that reduce the local water content. An expanding body of work has revealed that there is a water concentration threshold required for carbonation of brucite, forsterite [Mg_2SiO_4], and wollastonite [CaSiO_3] to proceed with wet supercritical CO_2 (e.g., Loring et al., 2011; Schaef et al., 2011; Felmy et al., 2012; Miller et al., 2013). Schaef et al. (2013a; 2011) documented that forsterite carbonation in wet supercritical CO_2 ceases when water films are too thin to behave like bulk water, and that brucite carbonation is arrested prior to completion due to water loss to nesquehonite. Pore scale observations of brucite carbonation at ambient conditions have also revealed that carbonate precipitates tend to stop growing upon reaching the gas-water interface (Chapter 4). If all mineral grains were coated with sufficiently connected water films, the initial available surface area should not decrease at low water saturation; however, once the water volume was consumed to below a critical threshold required to support carbonation, reaction would cease. This would reduce the reactive capacity but maintain an initial effective surface area comparable to that in water saturated media.

Here, we use the reactive transport model, MIN3P-DUSTY (Molins and Mayer, 2007) to evaluate whether a water limitation could explain the lack of carbonation at the top of the column, and by what mechanism it likely occurs. Three “end-member” conceptual models based on the above discussion are explored: 1) a “base case” that assumes the reaction is limited by surface passivation but is independent of water saturation, 2) a “dry pore” model that defines a portion of the brucite as unreactive because it resides in effectively dry pores,

and 3) a “water film” model that assumes all brucite as initially available for reaction, but the reaction stops prematurely due to the loss of water to hydrated Mg-carbonates (Fig. 6.10). The effect of particle movement documented in microfluidic experiments (Chapter 4) are neglected, as the large size of the brucite grains meant that the majority likely bore the skeletal load of overlying material.

6.4.2.3 Conceptual models of water-limited carbonation

Base case. The first conceptual model represents the extent of reaction that would be achieved if water content had no effect on reactivity. The extent of carbonation depends primarily on the distance from the CO₂ source and duration of exposure to the CO₂-rich gas stream, and is limited by surface passivation only. The equation derived from our previous, smaller scale column experiments to model surface passivation with negligible water limitations is employed (Eq. 6.5; Chapter 5):

$$k_{eff}^t = k^0 SA \left[1 - \left(\frac{\varphi^0 - \varphi^t}{\varphi^0 - \varphi^p} \right)^5 \right] \quad (\text{Eq. 6.5})$$

for $\varphi^t \leq \varphi^p$, where k_{eff}^t is the effective ‘threshold’ rate constant (L s⁻¹), k^0 is the initial reaction rate constant equal to 10^{-6.13} L s⁻¹ m⁻² (after Pokrovsky et al., 2005b), SA is the brucite surface area (m²), and φ^0 and φ^p are the initial brucite volume fraction and a threshold brucite volume fraction at which the reaction rate becomes negligible due to surface passivation. Here, k_{eff}^t replaces k_{eff}^0 in Equation 6.2. This formulation is referred to as the ‘threshold’ model, and provides a relatively constant reaction rate, followed by a rapid shutdown of reaction at a threshold degree of brucite conversion (represented by the volume fraction of brucite; Fig. 6.8D), which is attributed to surface passivation (Chapter 5).

Dry pore model. The dry pore model assumes that some mineral grains are not exposed to reactive fluid, resulting in a lower effective initial brucite volume fraction and surface area. Here, it is assumed that the fraction of brucite available for reaction is proportional to the

fraction of water filled pore space (Fig. 6.10; Eq. 6.6). The threshold volume fraction (φ^p) is also proportional to the water filled pore space, such that the same extent of carbonation (i.e., percent conversion of brucite to carbonate) occurs prior to passivation (Eq. 6.7).

$$\varphi_z^0 = \varphi^0 \times S_w \quad (\text{Eq. 6.6})$$

$$\varphi_z^p = \varphi^p \times S_w \quad (\text{Eq. 6.7})$$

Where φ_z^0 and φ_z^p are the effective initial and threshold volume fractions at a depth 'z' in the column, and S_w is the water saturation (fraction of pore volume occupied by water). The variables φ_z^0 and φ_z^p are substituted into Equation 6.5 in place of φ^0 and φ^p , respectively.

Water film model. In the third conceptual model, it is assumed that all brucite grains are coated with sufficiently connected water films such that the initial effective volume fraction and surface area are the same as in the base case under water-unlimited conditions (Fig. 6.10). However, the progressive loss of water due to uptake into the solid phase decreases the volume of water in the vicinity of reactive surfaces over time until the reaction cannot proceed. Here, carbonation ceases when the local water saturation reaches a threshold value. Thus, the threshold function was again employed but the threshold volume fraction was a function of water saturation instead of surface passivation (Eq. 6.8):

$$\varphi_z^p = \varphi^0 - 0.102S_w \quad (\text{Eq. 6.8})$$

This effectively reduces the reactive capacity of the porous medium, by decreasing the volume fraction of brucite available as a function of water saturation (Eq. 6.8). For simplicity, the dependence of this threshold brucite volume fraction was expressed as a linear function of water saturation (Eq. 6.8), with the slope fitted between endpoints at zero water saturation, where no reaction will occur, and an upper saturation limit above which water is

no longer limiting (slope = 0.102; see A4 Fig. A4.8). At the experimental conditions, surface passivation is expected to limit the extent of brucite conversion to ~60%, when not limited by water availability (i.e., above the upper saturation limit; Chapter 5; A4 Fig. A4.8). We use an empirically derived value from the experiments of 20% saturation as the upper saturation limit for water-limited conditions. This is in fairly good agreement with both the stoichiometric limit (17%) and water thresholds reported in previous studies under similar conditions (Assima et al., 2013a; Chapter 5). Above this limit, an unmodified version of the base case threshold model accounting for passivation alone is employed (Eq. 6.5). Below this limit, Equation 6.8 is substituted for φ^p in Equation 6.5. The model was modified to include water as a reactant during precipitation of artinite, such that the water saturation evolved as carbonates precipitated. The net water removal from both nesquehonite and artinite precipitation was attributed to artinite, as it precipitated in greater quantities.

6.4.2.4 Reactive transport modeling of water-limited carbonation

Modeling results from each scenario were compared to experimental CO₂ breakthrough curves (Fig. 6.11) and solid phase brucite and CO₂ abundance data (Fig. 6.12). Model results for individual carbonate minerals are provided in Appendix 4 (A4 Fig. A4.9). The base case model reproduces the experimental data for the base and middle of the column well, where the water saturation exceeds ~15% (Fig. 6.11A). This is consistent with the extent of carbonation being limited primarily by surface passivation where water saturation is highest (i.e., base and middle). However, it is clear that the base case model overestimates the reactive capacity for the drier top of the column, as evidenced by the delayed CO₂ breakthrough and the homogeneous extent of carbonation predicted at all depths (Figs. 6.11A and 6.12). This implies that factors other than surface passivation by nesquehonite are limiting reaction in these areas.

Conversely, the dry pore model underestimates the extent of carbonation and the instantaneous rate, as indicated by the premature breakthrough and excessive $p\text{CO}_2$ during stage 2 at the middle and top of the column (Figs. 11B and 12). The proportional relationship

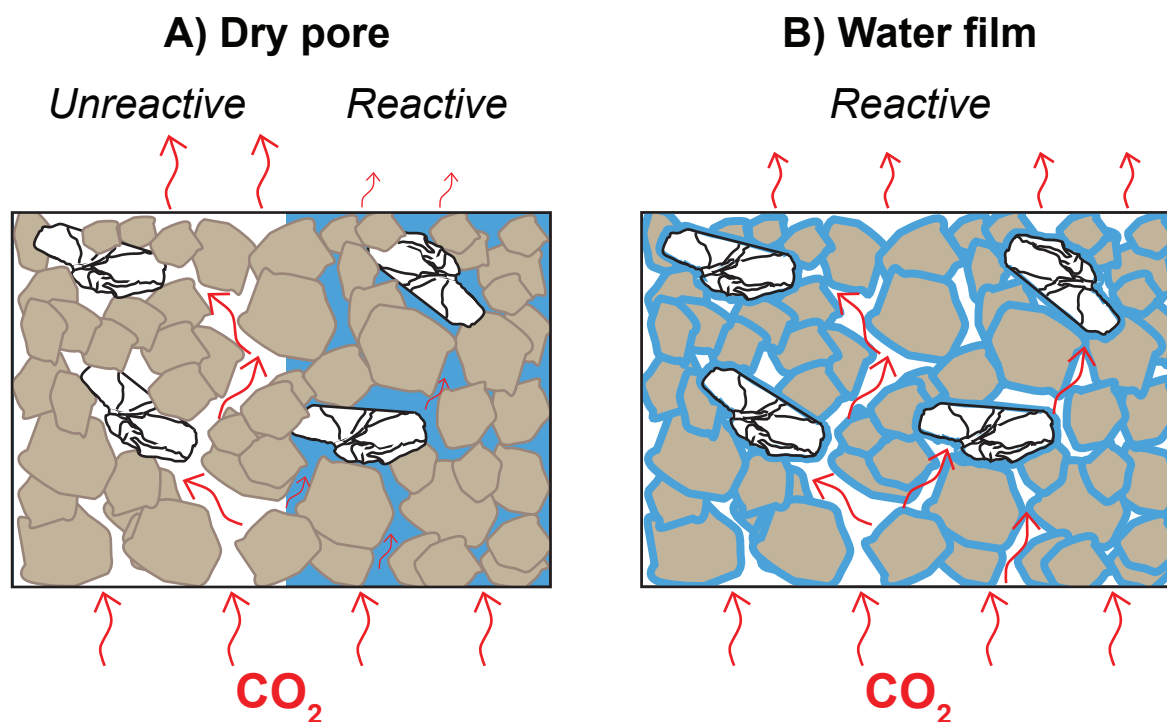


Figure 6.10. Conceptual models of water limited carbonation. A) Dry pore model. B) Water film model.

between water saturation and reactive capacity is clearly an oversimplification; the fraction of brucite with access to water must exceed the bulk saturation. This implies that capillary and electrostatic forces provide sufficiently connected water films to coat and connect the majority of grains (e.g., Tokunaga, 2011), providing exposure to reactive fluid. Consistent with this, the water film model produces excellent agreement between the modeled and experimental data (Figs. 6.11C and 6.12). In order to reproduce the experimental data, an initial surface area equal to that in water-unlimited conditions was required to account for the lack of CO_2 breakthrough at the top of the column during the first ~ 100 h (i.e., water film model). This implies that the lack of reaction cannot be attributed to a lack of wetted surfaces. Instead, low water content appears to primarily limit the extent of reaction possible rather than the reactive surface area, which has important implications for quantifying reactive surface area in the unsaturated zone. Simply decreasing the effective surface area, as is often the approach, does not represent reaction progress well. Because brucite carbonation is a coupled dissolution-precipitation

reaction, the restricted area within which precipitates can form at low water content, and the corresponding water loss during precipitation results in a premature cessation of the reaction compared to surface passivation alone. The precipitation of hydrous Mg-carbonates therefore provides a negative feedback on reaction progress due both to surface passivating effects and the removal of water.

6.4.3 Preferential flow paths

The anomalously early breakthrough documented at the middle sensor of the 60% saturated column, and the heterogeneity in reaction extent in all columns is indicative of preferential flow paths. Orange coloration visibly identifies narrow (~5 cm diameter) channels of highly reacted material surrounded by white, low to moderately carbonated material (Fig. 6.13). Although some channeling was observed in the 35% saturated columns, the process was most extreme in the 60% saturated column. This is attributed to the higher percentage of water filled pores that effectively block gas transport (Collin and Rasmuson, 1988); therefore a limited volume is available for the gas to flow. Because the bases of the columns were at or close to 100% water saturation, gas flow into the columns necessitated displacement of pore water. It is well known that the differences in viscosity between two fluids, such as the supplied gas and the pore water, leads to instabilities at the their interface (Hill, 1952; Marulanda et al., 2000). This may trigger the development of viscous fingers in the direction of flow and thus heterogeneous distribution of the invading fluid in the porous medium (Hill, 1952; Marulanda et al., 2000). Because the gas flow in the experiments was upward, and it has a much lower density and viscosity than the displaced water, the invading front was inherently unstable and should lead to fingering (Hill, 1952; Kueper and Frind, 1988; Marulanda et al., 2000). Although the importance of viscosity and density differences has been demonstrated in homogeneous media (Marulanda et al., 2000 and references therein), in heterogeneous porous media, viscous fingering becomes less important, and flow paths are instead governed by the permeability field (Kueper and Frind, 1988). It is plausible that small-scale heterogeneities in

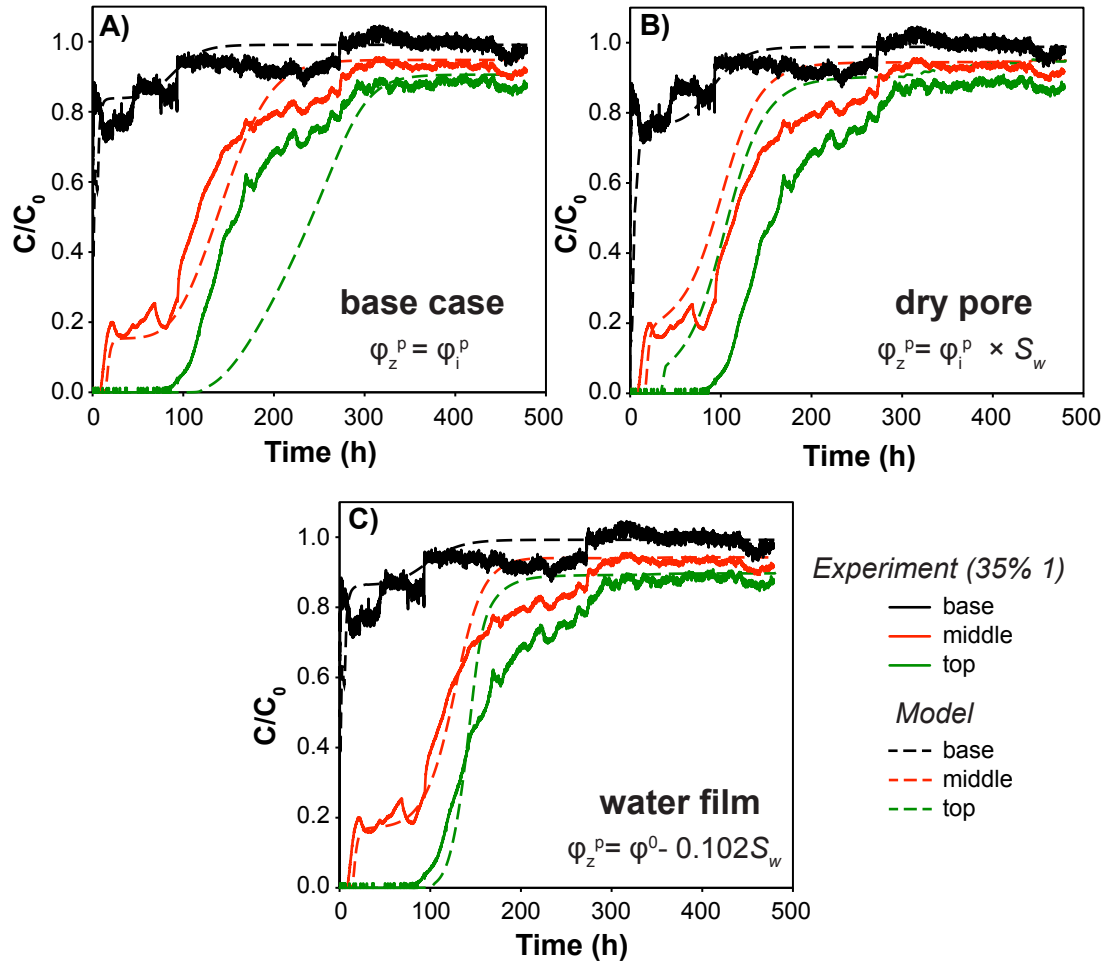


Figure 6.11. Comparison of modeled versus experimental CO_2 breakthrough curves from 35% 1. Black, red, and green lines represent CO_2 breakthrough curves from the base, middle, and top of the column. Solid and dashed lines represent experimental and modeled data, respectively. A) Results from the base case model. B) Results from the dry pore model. C) Results from the water film model.

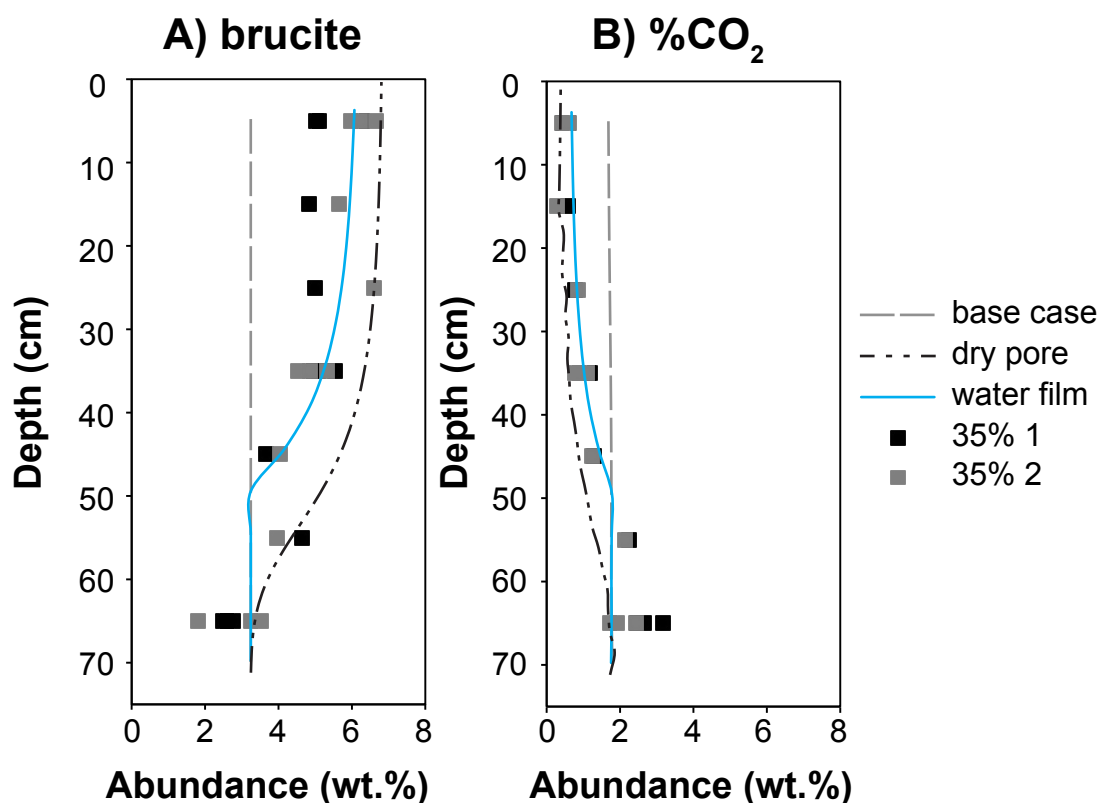


Figure 6.12. Comparison of modeled versus experimental brucite (A) and secondary phase CO₂ (B) abundance profiles from 35% 1 and 2. The black and grey squares illustrate measured brucite abundance in 35% 1 and 2, respectively. The grey dashed and black dash-dot lines represent the base case and dry pore models, respectively, and the solid blue line represents the water film model.

the porous medium lead to preferential channelization of the flow along more permeable paths. For instance, the highly carbonated region along the column wall (Fig. 6.13C) is attributed to channelization between the porous media and the column wall. Conversely, the smaller diameter highly carbonated zones visible towards the middle of the column (Fig. 6.13C) could be the result of instabilities at the fluid interface. Although care was taken to ensure the porous media in the column experiments was homogeneous, it is likely that small-scale heterogeneities in permeability existed.

Initial intrinsic and relative permeability distributions are likely to control the early

infiltration of the porous medium by the gas phase, but the question as to how these initial fingers will evolve during carbonation due to reaction induced changes in porosity and permeability provides additional complexity. Mineral dissolution and precipitation can lead to positive or negative feedbacks that enhance or dampen finger development; a process known as reactive-infiltration instability (e.g., Daccord and Lenormand, 1987; Ortoleva et al., 1987; Daccord, 1987; Kelemen et al., 1995; Dipple and Gerdes, 1998; Kalia and Balakotaiah, 2007). Despite the removal of water from the pore space during hydrated Mg-carbonate precipitation, a net decrease in gas-filled pore volume during carbonation is expected due to the large solid volume increase, irrespective of the type of Mg-carbonate mineral formed (A4 Fig. A4.10). Yet, the persistence of the viscous fingers implies that permeability remained greater within the fingers than in the surrounding media, despite the porosity reduction. This is attributed to the fact that precipitation would occur in water filled pores within the fingers (e.g., Chapter 4), thus the majority of pore space clogging would not occur in the gas-filled pores through which the gas was flowing. Moreover, the evaporative removal of water from the pore space would be greatest in the fingers where the gas flux was highest, thereby increasing the gas filled pore volume and relative permeability with respect to the gas phase; a positive feedback. The implication of these effects is that a large proportion of the reactive material is inaccessible, resulting in a reduction of both reactive capacity and effective surface area. The reduced reactive capacity is evidenced by the lower mass of CO₂ sequestered in the 60% saturated column despite the minimization of water-limited conditions. In practice, this is equivalent to the 'dry pore model,' except the number and distribution of channels cannot be estimated *a priori*.

6.5 Implications

6.5.1 Mineral dissolution-precipitation reactions in the vadose zone

Quantification of reactive surface area, upon which mineral weathering reactions responsible for nutrient and carbon cycling and contaminant attenuation depend (Stipp, 1998;

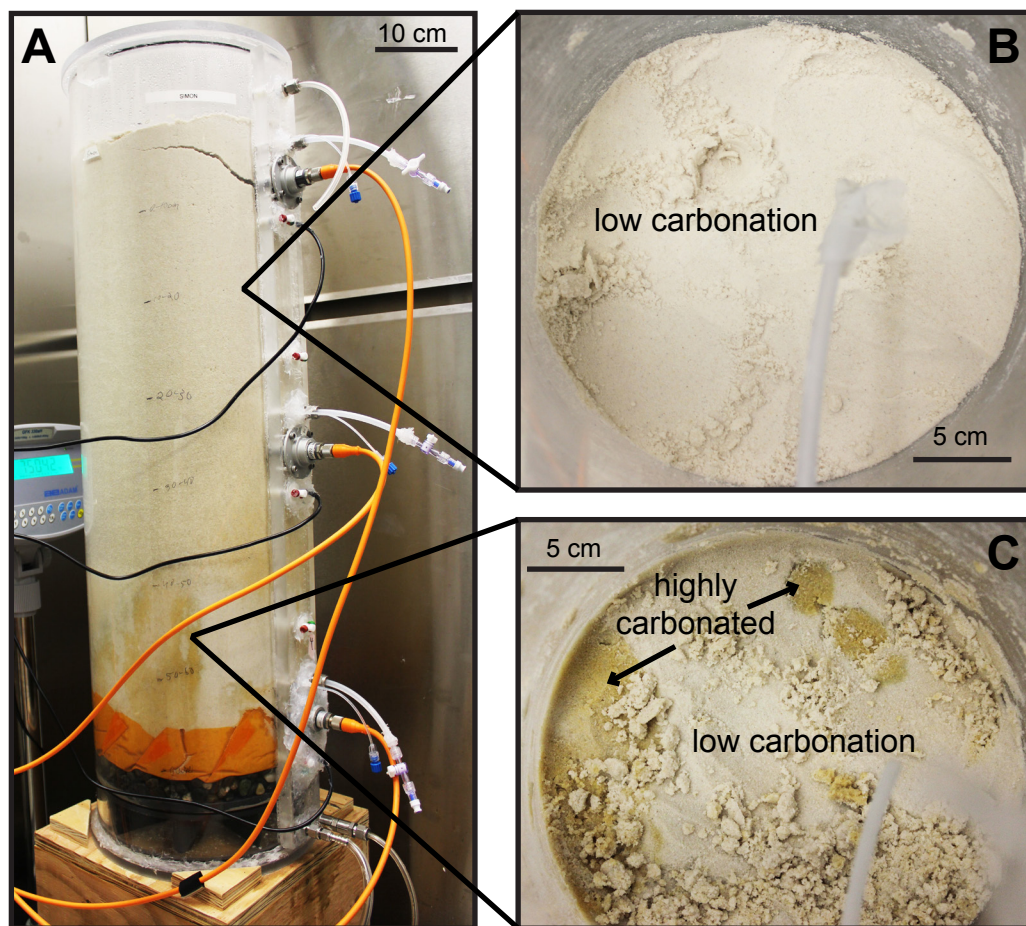


Figure 6.13. Photographs of the 60% saturated column at the conclusion of the experiment. A) Photograph of the column exterior showing reaction fingers: narrow zones of highly reacted material typified by an orange coloration. Off-white areas are zones of poor to moderately carbonated material. The bright orange area seen from the exterior at the column's base is the mesh that separates the reactive material from the gravel layer. Map view of the solid materials at the conclusion of the experiment during excavation near the top of the column (B) and near the base of the column (C). Orange colored reaction fingers are evident near the base of the column, but are not visible near the top of the column to the overall lesser extent of reaction, which was insufficient to induce a visible color change.

Cubillas et al., 2005; McKinley et al., 2006; Manning, 2008; Maher et al., 2009; Wilson and Bish, 2012), is complicated by low water availability in the unsaturated zone and changes in physical surface area with reaction progress. Reactive transport modeling revealed that low water saturation does not significantly reduce reactive surface area; rather it reduces the reactive capacity of the porous medium. Omission of this effect in reactive transport models may result in significant over prediction of the extent of reaction. Simply decreasing the effective surface area, as is often the approach, does not represent reaction progress well; the reactive capacity must also be considered. Moreover, the maintenance of reactive surface area despite considerable consumption of the reactive phase has implications for quantifying the evolution of reactive surface area. In the case of brucite, surface area is better represented as being constant, due in part to the roughening and fracturing of grains during reaction rather than assumed to decrease with decreasing geometric grain size. Similar mechanisms may occur during dissolution of feldspars with exsolution lamellae (Lee et al., 1998) or due to reaction induced fracturing during natural or engineered carbonation of Mg-silicates (Kelemen et al., 2011; Beinlich and Austrheim, 2012).

6.5.2 CO₂ sequestration

Local water saturation is significantly altered during injection of CO₂ into subsurface formations for sequestration purposes (Loring et al., 2011; Schaef et al., 2011; Van Pham et al., 2012; Schaef et al., 2013a; Miller et al., 2013; Thompson et al., 2013; Thompson et al., 2014), and near surface CO₂ sequestration strategies and natural systems will also be affected by rainfall and evaporation. The limited extent of reaction at low water contents implies that the capacity of such CO₂ sequestration strategies will be strongly restricted by the available volume of water. Such effects may also be relevant for precipitation of hydrated clays, sulfates, and zeolites that have water in their crystal structures. Conversely, at high water saturation, preferential flow path development could significantly reduce the reactive capacity when CO₂ is injected into porous media, although this could in part be controlled by the rate of injection

(e.g., Ji et al., 1993). Preferential flow paths could likely be redirected by the addition of water, for example, by rainfall or process water recharge in mine tailings, and could be minimized via injection of gas only above the water table in engineered systems.

7. Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining⁶

7.1 Introduction

Storage of CO₂ in carbonate minerals has been recognized as a safe and effective method for mitigating rising concentrations of atmospheric greenhouse gases (Seifritz, 1990; Lackner et al., 1995; Lackner, 2003). Unlike traditional Carbon Capture and Storage (CCS), which relies predominantly upon stratigraphic trapping of injected supercritical CO₂ within rock formations, carbon mineralization technologies utilize direct production of carbonate minerals as traps for CO₂. Since carbon mineralization was first proposed as a method for storing CO₂ (Seifritz, 1990), most of the work on this subject has focused on the development of rapid, large-scale *ex situ* methods for trapping and storing CO₂ at industrial point sources (reviewed in Huijgen and Comans, 2003; IPCC, 2005; Huijgen et al., 2005; Sipilä et al., 2008; Power et al., 2013b). Most processes developed to date are based on reaction of CO₂ with naturally occurring non-carbonate minerals such as silicates, hydroxides or oxides. Weathering of these minerals in nature is generally a slow process and high temperatures and pressures are needed to induce carbon mineralization reactions on the short timescales (i.e., hours) required for development and deployment of industrial carbonation reactors (Sipilä et al., 2008; Zevenhoven et al., 2011). Although rapid and technologically feasible, the financial viability of this approach to carbon mineralization is currently limited by low carbon prices (Power et al., 2013a; Power et al., 2013b).

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Recent research has focused increasingly on two alternative approaches: (1) *in situ* carbon mineralization and (2) *ex situ* carbon mineralization at industrial sites. *In situ* carbon mineralization aims to promote subsurface carbonation by injection of CO₂, or solutions bearing dissolved CO₂, into mafic and ultramafic formations (e.g., Cipolli et al., 2004; Kelemen and Matter, 2008; Gislason et al., 2010). *Ex situ* carbon mineralization at industrial sites focuses on low-temperature and low-pressure carbonation of alkaline industrial wastes such as smelter slag, fly ash, alkaline and saline brine, construction waste, and mine tailings (e.g., Wilson et al., 2006; Manning, 2008; Power et al., 2009; Huntzinger et al., 2009; Wilson et al., 2009a; Wilson et al., 2009b; Renforth et al., 2009; Ferrini et al., 2009; Power et al., 2010; Zhao et al., 2010; Ballirano et al., 2010; Wilson et al., 2010; Pronost et al., 2011; Renforth et al., 2011; Wilson et al., 2011; Power et al., 2011b; Bobicki et al., 2012; Pronost et al., 2012; Harrison et al., 2013a; Chapter 2; Manning and Renforth, 2013).

Carbonation of the mineral waste from ultramafic mines has been documented previously (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2009b; Wilson et al., 2011; Pronost et al., 2012; Beinlich and Austrheim, 2012; Oskierski et al., 2013); however, previous estimates of carbonation rates have generally relied on small sample sets and have not been explained within the context of geochemical modeling. Complementary laboratory experiments and reactive transport modeling have recently been developed to investigate and quantify controls on the rate of carbon mineralization in mine tailings (e.g., Wilson et al., 2010; Pronost et al., 2011; Bea et al., 2012; Assima et al., 2013a; Assima et al., 2013b; Harrison et al., 2013a; Chapter 2). Thus, a detailed framework now exists for assessing, monitoring and modeling carbon mineralization in mine tailings. Here, for the first time, we apply isotopic and crystallographic carbon accounting methods and reactive transport modeling to quantitatively assess the rate of, and controls on, carbon mineralization on the scale of a large operating tailings facility at the Mount Keith Nickel Mine, Western Australia. This represents the first implementation of a detailed framework for carbon accounting during carbon mineralization via air capture in an active industrial setting and on a landscape scale.

At the Mount Keith Nickel Mine, the hydrated Mg-carbonate mineral, hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], develops as a weathering product within ultramafic mine tailings. Consequently, accounting of the amount of atmospheric CO₂ that is being trapped and stored within this mineral could be used to offset the mine's greenhouse gas emissions. The isotope system (i.e., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and F^{14}C) employed by Wilson et al. (2009a) has been used to assess capture and storage of atmospheric CO₂ within hydromagnesite in the tailings at Mount Keith. Further to this, quantitative phase analysis using the Rietveld method and powder X-ray diffraction (XRD) data are used to estimate the amount of hydromagnesite in the tailings. Quantification of hydromagnesite at Mount Keith is non-trivial, because the mineral content of mine tailings is generally heterogeneous due to frequent changes in ore mineralogy, processing procedures, and tailings management practices. The mineralogy of tailings piles also changes with time as tailings react with the atmosphere and meteoric and process waters to produce secondary mineral phases. As a result, geostatistical methods that rely on the presence of regular and predictable geological structures cannot be used to predict the mineralogy of a mine tailings pile. Thus, in order to estimate the total amount of CO₂ captured from the atmosphere and stored within secondary carbonate mineral phases at Mount Keith, it is necessary that the mineralogy of its tailings storage facilities be well constrained. We have constructed a database of quantitative mineralogical results for a large suite of tailings samples, taken from various depths below the surface of the tailings storage facility at Mount Keith.

Because the ages are known for many of the tailings flows at Mount Keith, we have been able to use our quantitative mineralogical results to build a time-dependent reactive transport model that describes the geochemical evolution of its tailings storage facilities (Bea et al., 2012; this study). From this model, we illuminate the mechanisms governing carbon mineralization and obtain an empirical rate for hydromagnesite precipitation. Finally, the reactive transport model has been used to assess potential methods by which tailings management practices could be tailored to enhance carbon mineralization and maximize offsetting of greenhouse gas emissions at Mount Keith.

7.2 Locality and sampling strategy

7.2.1 The Mount Keith Nickel Mine

The MKD5 orebody at Mount Keith is located in the North Eastern Goldfields district of Western Australia (Fig. 7.1) and is the largest nickel producer in Australia (Grguric, 2003). The deposit at Mount Keith occurs in the NNW/SSE-trending Agnew–Wiluna greenstone belt in the Archaean Yilgarn Craton (Hill et al., 1990). The MKD5 orebody is hosted by komatiitic peridotite (primarily dunite), which attained mid–upper greenschist facies as a result of regional metamorphism (Barrett et al., 1977). Retrograde serpentinization and carbonation of the host peridotites resulted from infiltration by H₂O–CO₂-rich fluids (Barrett et al., 1977; Grguric et al., 2006). Resulting metamorphic assemblages (from proximal to distal) are (1) talc–magnesite, (2) antigorite–magnesite, and (3) lizardite–brucite–hydrotalcite group (Grguric et al., 2006).

Conventional, staged-cutback, open pit mining methods are practiced at MKD5, yielding approximately 11 Mt of ore annually (Grguric, 2003). The mining operation at MKD5 produces approximately 370 000 t of greenhouse gases (cited as CO₂ equivalent) and approximately 11 Mt of ultramafic tailings each year (BHP Billiton, 2005). Ore from the MKD5 deposit is processed using froth flotation methods to concentrate sulfide minerals (Grguric et al., 2006). Additives used in processing include citric and sulfuric acids, guar gum, Na-dithionite, Na-ethyl xanthate, and (historically) soda ash. In 2004, ore reserves contained 0.52 wt.% nickel (Grguric et al., 2006), primarily in high-Ni pentlandite [(Fe,Ni)₉S₈], godlevskite [(Ni,Fe)₉S₈], heazlewoodite [Ni₃S₂], and millerite [NiS]. Recovery of these minerals from the flotation circuit is typically about 70% (Grguric et al., 2006). The material rejected from the processing plant is piped to one of two tailings storage facilities (TSF2, which was the only facility in operation at the time of sampling), and is suspended in the hypersaline process water used in the flotation circuit. Tailings are deposited from spigots located on risers at nine points in TSF2 (Fig. 7.1A).

The tailings storage facility at Mount Keith was constructed in two phases. The two cells of TSF1 (Fig. 7.1A) were the sole receptacles for tailings from July 1994 until the facility was decommissioned in January 1997 (Stolberg, 2005). A centralized discharge tailings storage

facility (TSF2) was commissioned to replace TSF1 by January 1997 (Stolberg, 2005) and remains in operation today. Along the circumference of TSF2, the outer 100 to 400 m of the compound are dedicated to catching and storing tailings in the event that mineral waste from the interior of the facility should overflow. This design feature has been effective and provides

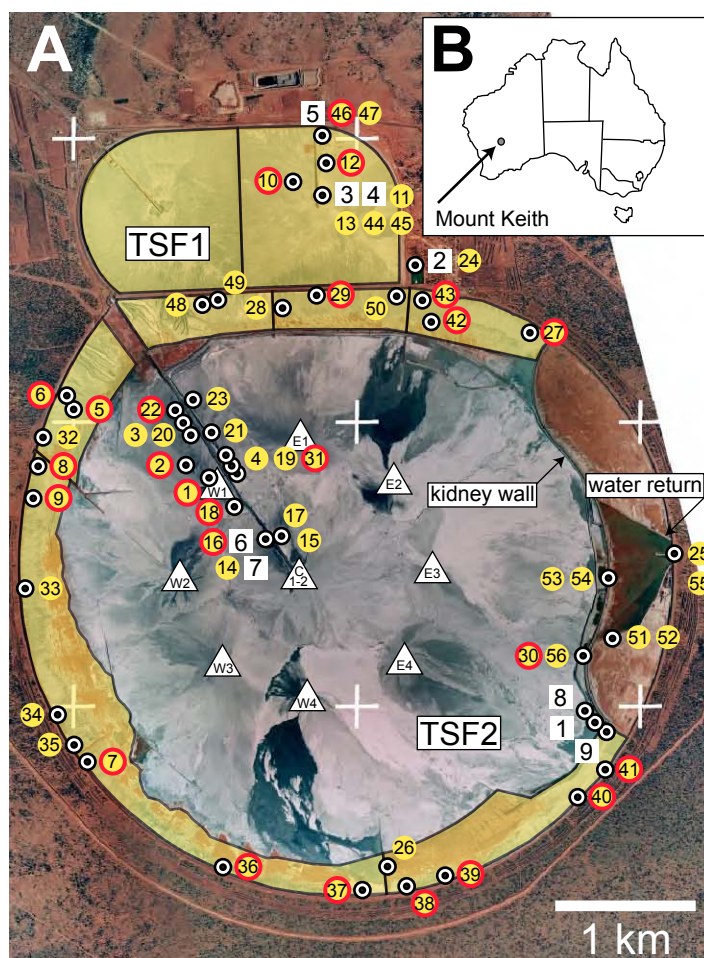


Figure 7.1. The Tailings Storage Facilities (TSFs) at Mount Keith (A). Location of Mount Keith Nickel Mine within Australia (B). The roughly circular facility in (A) is TSF2 and the smaller, adjoining facility is TSF1. Samples were collected at 59 locations in TSF1 and TSF2. Sampling in TSF2 was done along the perimeter of the facility and on both sides of a radial access road. Sampling in TSF1 was done proximal to the access road in Cell 2 (the right-most cell of TSF1). Squares indicate sites sampled in 2005; circles indicate sites sampled in 2006; borders on circles indicate sites for which Rietveld refinements have been done; triangles indicate locations of risers from which tailings are deposited. Shading denotes regions of the TSFs in which deposition of tailings had ceased as of 2006.

snapshots of tailings compositions from several overflow events. Tailings in the various overflow cells of TSF2 had been permitted to weather, without addition of new tailings or process water, for periods of one, three, and between seven and eight years prior to sampling in 2006. At the time of sampling, tailings in the interior of TSF2 (along the radial access road, Fig. 7.1A) had last been deposited approximately zero or one half years prior to collection.

7.2.2 Strategy for sampling at Mount Keith

Limited sampling of the tailings storage facilities at Mount Keith was begun in April 2005. More extensive sampling was done in September and October of 2006. In excess of 800 samples were collected from TSF2 and the older, now-decommissioned TSF1. Bea et al. (2012) describe detailed quantitative mineralogical results and reactive transport modeling of TSF1.

At the time of fieldwork, large regions of TSF2 were saturated with process water, making these regions of the tailings facility inaccessible for sampling. In order to compensate for incomplete access to the tailings at Mount Keith, sampling of the main tailings storage facility (TSF2) was carried out along a radial maintenance road and around the perimeter of the roughly circular facility (Fig. 7.1A). Samples were collected at random intervals along these two paths in TSF2. Tailings were primarily sampled by collection of single cores, coring on 5 m x 5 m and 10 m x 10 m grids (after Roselle et al., 1999) and from vertical profiles on exposed surfaces and excavated trenches. Further detail is available in the Supporting Information (SI)⁷.

To the best of our knowledge, all of the tailings (at the surface and at depth) sampled from the overflow cells around the exterior of TSF2 are of a specific age (either one, three, or between seven and eight years). Contrastingly, only the ages of tailings sampled from near the surfaces in the central regions of TSF2 are well constrained (as zero or one half years).

⁷The Supporting Information to the Wilson et al. (2014) *International Journal of Greenhouse Gas Control* article is available with the online version of the paper: doi:10.1016/j.ijggc.2014.04.002. Supplementary data relevant to the reactive transport modeling is included as Appendix 5 (A5) in this thesis.

7.3 Analytical and modeling methods

Qualitative and quantitative mineralogy were obtained from powder X-ray diffraction (XRD) data. Quantitative phase analysis with the Rietveld method (Rietveld, 1969; Hill and Howard, 1987; Bish and Howard, 1988) was done on 172 samples of mine tailings from TSF2 at the Mount Keith Nickel Mine. Samples for Rietveld refinement were selected to optimize coverage of the accessible regions of the tailings storage facility. A random number generator was used to select subsets of samples collected from 5 m x 5 m and 10 m x 10 m grids for quantitative phase analysis.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were used to image and characterize mineral habits and textural relationships amongst minerals in thin section. Stable carbon and oxygen isotopic data were obtained from specimens of tailings, waste rock, ore, process additives and water. Radiocarbon data were collected from specimens of CO₂ that were isolated from magnesite and hydromagnesite in bulk tailings using a selective acid extraction procedure. All radiocarbon data were collected using the Single Stage Accelerator Mass Spectrometer (SSAMS) at The Australian National University. Detailed analytical methods are provided in the Supporting Information.

The reactive transport code MIN3P (Mayer et al., 2002; Bea et al., 2012) was employed to identify the processes governing hydromagnesite precipitation in the active tailings storage facility at Mount Keith, and to estimate the rate of CO₂ fixation. MIN3P is a multicomponent reactive transport code that allows direct coupling between transport and reaction processes (Mayer et al., 2002). It was recently modified by Bea et al. (2012) to better represent the influence of dynamic atmospheric conditions on reaction progress by incorporating energy balance equations and vapor transport. Mayer et al. (2002) and Bea et al. (2012) provide complete descriptions of the governing equations and verification examples for MIN3P.

7.4 Qualitative mineralogical results and field observations

7.4.1 Qualitative mineralogy of Mount Keith mine tailings

Tailings at Mount Keith are composed primarily of serpentine minerals, antigorite, lizardite and minor chrysotile $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$, with hydrotalcite-group minerals including iowaite $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$ and woodallite $[\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}]$ with occasional pyroaurite $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$, stichtite $[\text{Mg}_6\text{Cr}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$, and uncommon mountkeithite $[(\text{Mg},\text{Ni})_{11}(\text{Fe},\text{Cr})_3(\text{OH})_{24}(\text{SO}_4,\text{CO}_3)_{3.5} \cdot 11\text{H}_2\text{O}]$. A solid solution exists amongst iowaite, woodallite, pyroaurite and stichtite and ideal end-member compositions are generally not observed at Mount Keith (Grguric, 2001). Minor amounts of brucite, chrysotile, talc, magnetite, chromite, quartz, magnesite, dolomite, and calcite are common. Trace vermiculite is also observed in the tailings. Sulfide minerals have not been detected with XRD to a limit of approximately 0.5 wt.%. These observations are consistent with ore mineralogy (Grguric, 2003).

Efflorescences of secondary minerals are abundant near surfaces within the tailings storage facilities and include carbonate minerals, halide minerals and sulfate minerals (listed in SI Tables S1 and S.2). Efflorescences of sulfate minerals commonly form at the surface of mine tailings during dry conditions or in arid climates, and are leached from tailings during rainfall events (Jambor et al., 2000). At Mount Keith, hydromagnesite, halite, hexahydrite $[\text{MgSO}_4 \cdot 6\text{H}_2\text{O}]$, and blödite $[\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$ dominate these efflorescences, and are commonly associated with lesser amounts of epsomite $[\text{MgSO}_4 \cdot 7\text{H}_2\text{O}]$, konyaite $[\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}]$, löweite $[\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13} \cdot 15\text{H}_2\text{O}]$, and gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$. Sanderite $[\text{MgSO}_4 \cdot 2\text{H}_2\text{O}]$, starkeyite $[\text{MgSO}_4 \cdot 4\text{H}_2\text{O}]$, pentahydrite $[\text{MgSO}_4 \cdot 5\text{H}_2\text{O}]$, and carnallite $[\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}]$ are less common and have only been observed at low abundance. Kainite $[\text{Mg}(\text{SO}_4)\text{KCl} \cdot 3\text{H}_2\text{O}]$ and anhydrite $[\text{CaSO}_4]$ may or may not be present near detection in a very few of the samples analyzed. The hydration states of sulfate minerals are strongly dependent on temperature and relative humidity (e.g., Chou and Seal, 2003; Chipera and Vaniman, 2007; Chou and Seal, 2007) and double salts are known to decompose to single salts (e.g., konyaite and blödite may decompose

to produce thenardite, hexahydrite and amorphous phases; Mills et al., 2010). Thus, the relative abundances of hydrated sulfate minerals measured in the laboratory may not reflect abundance in the field.

7.4.2 Occurrence of hydromagnesite mineralization

Hydromagnesite was detected by XRD in the majority of samples, but is more commonly found at high abundance in samples of shallow tailings. SEM images of Mount Keith mine tailings commonly show fine crystals of hydromagnesite precipitating at the surface of grains of serpentine (Fig. 7.2). In some instances, this hydromagnesite infills both fine cracks and broad fissures in serpentine grains (Fig. 7.2A). The latter textures suggest that hydromagnesite may be forming by replacement of serpentine. Micrometer-scale crystals of hydromagnesite radiate out into the spaces between tailings grains and commonly cement them together (Fig. 7.2B). These textures are similar to those described by Wilson et al. (2009a) for dense cements of hydromagnesite and dypingite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$ that form at depth within tailings

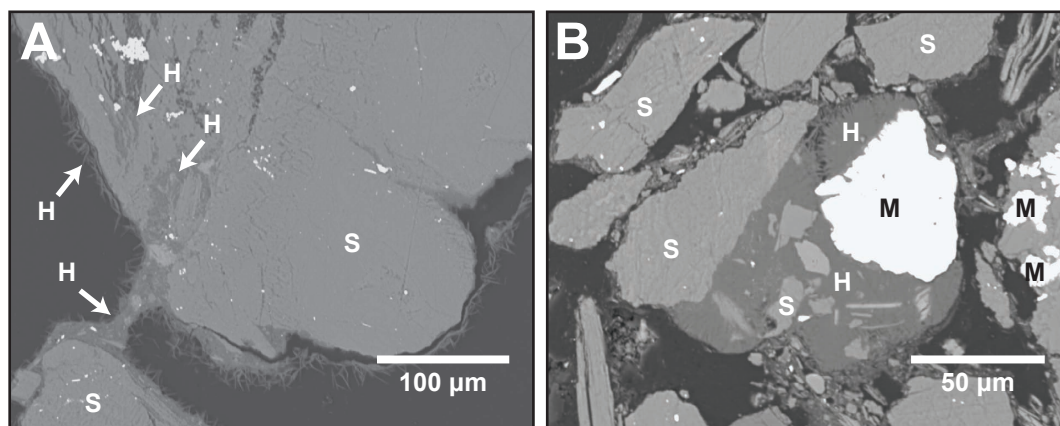


Figure 7.2. Backscattered electron images of hydromagnesite in Mount Keith mine tailings. Both (A) and (B) are from a particularly hydromagnesite-rich sample, 06MK9-9. (A) Hydromagnesite crystals precipitating at the surface of larger grains of serpentine and infilling cracks and fissures within them. (B) Hydromagnesite cementing both fine and larger grains of serpentine and magnetite together. H – hydromagnesite; M – magnetite; S – serpentine.

at the Clinton Creek chrysotile mine, Yukon, Canada. The textural relationship between hydromagnesite and gangue minerals such as serpentine confirms the secondary origin of hydromagnesite as a weathering product at Mount Keith.

Secondary hydromagnesite is typically concentrated within and just below efflorescent crusts of sulfate minerals; however, hydromagnesite persists at depth within the tailings at Mount Keith whereas sulfate minerals generally do not. Although tailings that are heavily cemented with hydromagnesite commonly occur near the surface of TSF2, hydromagnesite-rich samples are also encountered at depth within the tailings storage facility.

Excavating trenches within TSF2 to collect profile samples reveals distinct horizons of tailings material. Within these profiles, layers of clay and silt sized tailings commonly overlay layers of sand sized tailings. These well-sorted layers are likely indicative of mass settling within tailings flows during distinct depositional events [see upper 2 m of the profile at sampling site 1 (i.e., 06MKP1 within 0.5-year old tailings)], which is illustrated in Figure 7.3A and 7.3B. Tailings flows consisting of fine and coarse layers range from 1 cm to 40 cm thick. The most recently deposited tailings in 06MKP1 are covered by an efflorescent crust of blödite and halite and are enriched in hydromagnesite (samples labeled 1–3 in Fig. 7.3A). Hydromagnesite and sulfate minerals are not detectable in the layers of fine sand (4) and coarse sand (5) beneath the surficial samples. However, hydromagnesite is present in deeper samples (6–8) that are associated with filled desiccation cracks (located between samples 7 and 8). Again, hydromagnesite is absent from sample 9, which grades into medium to coarse sand, but it reappears in sample 10. Although sample 10 is of coarse sand, it is a thin horizon and is in contact with a deeper, silty layer (11) that also contains hydromagnesite. The same trend of coarsening grain size with increasing depth occurs between samples 11 and 14, all of which contain hydromagnesite. Filled desiccation cracks appear once again between sample 14 and the fine-grained, hydromagnesite-rich tailings from sample 15. Beneath this level, at a depth of approximately 160 cm, the tailings become darker in color and smell faintly of organics.

Desiccation cracks are a common feature within mine tailings at the surfaces of TSF2.

Within weeks to months of tailings deposition, desiccation cracks begin to appear within the upper few centimeters of new tailings flows. Shallow, distantly spaced desiccation cracks can be seen in the newly deposited tailings at sampling site 30 (Fig. 7.3C). Stolberg (2005) notes that such cracks form within one month in column experiments conducted on water-saturated tailings from Mount Keith when these are left to drain. After approximately 6–12 months, many more cracks will have propagated within the hardened efflorescences on tailings surfaces (Fig. 7.3D). If the tailings are left exposed for a significant amount of time, the desiccation cracks can become deeper features as efflorescent sulfate minerals are leached from the surficial tailings, leaving behind hardened blocks and layers of hydromagnesite-cemented tailings (Fig. 7.3E).

The prevalence of desiccation cracks at tailings surfaces, the preservation of infilled desiccation features at depth, and the higher abundance of hydromagnesite within deep samples such as 06MKP1-8 and 06MKP1-15 indicate that the horizons from which they were taken were once exposed at the surface. It is particularly notable that these former surfaces and the horizons adjacent to them are enriched in hydromagnesite compared to the hydromagnesite-poor horizons of tailings that separate them. While hydromagnesite is most abundant near tailings surfaces, including former tailings surfaces, observations of hydromagnesite in deep, sandy horizons suggests that it may continue to precipitate or become reworked at depth.

7.4.3 Consequences of timing and depth of tailings deposition for hydromagnesite formation

Most of the sampling in TSF2 was done to depths between zero and 130 cm using a sediment-coring device. The ~35-meter tall W1 riser (near sampling sites 1 and 2, Fig. 7.1A) was buried in tailings to a depth of 19 m at the time of sampling. This represents an average deposition of approximately 2 m of tailings each year from the time TSF2 was commissioned up until the time of sampling. However, mine tailings deposits are commonly less than 1 m deep within the exterior overflow cells and at the edges of the large central cell of TSF2. Mining at Mount Keith produces approximately 11 Mt of tailings each year. If this mass of

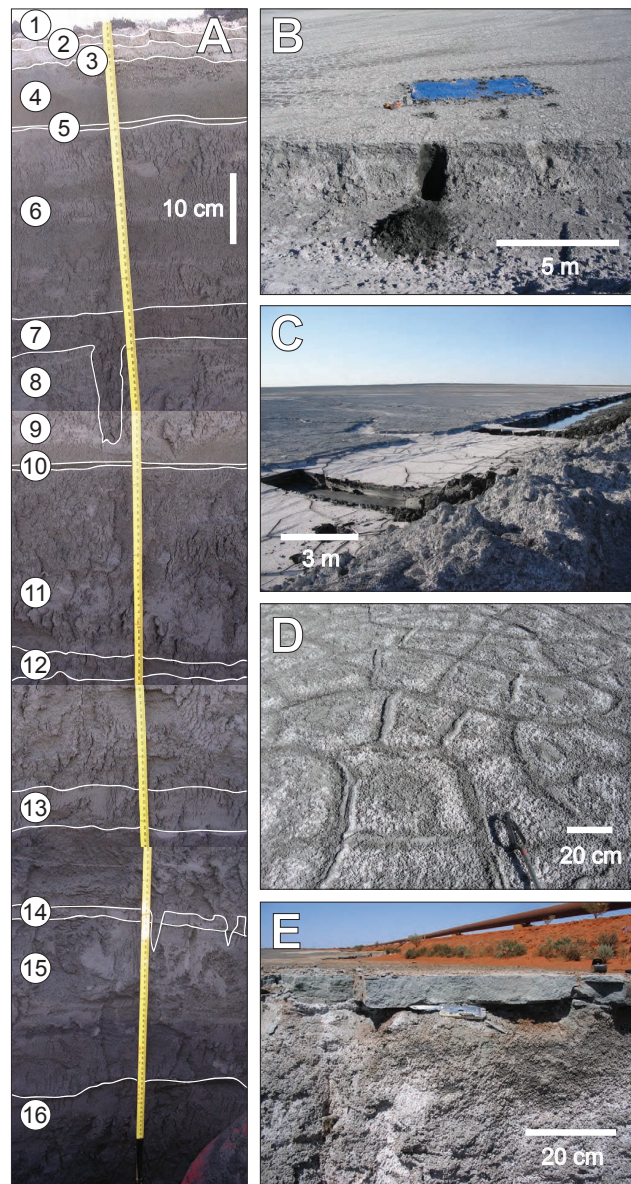


Figure 7.3. Mount Keith mine tailings at the surface and at depth within TSF2. The upper half of the profile at sampling site 1 (06MKP1) (A). Numbers label specific samples (e.g., “1” denotes sample “06MKP1-1”) and white lines separate distinct horizons. (B) The profile excavation from (A) and a 5 m x 5 m grid sample (delineated by the blue tarpaulin) at sampling site 1. (C) Backhoe excavation at sampling site 30, showing near surface water and meter-scale desiccation cracks. (D) An older surface in TSF2 (~1-year old) showing well-developed efflorescences and more pervasive desiccation features. (E) The 7–8-year old surface of TSF2 at sampling site 9 (showing sample 06MK9-6), which is heavily cemented with hydromagnesite.

tailings were deposited uniformly throughout TSF2 it would be approximately 50 cm in depth. After 10 years (i.e., from January 1997 to October 2006) of uniformly thick deposition, tailings deposits would be 5.0 m deep. Clearly, the deep deposits that surround risers are not typical of all regions within TSF2, which suggests that depths on the order of meters are more common than those on the order of decameters.

Stolberg (2005) gives values of 3.0 to 3.8 m for the depth of the tailings deposited near the center of Cell 2 in the now unused TSF1 (i.e., the rightmost cell in Fig. 7.1A) and values as high as 10 m for the depth of tailings near discharge points along the perimeter of Cell 2. As such, deep grid samples in TSF1 and, similarly, near the risers in TSF2 would most likely be accessing tailings deposited within one year of last deposition at the surface. Following this line of reasoning, we have attributed the same ages known for the surface deposits to the deeper tailings in our analyses.

Mount Keith experiences an average pan evaporation of 2,400 mm yr⁻¹ and limited rainfall (220 mm yr⁻¹ on average), most of which is lost to evapotranspiration (Stolberg, 2005). The location of the watertable within most regions of TSF2 was difficult to assess by coring; however, the water table was observed at an elevation of 524.3 m above sea level at both sampling site 30 and at the water return pond (sampling site 25). At sampling site 30, samples collected with a backhoe excavator were saturated with water, indicating that they had been collected from beneath the vadose (unsaturated) zone. Recently deposited tailings from some areas of TSF2 were wetted beneath efflorescent crusts, and holes cored through these damp tailings had a tendency to swell shut within minutes of sampling, but standing water was not observed. This suggests that in parts of TSF2, only the upper few meters of tailings are unsaturated.

Darkly colored, anoxic samples were collected from the base of the profile at sampling site 1, from the base of the backhoe trench at sampling site 30 (Fig. 7.3C) and from shallow depth (i.e., < 20 cm) near the water return pond. These samples may reflect a prevalent compositional change within the deeper, anoxic tailings that are located within the saturated

zone of TSF2. Hydromagnesite was present within the anoxic samples from sites 1 and 30 at abundances comparable to those in the unsaturated zone, suggesting that hydromagnesite is relatively insoluble within the saturated zone of TSF2 and would persist at depth following burial. Thus, estimates of hydromagnesite abundance, made predominantly from samples collected from within the vadose zone, should still apply to deeper, saturated tailings.

7.5 Analytical results

7.5.1 Rietveld refinement results

Rietveld refinement results for tailings from Mount Keith are shown in Figures 7.4 through 7.7 and the complete dataset is available in SI Table S5. Refined abundances and median abundances for hydromagnesite are plotted in Figure 7.4 for tailings of five different ages (i.e., 0 years, 0.5 years, 1 year, 3 years and 7 to 8 years). Shaded envelopes denote the median plus or minus the median absolute deviation of mineral abundance (e.g., Upton and Cook, 2008) for depth intervals (in cm) of [0, 25), [25, 50), [50, 75), [75, 100), [100, 125), [125, 150), and [150, maximum depth]. Data are plotted similarly in Figures 7.5 through 7.7. Results for 10-year old tailings from TSF1 are discussed and modeled by Bea et al. (2012). We use the median and median absolute deviation (MAD) as measures of central tendency because Rietveld refinement results produce a sparse set of log-normally distributed data. Statistical analyses are discussed in more detail in the Supporting Information.

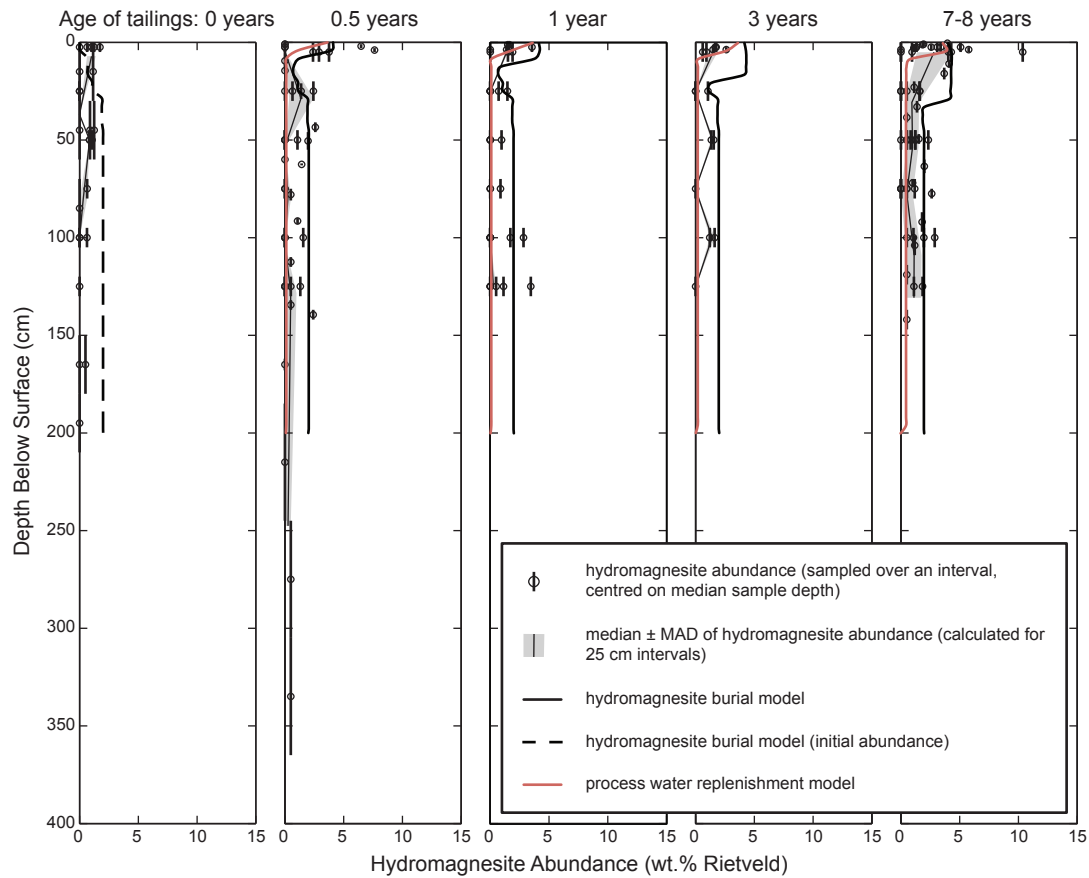


Figure 7.4. Variation of hydromagnesite abundance with depth beneath the surface of TSF2 over time. Age is measured relative to 2006, the date of sampling. Open circles indicate the median depth from which a sample was taken. The associated vertical lines represent intervals of depth over which individual samples were collected. Lines drawn through the data for tailings of each age connect points that denote the mean depth of sampling (based on median depths for individual samples) and the median abundance of hydromagnesite for samples from similar depths. Shaded regions are the median value $\pm$ the median absolute deviation. Black and red lines represent model output from modeling of the hydromagnesite burial and process water replenishment hypotheses, respectively.

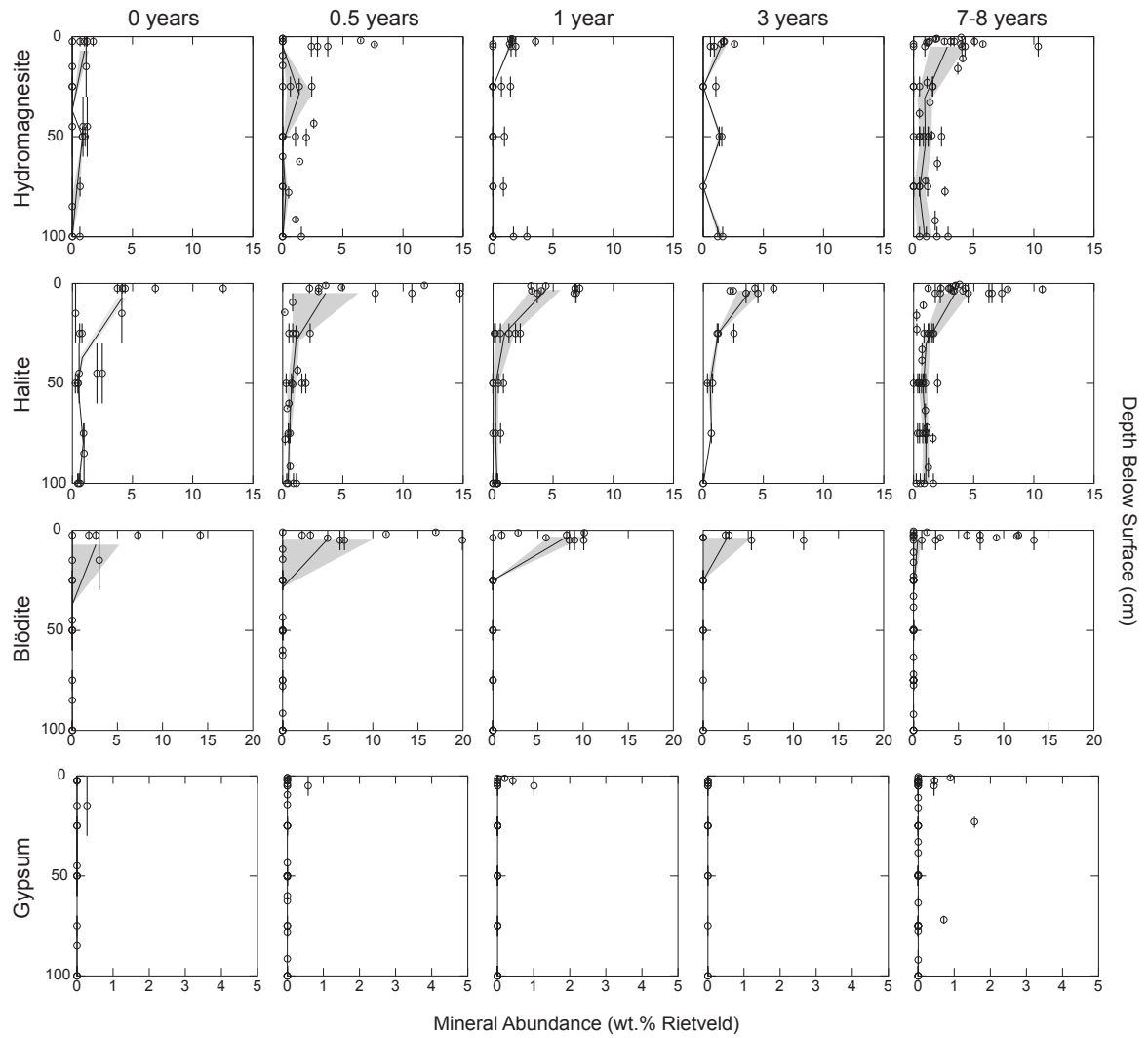


Figure 7.5. Variation of the abundance of select secondary minerals (hydromagnesite, halite, blödite and gypsum) with depth beneath the surface of TSF2 over time. Age is measured relative to 2006, the date of sampling.

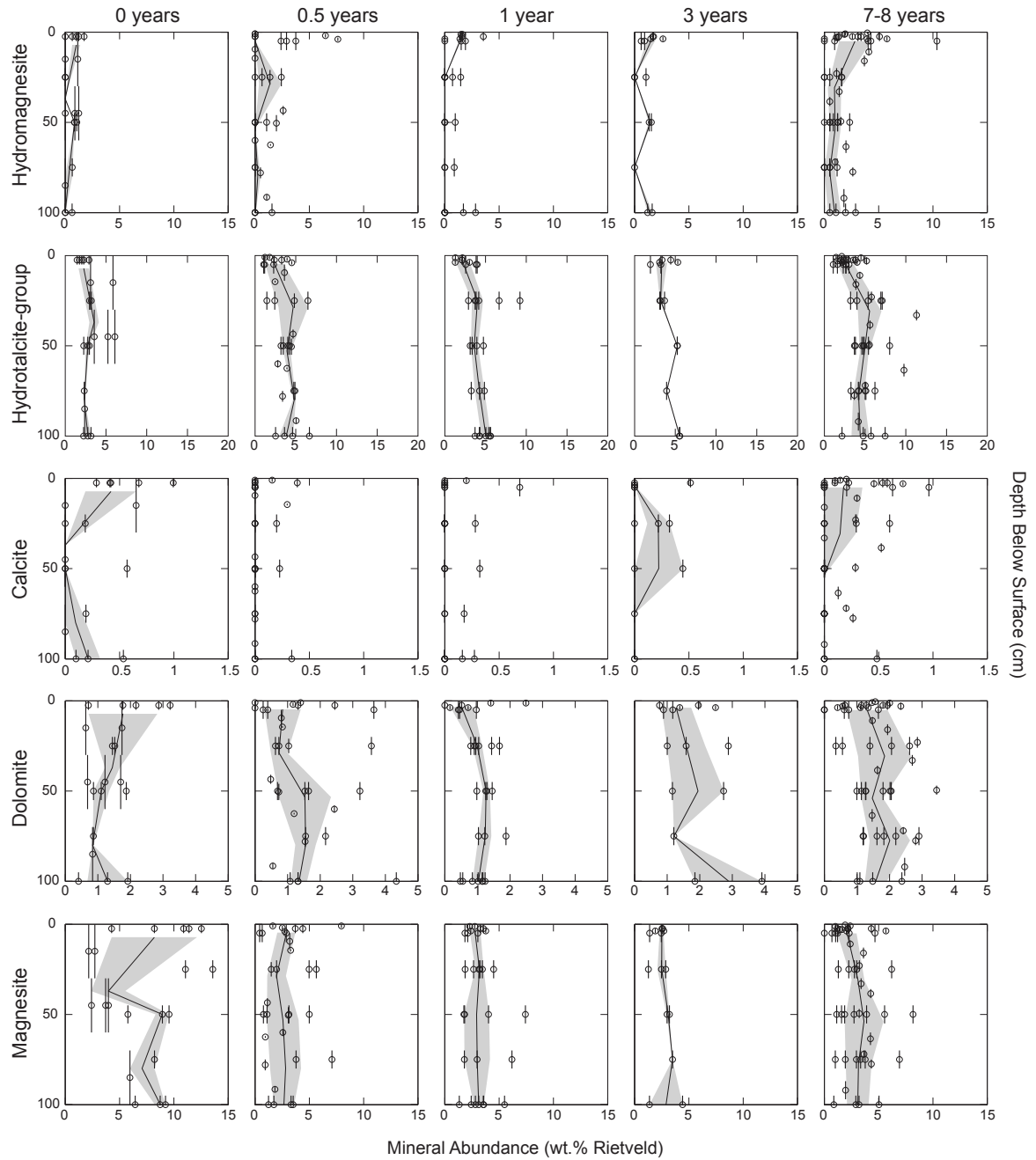


Figure 7.6. Variation of the abundance of gangue carbonate minerals (hydrotalcite-group, calcite, dolomite and magnesite) compared to hydromagnesite abundance with depth beneath the surface of TSF2 over time. Age is measured relative to 2006, the date of sampling.

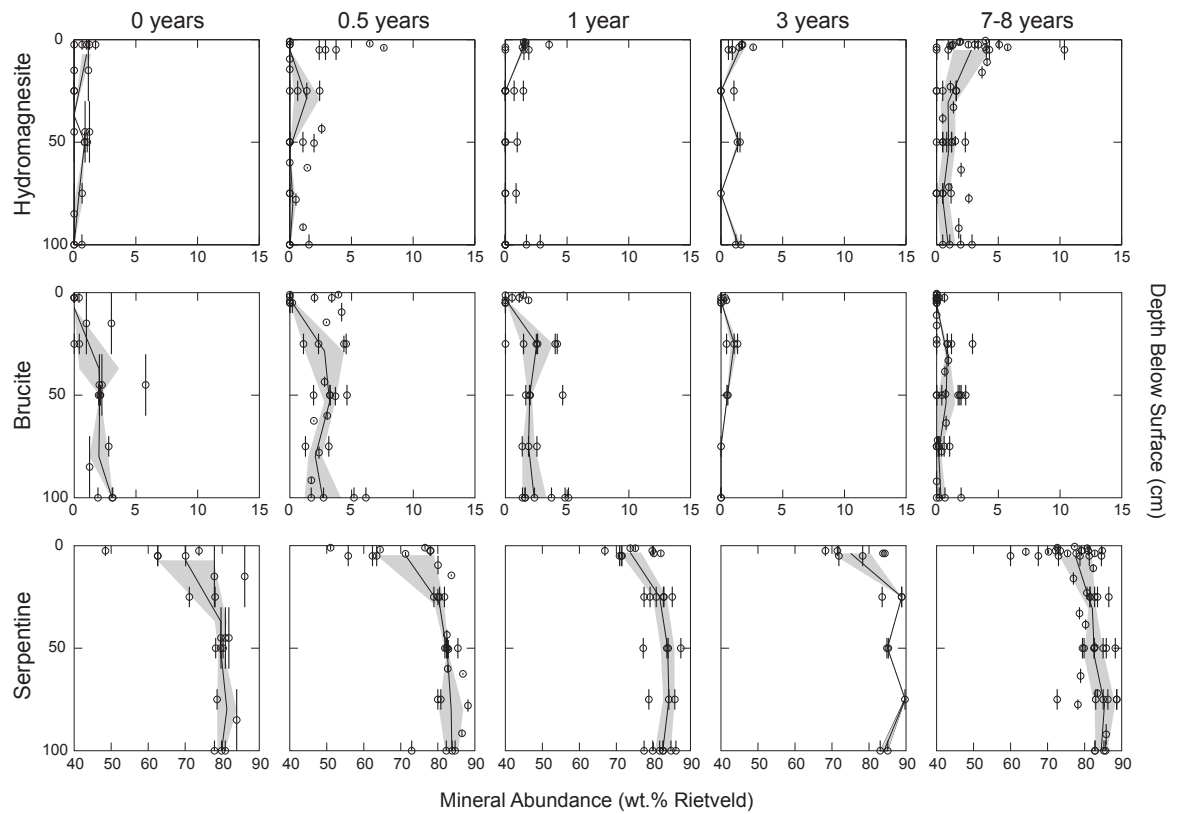


Figure 7.7. Variation of the abundance of brucite and serpentine-group minerals compared to hydromagnesite abundance with depth beneath the surface of TSF2 over time. Age is measured relative to 2006, the date of sampling.

7.5.2 Stable isotopic results

The $\delta^{13}\text{C}$ values for carbonate minerals from Mount Keith mine tailings (see Fig. 7.8 and SI Table S6) vary from -8.56‰ to +1.04‰ (VPDB), with $\delta^{18}\text{O}$ ranging from 7.81‰ to 39.89‰ (VSMOW). One specimen of bedrock magnesite from a sample of waste rock is characterized by $\delta^{13}\text{C}_{\text{VPDB}} = -6.52\text{‰}$ and $\delta^{18}\text{O}_{\text{VSMOW}} = 7.91\text{‰}$. A specimen of iowaite (a hydrotalcite-group mineral) from the mine pit gives values of $\delta^{13}\text{C}_{\text{VPDB}} = -2.83\text{‰}$ and $\delta^{18}\text{O}_{\text{VSMOW}} = 16.11\text{‰}$. Specimens of late-stage Ni-dolomite alteration give $-6.58\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -5.78\text{‰}$ and $26.35\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 27.86\text{‰}$ ($\delta^{13}\text{C}_{\text{av}} = -6.16\text{‰}$ and $\delta^{18}\text{O}_{\text{av}} = 27.30\text{‰}$). Bedrock magnesite, isolated from tailings by selective acid dissolution, gives values of $-6.79\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -1.23\text{‰}$ and $10.33\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 18.98\text{‰}$ ($\delta^{13}\text{C}_{\text{av}} = -4.11\text{‰}$ and $\delta^{18}\text{O}_{\text{av}} = 13.27\text{‰}$). Notably, magnesite extracted from bulk tailings is slightly more enriched in ^{13}C and significantly enriched in ^{18}O over the specimen of pure magnesite that was sampled from waste rock. Duplicate analyses of one sample of soda ash (used historically as an industrial process chemical) give average values of $\delta^{13}\text{C}_{\text{VPDB}} = -8.69\text{‰}$ and $\delta^{18}\text{O}_{\text{VSMOW}} = 17.73\text{‰}$. Dissolved inorganic carbon in tailings water gives values of $-8.16\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -6.20\text{‰}$ ($\delta^{13}\text{C}_{\text{av}} = -7.36\text{‰}$). Water from the processing plant gives values of -6.91‰ and -4.60‰ ($\delta^{13}\text{C}_{\text{av}} = -5.76\text{‰}$).

Analyses of bulk carbonate minerals give $-6.70\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -0.33\text{‰}$ and $14.16\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 31.97\text{‰}$ ($\delta^{13}\text{C}_{\text{av}} = -3.46\text{‰}$ and $\delta^{18}\text{O}_{\text{av}} = 22.60\text{‰}$). Hydromagnesite, isolated by selective acid extraction, is characterized by $-8.6\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq 1.0\text{‰}$ and $24.5\text{‰} \leq \delta^{18}\text{O}_{\text{VSMOW}} \leq 39.9\text{‰}$ ($\delta^{13}\text{C}_{\text{av}} = -3.0\text{‰}$ and $\delta^{18}\text{O}_{\text{av}} = 34.8\text{‰}$). On average, secondary hydromagnesite is enriched over magnesite by approximately 1‰ in $\delta^{13}\text{C}$ and approximately 22‰ in $\delta^{18}\text{O}$.

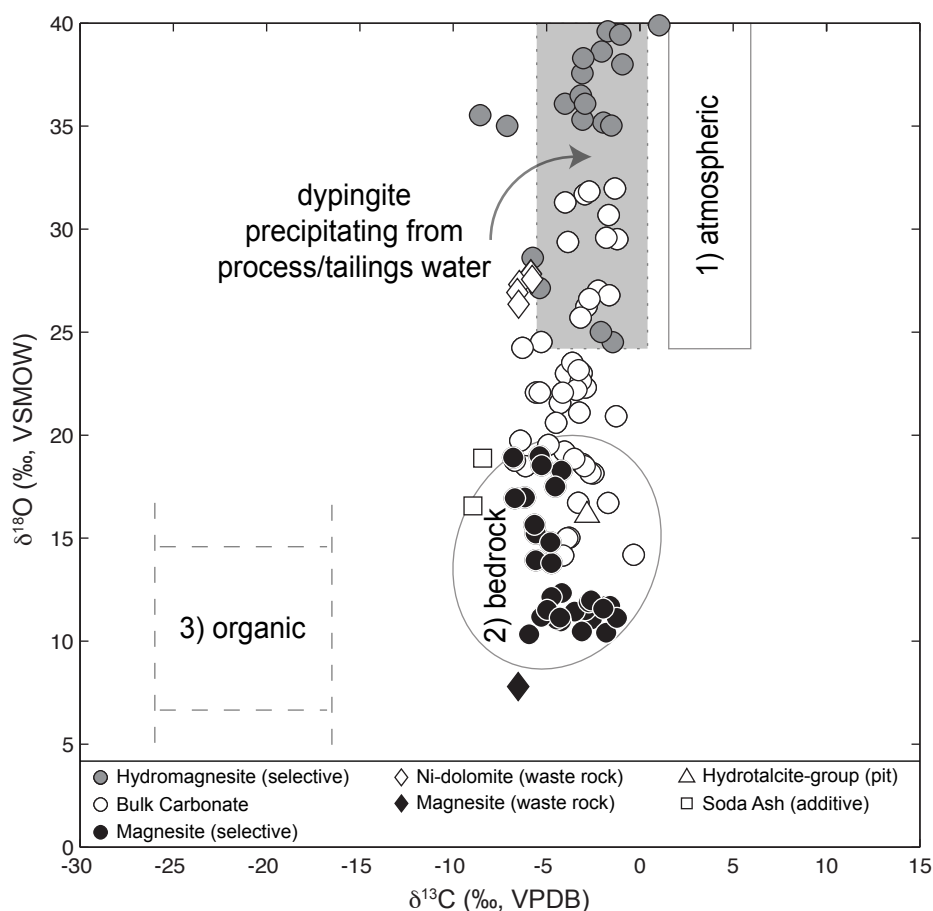


Figure 7.8. Stable oxygen and carbon isotope data for different modes of occurrence and mineralogy of carbonate minerals at Mount Keith. Numbers label fields for Mg-carbonate minerals in equilibrium with specific reservoirs for carbon. Measurement errors (as 2σ) are typically smaller than the symbols employed.

7.5.3 Radiocarbon results

The $F^{14}C$ values for carbonate minerals at Mount Keith range from 0.004 to 1.052 and are given in Figure 7.9 and SI Table S6. Average values of $F^{14}C$ and $\delta^{13}C_{VPDB}$ are plotted for samples on which replicate analyses have been done. Because $\delta^{13}C$ data for four specimens of magnesite are not available, radiocarbon results are plotted for two of these specimens only (i.e., CO₂ selectively extracted from magnesite in samples 06MKG-2-7-3 and 06MKG10-5-1).

One specimen of bedrock Ni-dolomite gives an $F^{14}C$ of 0.004 and two specimens of highly pure bedrock magnesite are characterized by 0.005 and 0.009 (the latter value is

an average of two analyses). These results for highly pure bedrock carbonate minerals are consistent with ¹⁴C-free carbon and the level of atmospheric contamination expected from gas separation in our vacuum line and preparation of graphite samples. Carbon dioxide extracted from magnesite in four bulk samples of tailings is defined by $0.024 \leq F^{14}\text{C} \leq 0.365$ ($F^{14}\text{C}_{\text{av}} = 0.147$), the upper end of this range of values being significantly higher than expected from measurements on highly pure specimens. One specimen of soda ash (used historically as a process chemical in the flotation circuit at Mount Keith) has an $F^{14}\text{C}$ of 0.052. Analysis of CO₂

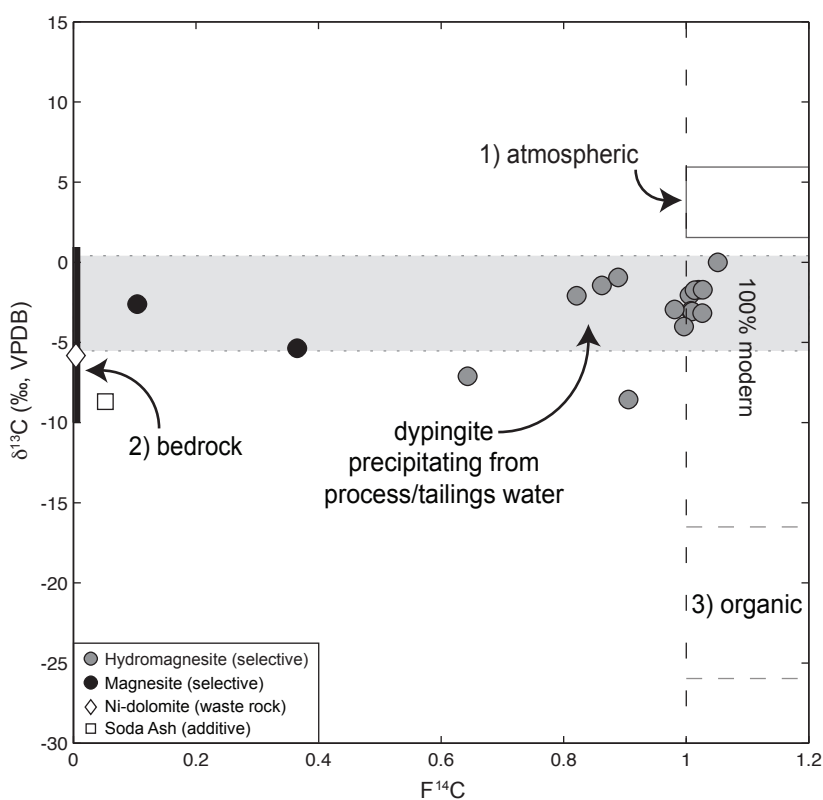


Figure 7.9. Stable carbon ($\delta^{13}\text{C}$) and fraction modern carbon ($F^{14}\text{C}$) data for secondary precipitates of hydromagnesite, bedrock carbonate minerals, and soda ash (a process additive) from Mount Keith. Numbers label fields for Mg-carbonate minerals in equilibrium with specific reservoirs for carbon. Values for $\delta^{13}\text{C}$ were determined in the Pacific Centre for Isotopic and Geochemical Research at the University of British Columbia. Values for $F^{14}\text{C}$ are corrected for machine fractionation using AMS results for $\delta^{13}\text{C}$. Measurement errors are typically smaller than the symbols employed.

selectively extracted from hydromagnesite is characterized by $0.572 \leq F^{14}\text{C} \leq 1.052$ (average $F^{14}\text{C} = 0.921$).

7.6 Discussion of mineralogical and isotopic results

7.6.1 Mineralogical change and formation of hydromagnesite

7.6.1.1 Occurrence of efflorescent minerals

The most common and abundant efflorescent phases at Mount Keith are secondary hydromagnesite, sulfate minerals and halite. The distribution of these phases changes with depth below the tailings surface and evolves with time since deposition of tailings in TSF2.

The abundances of both hydromagnesite and halite in tailings of all ages are greatest within 0 to 25 cm of the surface (Figs. 7.4 and 7.5). This is consistent with previous observations and model results, which indicate that secondary efflorescent minerals are more likely to form within an evaporative horizon at the contact between tailings and the atmosphere (e.g., Acero et al., 2007; Acero et al., 2009; Bea et al., 2012). The abundance of hydromagnesite becomes relatively constant at depths below 25 cm in tailings of each age. However, high abundances of hydromagnesite are sometimes measured at greater depths (Fig. 7.4), which may reflect partial preservation of crusts from former tailings surfaces or ongoing precipitation at depth. It is also possible that hydromagnesite from buried crusts is being reworked at depth as the tailings settle under their own weight. Both hydromagnesite and halite may also be remobilized to some extent by water percolating through the tailings (primarily process water in TSF2, with some influence from meteoric water). Quantitative mineralogical results also show that the mean abundance of hydromagnesite within the upper 25 cm increases with time since deposition of tailings. Thus, hydromagnesite precipitation is an ongoing process in TSF2.

It is notable that hydromagnesite abundance follows a similar trend to that for halite (Fig. 7.5). The formation of halide crusts within tailings in arid climates is known to result from strong capillary transport of aqueous species toward tailings surfaces (Dold, 2006). As with hydromagnesite, the highest concentrations of halite occur at shallow depths, typically

above 25 cm (Fig. 7.5). Halite is also present at depth within the tailings and is found at low abundances in the vast majority of samples analyzed. This suggests that both halite and hydromagnesite remain saturated within tailings and are therefore relatively stable following burial under fresh tailings. Or it could imply that process water is already near saturation with respect to hydromagnesite prior to deposition of tailings, such that percolation of process waters does not significantly remobilize secondary phases.

Sulfate minerals precipitate in mine tailings as a consequence of oxidative weathering of primary sulfide minerals (e.g., Jambor and Blowes, 1998; Jambor et al., 2000). Blödite, hexahydrite and other sulfate minerals are common at the surface of 0- to 1-year old tailings, but persist only at reduced abundance in a few outlier samples at the surface of 3- and 7–8-year old tailings (Fig. 7.5). Sulfate minerals are scarce below 10 cm depth and are almost entirely absent below a depth of 25 cm. Gypsum, which is relatively insoluble compared to most sulfate minerals, appears to be the only sulfate phase that persists at depth, but it is uncommon and present only at low abundance (Fig. 7.5). Bea et al. (2012) demonstrate that sulfate minerals are absent from tailings in the non-operational TSF1 at Mount Keith. Without new input of tailings process water, rainfall events likely leach sulfate minerals from the surface of TSF1 within 10 years of deposition (consistent with observations by Jambor et al., 2000). The presence of sulfate minerals in surface crusts suggests that the older tailings flows around the perimeter of TSF2 may occasionally be exposed to fresh tailings water from the interior region of the storage facility. Additionally, the presence of anoxic, darkly colored tailings at depth within TSF2 suggests that surficial sulfate dissolution may be fueling microbial sulfur reduction in deeper tailings horizons.

Acero et al. (2007; 2009) demonstrate that the formation of efflorescent crusts of sulfate minerals reduces the permeability of mine tailings, which limits gas exchange with the atmosphere (i.e., evaporation, and O₂ and CO₂ diffusion). Thus, formation of efflorescences may be viewed as a self-limiting process that controls the depth to which alteration minerals may extend. Precipitation of carbonate and evaporite minerals, such as hydromagnesite and halite,

within tailings pores likely participates in controlling the rate and extent of mineralization.

Previous studies have also shown that efflorescent crusts may trap and concentrate upward diffusing gases such as CO₂ in pore spaces near tailings surfaces (Blowes et al., 1991; Tasse et al., 1997; Agnew and Taylor, 2000). Agnew and Taylor (2000) found that CO₂ concentrations in pore spaces beneath a crust of hydrated Fe-sulfate minerals at the Elura Ag-Pb-Zn Mine near Booroondarra, New South Wales, Australia, were up to 10 times that of atmospheric CO₂. This process only occurs where CO₂ is being generated at depth within tailings as a consequence of biodegradation of underlying organics or dissolution of carbonate minerals during biologically mediated oxidation of sulfide minerals. The undetectable quantities of sulfide minerals and high abundances of carbonate minerals within both fresh and weathered tailings suggest that neither process is significant at Mount Keith. Instead, it is more likely that the ubiquitous cracks and fissures that texture efflorescences allow for limited gas exchange between the deeper tailings and the atmosphere once efflorescences have formed.

7.6.1.2 Relationship of hydromagnesite to primary gangue minerals

Several gangue minerals including serpentine-group minerals, brucite, hydrotalcite-group minerals, magnesite and dolomite could act as sources of magnesium in hydromagnesite. Dissolution of bedrock (gangue) carbonate minerals could provide DIC into solution; essentially recycling previously fixed carbon into newly formed hydromagnesite. However, this would not constitute net sequestration of CO₂ within hydromagnesite, which requires a non-carbonate mineral source for both magnesium and carbon (Wilson et al., 2009a).

Variations in the abundances of mined bedrock calcite, dolomite, magnesite and carbonate-bearing hydrotalcite minerals with depth and time are plotted in Figure 7.6, and median values show no consistent trends in their distribution with depth or time. In almost all cases, the abundances of bedrock carbonate minerals stay relatively constant in comparison to results for secondary minerals such as hydromagnesite (Fig. 7.5), which typically show distinct and predictable behaviors with time and depth. Under the circumneutral pH conditions (i.e.,

pH of 5 to 8) that dominate within the tailings waters at Mount Keith, dissolution of bedrock carbonate minerals will proceed most readily for calcite, then dolomite, and least readily for magnesite (Palandri and Kharaka, 2004). Hydromagnesite is less resistant to dissolution in acidic solutions than magnesite (Königsberger et al., 1999). Hydromagnesite also dissolves rapidly in 5% acetic acid (Wilson et al., 2009a), an acid that has little effect on calcite, the least resistant of the bedrock carbonate minerals. Therefore, the near-constant abundance of less resistant bedrock carbonate minerals and the increasing abundance of hydromagnesite toward the surface of the tailings is very strong evidence that bedrock carbonate minerals are not being dissolved and remineralized as hydromagnesite in TSF2. Secondary Ca-bearing minerals (i.e., gypsum and anhydrite), which could form as a consequence of calcite (and dolomite) dissolution, are relatively uncommon in the tailings at Mount Keith, particularly when compared to the high abundances of secondary Mg-minerals. Only limited dissolution of calcite may be occurring, which indicates that bedrock carbonate minerals are not a significant source of carbon and magnesium in secondary hydromagnesite.

Weathering of serpentine-group minerals and brucite represents an alternative source of magnesium in TSF2. The compositional data for these minerals display a consistent trend toward decreasing abundance with proximity to tailings surfaces (Fig. 7.7). Abundances of brucite and serpentine minerals are relatively constant below a depth of approximately 25 cm in tailings aged 0 to 7–8 years, but decline rapidly within the upper 25 cm of the tailings. The decrease is coincident with increasing abundance of hydromagnesite. This effect is particularly marked for brucite, for which the median abundance and MAD decline to 0 wt.% for all surficial tailings aged 0 to 7–8 years. Contrastingly, brucite is typically present at 1.0–2.5 wt.% abundance throughout the deeper, less weathered samples from TSF2.

Median values for the abundance of serpentine decline by approximately 10 wt.% over the depth interval from 25 cm to 0 cm. This is, however, a proportionally minor decrease in the abundant serpentine minerals when compared to the complete loss of brucite. Bea et al. (2012) have shown that such trends can be caused by dilution of primary gangue minerals as secondary

minerals precipitate from tailings water, solutes and atmospheric gases. Significant input of new crystalline mass to previously unaltered tailings results in a dilution effect in mineral abundances. This occurs because Rietveld refinement results provide a relative measure of crystalline mass, normalized to 100% (w/w). Consequently, it is likely that significantly less than 10 wt.% of the serpentine is lost to weathering.

Weathering of brucite is known to produce hydromagnesite and other hydrated Mg-carbonate minerals under conditions of temperature and pressure that prevail at the Earth's surface (e.g., Hostetler et al., 1966; Xiong and Lord, 2008). Recent carbonation experiments (Zhao et al., 2010; e.g., Wilson et al., 2010; Hövelmann et al., 2012b; Harrison et al., 2013a; Chapter 2) indicate that brucite carbonation can be rapid at near-ambient pressures and temperatures, even in saline and alkaline brines similar to the tailings water at Mount Keith (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2). Bea et al. (2012) and Beinlich and Austrheim (2012) have also documented brucite carbonation in mine tailings from TSF1 at Mount Keith and in a sub-arctic mine shaft, respectively. Interestingly, no brucite was observed during SEM imaging of hydromagnesite-rich surface samples, which is consistent with the brucite abundance decreasing to 0 wt.% near tailings surfaces in TSF2. Grguric (2003) describes a common texture within Mount Keith ore whereby brucite forms coronas with magnetite that encompass sulfide blebs. Thus, the absence of brucite is explained by the (otherwise perplexing) overgrowths of hydromagnesite on magnetite grains (observed in Fig. 7.3B). This textural feature may play a role in limiting sulfide oxidation and carbonate mineral dissolution within Mount Keith tailings. Textural evidence from SEM imaging of particularly hydromagnesite-rich samples (Fig. 7.3A and B) also shows platy hydromagnesite crystals seeding from grains of serpentine minerals, which is consistent with serpentine carbonation. Carbonation of serpentine-group minerals in alkaline mine tailings is known to produce similar textures in brucite-free mine tailings (Wilson et al., 2009a). These results imply that the observed decreases in the abundances of both serpentine and brucite are very likely the result of two processes: (1) dissolution to produce secondary Mg-bearing minerals such as

hydromagnesite, and (2) a dilution effect caused by incorporation of water and atmospheric gases into these newly formed minerals.

7.6.2 Carbon reservoir fingerprinting

There are four potential sources of carbon in tailings from operating mines like Mount Keith: (1) atmospheric CO₂, (2) bedrock carbon from gangue carbonate minerals, (3) carbon from industrial additives, and (4) organic carbon (i.e., mine camp sewage, mined organic sediments, decay of local biota, or microbial metabolism). Net sequestration of CO₂ requires that there be a non-carbonate mineral source for cations and carbon. Thus, net sequestration of CO₂ can only occur in mine tailings when atmospheric carbon (either directly from the atmosphere or indirectly from modern organic matter) is fixed within the crystal structures of carbonate minerals. XRD techniques are well suited to identifying and quantifying carbonate minerals, but these techniques cannot discern which minerals are trapping and storing atmospheric CO₂ nor to what extent CO₂ is being sequestered. Stable and radiogenic carbon and stable oxygen isotope data can be used to: (1) identify the sources for CO₂ stored in carbonate minerals, (2) elucidate the mechanisms by which minerals form, and (3) trace the processes by which carbon is cycled.

7.6.2.1 Fingerprinting with stable isotopes

Stable isotopic data are plotted as $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{13}\text{C}_{\text{VPDB}}$ in Figure 7.8. Calculated and empirically derived fields for Mg-carbonate minerals plotting in isotopic equilibrium with metamorphic, atmospheric and organic sources of carbon (and oxygen) are also given in Figure 7.8. Please refer to the Supporting Information for a detailed description of the data used to define these fields.

The majority of the stable isotopic data for magnesite fall within the range of values expected for precipitation from a carbonate-bearing metamorphic fluid (Fig. 7.8), which is consistent with the known metamorphic origin for this mineral at Mount Keith. One specimen

of a hydrotalcite-group mineral (carbonate-bearing iowaite) has a similar stable isotopic signature to the specimens of magnesite. Specimens of Ni-dolomite are also similarly depleted in ¹³C, but are significantly enriched in ¹⁸O relative to the other bedrock carbonate minerals. This is consistent with their origin as fracture coatings and vug linings in oxidized ore (Grguric, 2003). Soda ash, which was used historically as a process chemical, is slightly depleted in ¹³C relative to bedrock carbonate minerals and gives δ¹⁸O values that are comparable to the upper range for specimens of magnesite.

Samples of bulk carbonate in mine tailings are consistently enriched in ¹⁸O relative to bedrock magnesite and many are enriched relative to Ni-dolomite. Analyses of hydromagnesite, done using selective acid extraction, indicate further enrichment in ¹⁸O (with some δ¹⁸O_{VSMOW} values reaching 40‰) accompanied by a small enrichment in ¹³C of ~1‰ on average. The significant enrichment of ¹⁸O in hydromagnesite relative to magnesite suggests precipitation in an evaporative environment. This is consistent with our interpretation that hydromagnesite forms as a secondary alteration mineral.

None of the data for hydromagnesite at Mount Keith fall within the fields defined for mineral precipitation in equilibrium with atmospheric CO₂ or organic carbon (i.e., mine camp sewage, which is disposed of in TSF2). However, most of the data for hydromagnesite are consistent with precipitation in equilibrium with DIC in process/tailings water at approximately 25°C. Because equilibrium carbon isotopic fractionation factors for hydromagnesite are not known, the fields for equilibrium precipitation of hydromagnesite from atmospheric CO₂ and DIC were estimated using the fractionation factor for dypingite [Mg₅(CO₃)₄(OH)₂·5H₂O], a structurally and chemically related mineral, which has been estimated to be $10^3 \ln \alpha_{\text{dypingite-HCO}_3^-} = (3.8 \pm 1.2)\text{‰}$ between 20°C and 25°C (Wilson et al., 2010; refer to the Supporting Information for details). Because seasonal temperature variations at Mount Keith are greater than the temperature range over which this fractionation factor was determined, it is reasonable to expect that the observed range of δ¹³C values should be broader than predicted here. Based on comparison with carbon isotopic fractionation factors between other carbonate minerals

and DIC, it is likely that inclusion of temperature dependence for dypingite-DIC fractionation would increase the breadth of this field to include all the remaining data for hydromagnesite. Although results are consistent with precipitation of hydromagnesite in equilibrium with process water and DIC, the ultimate source of carbon in DIC is not apparent from stable isotope data. Process water DIC and tailings water DIC at Mount Keith ($-8.16\text{‰} \leq \delta^{13}\text{C}_{\text{VPDB}} \leq -4.60\text{‰}$) are consistently depleted in ^{13}C relative to DIC in equilibrium with the atmosphere (i.e., $\delta^{13}\text{C}_{\text{VPDB}} \approx 0\text{‰}$ at 25°C). The observed carbon isotopic signature of DIC in process and tailings water may reflect (1) kinetic depletion of ^{13}C during diffusion of atmospheric CO₂ into solution (i.e., O'Neil and Barnes, 1971; Wilson et al., 2010; Harrison et al., 2013a; Chapter 2), (2) input of organic or soil CO₂ into the tailings waters, (3) the use of ^{13}C -depleted chemicals during processing, or (4) dissolution of ^{13}C -depleted bedrock carbonate minerals.

7.6.2.2 *Fingerprinting with radiocarbon*

F¹⁴C values for CO₂ selectively extracted from hydromagnesite range from 0.572 to 1.052 and all but one specimen has F¹⁴C > 0.8 (Fig. 7.9). A value of F¹⁴C = 1.06 reflects the ¹⁴C concentration of the atmosphere in 2006, the year of sampling at Mount Keith (Levin et al., 2008). Thus, the highest values in this range are consistent with a modern source for approximately 100% of the DIC-derived carbon in hydromagnesite. The average F¹⁴C value of hydromagnesite is $F^{14}\text{C}_{\text{av}} = 0.921 \pm 0.145$, which suggests that, on average, at least 87% of carbon in these samples has a modern source (relative to the 2006 atmosphere). The only known large reservoir for modern carbon at Mount Keith is the atmosphere and, based on our radiocarbon results, it can be concluded that almost all CO₂ mineralized as hydromagnesite originated from this source.

It is important to note that the excursion of some of these data below a F¹⁴C of unity suggests the possibility of: (1) partial dissolution and reprecipitation of bedrock carbonate minerals as hydromagnesite, (2) mixing with carbon-bearing process additives during mineral precipitation, or (3) contamination of CO₂ from modern hydromagnesite with CO₂ from

¹⁴C-free magnesite during selective acid extraction.

The very small amount of ¹⁴C measured in Ni-dolomite sample 06MKNi-dol ($F^{14}\text{C} = 0.004$) is consistent with the amount of atmospheric contamination typically observed in our vacuum line for samples of ¹⁴C-free bedrock carbonate minerals. The sample of soda ash has $F^{14}\text{C} = 0.052$, which could reflect sourcing of this process additive from a Quaternary evaporite deposit (Warren, 2006). Six specimens of magnesite give values of $0.005 \leq F^{14}\text{C} \leq 0.365$. Two of these analyses are of highly pure samples of magnesite found in waste rock at sampling sites 53 and 54 (i.e., 06MK53 and 06MK54), which give $F^{14}\text{C}$ values between 0.005 and 0.009. These values are consistent with vacuum line contamination of samples with $F^{14}\text{C} = 0$, as expected of bedrock magnesite that formed by carbonate alteration of serpentinized komatiite (Barrett et al., 1977; Grguric et al., 2006). The remaining analyses were done on CO₂ selectively extracted from magnesite in four samples of hydromagnesite-bearing tailings (06MKG2-6-3-mags, 06MKG2-7-3-mags, 06MKG10-5-1-mags, and 06MKP9-4-mags). Magnesite in these samples gives $F^{14}\text{C}$ values between 0.024 and 0.365. These values are higher than expected for bedrock magnesite at Mount Keith, which should not contain detectable ¹⁴C. Similarly to the few anomalously low $F^{14}\text{C}$ values for hydromagnesite, this deviation toward enrichment in ¹⁴C within magnesite could reflect (1) partial conversion of secondary hydromagnesite to magnesite or (2) contamination of CO₂ from ¹⁴C-free magnesite with modern CO₂ from residual, unreacted hydromagnesite during acid extraction.

The decomposition of hydromagnesite to magnesite has been inferred from observation of hydromagnesite playas on the Cariboo Plateau, interior British Columbia, Canada (e.g., Renaut and Long, 1989; Renaut, 1990; Renaut and Stead, 1991). Zhang et al. (2000) estimate that the conversion of hydromagnesite to magnesite requires tens to hundreds of years. However, it may be possible that some amount of recently precipitated hydromagnesite may undergo a transformation to magnesite on the decadal scale in the mine tailings at Mount Keith. In fact, the specimen of magnesite with the highest $F^{14}\text{C}$ value (i.e., 06MKG10-5-1-mags with $F^{14}\text{C}=0.365$) comes from the 10-year old surface of TSF1. In this case, the mixing

trend for magnesite in Figure 7.9 could result from precipitation of hydromagnesite and its decomposition to magnesite.

Alternatively, the finely intergrown nature of secondary hydromagnesite (i.e., as a cement between grains of primary tailings minerals) may be preventing complete reaction with phosphoric acid during sample processing. Subsequent processing of these samples at higher temperature and for a longer period of time would then dissolve not only the desired magnesite but also the residual, unreacted hydromagnesite. This would result in higher values of $F^{14}\text{C}$ than anticipated for magnesite. Furthermore, the finest fractions of less acid resistant bedrock carbonate minerals such as calcite, dolomite, and hydrotalcite-group minerals may be reacting to some extent during extraction of CO₂ from hydromagnesite. This would produce a dilution in ^{14}C , resulting in artificially low values of $F^{14}\text{C}$ for hydromagnesite and the incipient mixing trend in Figure 7.9. Thus, we interpret this trend as an artifact of the technique used for sample preparation, which suggests that some $F^{14}\text{C}$ values obtained for hydromagnesite are underestimated.

These observations are consistent with the results of previous isotopic studies, which conclude that dissolution of bedrock carbonate minerals does not contribute significantly to production of secondary Mg-carbonate minerals in neutral to alkaline mining environments (e.g., Wilson et al., 2009a; Wilson et al., 2011; Beinlich and Austrheim, 2012). Importantly, our radiocarbon results indicate that stable isotope data for Mount Keith carbonate minerals cannot be used to uniquely identify the source of carbon in hydromagnesite. Although radiocarbon data clearly identify a predominantly atmospheric source for carbon, $\delta^{13}\text{C}$ data indicate only that hydromagnesite is precipitating in equilibrium with DIC, but out of equilibrium with atmospheric CO₂ gas. Experiments by Wilson et al. (2010) and Harrison et al. (2013a; Chapter 2) demonstrate that kinetic depletion of ^{13}C occurs during dissolution of atmospheric CO₂ and hydroxylation of aqueous CO₂ to form bicarbonate in saline and moderately alkaline (pH < 11) solutions designed to emulate tailings water at Mount Keith. Mg-carbonate minerals that form from such carbon-limited solutions precipitate in isotopic equilibrium with ^{13}C -depleted

DIC (Figs. 7.8 and 7.9). Thus, although hydromagnesite at Mount Keith acts as a store for atmospheric CO₂, this is not immediately apparent due to the impact of diffusion on the $\delta^{13}\text{C}$ values of DIC. Most significantly, the stable isotopic data indicate that dissolution of atmospheric CO₂ into mine tailings water is kinetically limited, which suggests that carbon mineralization could be accelerated by increasing the supply of CO₂ into solution.

7.7 Reactive transport modeling of hydromagnesite formation in TSF2

7.7.1 Reactive transport model description and initial conditions

Field observations suggest that formation of hydromagnesite is promoted by evaporation and proceeds primarily within the upper 25 cm of tailings. As such, an atmospheric boundary condition was employed at the surface of a 2.0 m deep section of tailings to capture the effects of evaporation. Sinusoidal functions to represent seasonal fluctuations in relative humidity and temperature were employed for the atmospheric boundary based on data from a nearby weather station, similar to the method employed by Bea et al. (2012) to model the inactive TSF1 at Mount Keith. Rainfall events were applied to the tailings surface, in accordance with weather data recorded at a nearby weather station (Leinster Airport) in 2010 (after Bea et al., 2012; data from the Australian Government Bureau of Meteorology, 2013). A zero energy flux condition was applied at the base of the tailings, and a constant head boundary condition (pressure head = 0.0 m) was applied at the base of the tailings to simulate a water table depth at 2.0 mbgs, as is consistent with field observations. The model domain was initially saturated, and flow was 1-dimensional and vertical only. Refer to Appendix 5 (A5) for further detail regarding boundary and initial conditions.

The initial mineralogical composition utilized in the model was based on the afore-described quantitative mineralogical results, with initial abundances set to values representative of all profiles (A5 Table A5.1). Primary minerals included in the simulations comprised: serpentine (chrysotile), brucite, magnesite, calcite, and dolomite (A5 Table A5.1). An initial

value of 2.5 wt.% brucite was estimated based on its average abundance at depth within TSF2. Secondary phases that were allowed to precipitate included: hydromagnesite, halite, chalcedony, gypsum, blödite, epsomite, hexahydrite, and nesquehonite (A5 Table A5.1). Dissolution of the primary mineral phases were simulated as kinetically controlled reactions, whereas precipitation of secondary minerals was simulated as a quasi-equilibrium process.

Results from Bea et al. (2012) suggest that atmospheric CO₂ does not ingress past ~50 cm depth in TSF1 at Mount Keith. Yet, hydromagnesite was detected at reasonably high abundance at depths >50 cm in TSF2 (e.g., up to 4.1 wt.% in deep samples collected from 7.5 year old tailings profiles). As described previously, two distinct processes may be invoked to explain the occurrence of hydromagnesite at depth. First, both vertical and lateral fluxes of fresh process water may provide a source of DIC at depth, promoting further precipitation of hydromagnesite after burial. Second, the hydromagnesite within deep tailings samples may have precipitated at the surface when the tailings were first deposited and has persisted at depth following burial under fresh tailings. The plausibility and relative importance of each of these two mechanisms was examined using MIN3P.

In order to estimate the abundance of hydromagnesite that could be derived from process water alone, no hydromagnesite was initially present at depth for simulation of the process water replenishment hypothesis. An average tailings deposition rate of 50 cm yr⁻¹ was estimated based on 11 Mt yr⁻¹ of tailings deposited evenly over the ~16.6 km² area of TSF2. Field observations of excavated profiles (Fig. 7.3) indicate that tailings flows are ~10 cm thick on average, suggesting that there are five flows per year that are exposed at the surface for an average of ~70 days prior to burial. One-year long simulations of tailings containing no initial hydromagnesite suggest an average of ~1.95 wt.% hydromagnesite could form within 70 days in the upper 10 cm of the tailings. As such, to simulate the hydromagnesite burial hypothesis, an initial hydromagnesite content of 1.95 wt.% was assigned for depths >50 cm to account for historical hydromagnesite formation during tailings deposition, and in the upper 10 cm, hydromagnesite abundance was set to decline linearly from 1.95 wt.% to 0.00 wt.%.

The initial chemistry of the pore water and fresh process water was set to represent the process water chemistry as indicated by Stolberg (2005) and Bea et al. (2012); it was relatively alkaline (pH = 8.85) and highly saline ([Na⁺] = 0.8 M; A5 Table A5.2). Process water DIC was initially constrained to be in equilibrium with atmospheric $p\text{CO}_2$ ($\approx 3.45 \times 10^{-4}$ atm), and was therefore initially out of equilibrium with the tailings minerals. The upper boundary solution (i.e., rainfall) chemistry was equal to meteoric water composition at equilibrium with atmospheric $p\text{CO}_2$ (after Bea et al., 2012; see Appendix 5). All solutions were in equilibrium with atmospheric $p\text{O}_2$ (0.21 atm).

Because the simulations were 1-dimensional, a horizontal flux for process water replenishment could not be applied. Therefore, recharge of process water was represented by a constant influx of water spread equally throughout the model domain with vertical flow only. Flow is dominantly vertical in the unsaturated zone, where it is influenced primarily by gravity and evaporation, thus a horizontal process water flux is only expected within the saturated zone. Horizontal flow would occur only for fresh tailings that have not yet drained, as well as tailings at depth within the saturated zone. Thus, although the application of a constant flux throughout the upper 2 m of the tailings is a physically improbable scenario, it allowed assessment of the maximum possible extent to which introduction of DIC at depth may affect carbon mineralization, for a given rate of process water recharge. The physical parameters used in the simulations are summarized in Appendix 5.

Stolberg (2005) measured the vertical hydraulic conductivity of two TSF2 tailings samples, which provided an average saturated hydraulic conductivity (K_{sat}) of 4.88×10^{-8} m s⁻¹. This K_{sat} value was used for all simulations without process water replenishment (A5 Table A5.3). Stolberg (2005) noted, however, that the horizontal hydraulic conductivity could be 10–100 fold greater than the vertical conductivity. This is due to the manner of tailings deposition, which creates horizontal layers of distinct grain size (Fig. 7.3) that lead to higher conductivity in coarse-grained layers. This magnitude of anisotropy is consistent with that estimated for other base metal tailings (Yanful and St-Arnaud, 1992). Consequently, a hydraulic

conductivity of $4.88 \times 10^{-6} \text{ m s}^{-1}$ was used for the process water replenishment simulation in order to model the maximum lateral process water flux that could be expected in TSF2 (A5 Table A5.3). Assuming any lateral process water flux is primarily driven by the change in elevation (~14–16 m) across the 4600-meter diameter storage facility, the maximum process water flux at this horizontal K_{sat} is $1.7 \times 10^{-8} \text{ m s}^{-1}$, or $3.4 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$ through the model domain (2 m² cross section). This flux was divided equally throughout the model domain for the process water replenishment simulation, with a constant chemical composition equal to the initial process water composition. The potential effects of reactions occurring up-gradient of the model domain on cation and DIC concentration are neglected; therefore, these simulations represent the maximum DIC flux that would be possible. No replenishment of process water was applied to model the hydromagnesite burial hypothesis.

7.7.2 Reactive transport modeling results and discussion

7.7.2.1 Mineral dissolution and hydromagnesite precipitation rates

In all simulations, the majority of hydromagnesite precipitation is predicted to occur within the top 25 cm of the tailings, owing to the evapoconcentration of solutes (e.g., Mg²⁺), dissolution of primary minerals, and the ingress and dissolution of atmospheric CO₂ (Fig. 7.4), as is consistent with field data. Simulated aqueous magnesium concentrations reach up to 1.0 M at the tailings surface after 7.5 years, which is a tenfold increase over the initial concentration. CO₂ dissolution results in a pH decline near the tailings surface and drives brucite dissolution, leading to the development of a brucite-depleted zone in the near-surface tailings. Mass balance calculations indicate that ~87% of magnesium contained in hydromagnesite is sourced from brucite dissolution, with the balance from magnesium initially present in the pore water. This implies that modest carbon mineralization may still derive from the Mg-rich waters alone, even once the supply of brucite is exhausted, but would be limited by the rate of replenishment of Mg-rich water. The model predicts no serpentine dissolution, as supersaturated conditions existed throughout the tailings pile in the simulations. Textures observed in field samples,

however, indicate that a small percentage of the serpentine is carbonated. Passive serpentine carbonation has also been documented in chrysotile and kimberlite-hosted diamond mine tailings that lack brucite (Wilson et al., 2006; Wilson et al., 2009a; Wilson et al., 2009b; Wilson et al., 2011).

A possible explanation for the discrepancy is that there are microenvironments differing in chemistry from the bulk solution that are not captured by the model. For instance, local sulfide oxidation in the near surface could generate acidity, and promote chrysotile dissolution. In addition, there may be complexation effects with organic process water additives that are not adequately accounted for in the model; increased complexation of aqueous magnesium would promote serpentine dissolution. As mentioned previously, the formation of hardpans of efflorescent minerals could also lead to the development of regions with locally elevated $p\text{CO}_2$, by inhibiting gas transport, although this would only occur if CO_2 were generated at depth (e.g., Blowes et al., 1991). Nevertheless, brucite dissolution is sufficient to account for the abundance of hydromagnesite observed (Fig. 7.4), suggesting that brucite is the primary source of magnesium for carbon mineralization. This is consistent with experimental evidence for the carbonation of brucite in chrysotile mining residues, which demonstrates much greater reactivity of brucite compared to that of chrysotile (Pronost et al., 2011; Assima et al., 2013a).

This observation also has important implications for silicon cycling at Mount Keith because it implies that the mass of silica being mobilized and cycled (via serpentine dissolution) is likely to be considerably less than that of magnesium or carbon. Weathering and carbonation reactions may be limited by accumulation of silicic acid in solution, although Schuiling et al. (2011) propose that silica saturation may be minimized by precipitation of secondary mineral phases or uptake by the biosphere. At Mount Keith, the silica produced by weathering of serpentine is likely to take the form of opal-A (amorphous silica) or silicic acid, which may remain in solution or be taken up by aquatic microorganisms. Formation of opal-A has been observed previously in ultramafic weathering systems, such as the Woodsreef Chrysotile Mine in New South Wales, Australia (Oskierski et al., 2013) and uptake of silicic acid by diatoms,

which produce silica frustules, has been documented at the Clinton Creek Chrysotile Mine, Yukon, Canada and in hydromagnesite–magnesite playas in ophiolitic terrane near Atlin, British Columbia, Canada (Power et al., 2007; Power et al., 2009; Power et al., 2011a). We were unable to quantify the amount of amorphous silica at Mount Keith, because it is difficult to detect with XRD, which is best suited to identification and quantification of well-ordered crystalline solids and can only detect amorphous material at considerably higher abundances than those anticipated for silica production at Mount Keith.

The model predicts relatively rapid brucite dissolution in the near surface environment, with brucite completely removed within ~170 days in the upper 2 cm of the tailings. Correspondingly, ~4 wt.% hydromagnesite is predicted to form within this horizon during this time. With an estimated exposure time of ~70 days at the surface, brucite dissolution at this rate would result in incomplete consumption of brucite prior to burial, leaving up to ~45% of the brucite unreacted (i.e., ~1.1 wt.% remaining), which is consistent with field observations (Figs. 7.7 and 7.10).

The brucite dissolution rates were calibrated to mimic those observed for reaction of brucite with CO₂ in air in slurry reactor experiments conducted by Harrison et al. (2013a; Chapter 2), which was achieved by adjusting the effective surface area of brucite in the model. The reactive surface area employed in the model was 0.3 m² g⁻¹, compared to a BET measured value of 9.35 m² g⁻¹ for bulk tailings (Power et al., 2011b). The reactive surface area of brucite in tailings is expected to be lower than this bulk value, as the presence of minerals with typically high surface areas, such as chrysotile, may skew the measurement toward higher values. Moreover, BET measurements commonly overestimate reactive surface area due to variable reactivity of surface features (e.g., Brantley and Mellot, 2000; Gautier et al., 2001; Luttge and Arvidson, 2008). Although this provides net rates consistent with field observations over year-long time spans, it is likely that the instantaneous brucite dissolution and hydromagnesite precipitation rates calculated by the model are overestimated in comparison to actual reaction rates in the field. This is because the exposure and accessibility of brucite surfaces to CO₂

would likely be lower in tailings than in a continuously stirred batch reactor owing to unequal porewater distribution and possible surface passivation effects.

Precipitation of secondary hydromagnesite at the surfaces of brucite grains may decrease their reactivity, as has been documented for oxide and carbonate coatings that form on pyrite in mine tailings and granular iron in permeable reactive barriers, respectively (Nicholson et al., 1990; Jeen et al., 2006). This effect is not explicitly accounted for in the model. In addition, it should be noted that the experimental results of Harrison et al. (2013a; Chapter 2) are for carbonation of brucite to nesquehonite rather than to hydromagnesite, the latter of which is observed at Mount Keith. This change in mineralogy is primarily a function of the difference in temperature between the laboratory (23°C) and the field where air temperatures may exceed 40°C. Under ambient $p\text{CO}_2$, and temperatures exceeding approximately 40°C, hydromagnesite is favored to form over nesquehonite (Hänchen et al., 2008). Nonetheless, experiments demonstrate that although the hydration states of the resulting Mg-carbonate minerals differ as a function of temperature, the mechanism by which brucite is replaced and the stable isotopic signatures of carbonate minerals are comparable (Wilson et al., 2010; Harrison et al., 2013a; Chapter 2). Thus, the results of Harrison et al. (2013a; Chapter 2) provide a reliable baseline for calibrating model results for Mount Keith.

Although the quantitative mineralogical and isotopic data do not provide adequate temporal and spatial resolution to precisely constrain the instantaneous rate of brucite dissolution, the average annual rates are in good agreement with field observations. An average hydromagnesite precipitation rate for the upper 10 cm of tailings of ~4 wt.% yr⁻¹ is estimated for TSF2 based on quantitative mineralogical data and modeling results. This corresponds to a CO₂ sequestration rate of ~39 800 t CO₂ yr⁻¹ in the upper 10 cm of tailings, or ~11% of annual mine emissions.

7.7.2.2 Occurrence of hydromagnesite at depth

Based on agreement with mineralogical data, the modeling results indicate that the presence of hydromagnesite at depth is more likely attributable to burial and reworking of material originally precipitated near the tailings surface as opposed to introduction of fresh DIC in replenished process water (Fig. 7.4).

The modeled influx of replenished process water, containing atmosphere-equilibrated DIC, is able to drive formation of hydromagnesite at depth without invoking the transport of CO₂ directly from the atmosphere. However, the rate of precipitation is insufficient to explain the observed abundance of hydromagnesite at Mount Keith (Fig. 7.4). A two-fold increase in DIC flux provided by process waters would be necessary to produce observed abundances of hydromagnesite. This is only possible by having either (1) a higher DIC content in the process water than has been observed at Mount Keith or (2) a two-fold increase in the flux of water to the tailings in TSF2.

There is no evidence to suggest that the initial influx of process water has an elevated DIC content relative to tailings waters. Moreover, even if the process water flux were doubled, the concentration of DIC initially present in the process water would become progressively depleted along the flow path as a consequence of hydromagnesite precipitation. This suggests that, except in the case of tailings located immediately adjacent to risers, the modeled DIC concentrations in the process water supplied to deep tailings likely substantially overestimated the actual DIC concentrations in TSF2. Tailings that are down-gradient along the flow path would receive little DIC in process waters to drive hydromagnesite precipitation, suggesting the modeled amount of hydromagnesite precipitation in these simulations is overestimated. Field measurements of DIC at depth would provide better constraint as to whether DIC is replenished and available for precipitation of hydromagnesite; but tailings pore waters were generally inaccessible at the time of sampling owing to the depth of the water table below the surface of TSF2.

Therefore, it is more likely that the majority of the hydromagnesite documented at depth

within TSF2 was initially precipitated near the tailings surface, but has become reworked upon burial. On the scale of the entire tailings impoundment, only negligible precipitation of hydromagnesite may occur due to lateral recharge of DIC-rich process water. Process water DIC may only play a role in hydromagnesite production near risers in the interior of TSF2, where tailings flows are thicker and fresh tailings are generally only exposed to the atmosphere for short periods. Recharge of process water DIC is less likely toward the edges of TSF2; however, the thin tailings flows deposited far from the risers provide an ideal environment for hydromagnesite precipitation via ingress of atmospheric CO₂.

Modeling also predicts that tailings waters may become temporarily undersaturated with respect to hydromagnesite following rainfall events, which could lead to dissolution and redistribution of this phase at depth. Thus, a geochemical mechanism exists by which hydromagnesite may become reworked and more homogeneously distributed within tailings due to transient dissolution of hydromagnesite in near-surface tailings.

7.8 Potential for accelerating carbon mineralization

Quantitative mineralogical results, microscopy and all simulations suggest that the majority of atmospheric CO₂ fixation at Mount Keith occurs via carbonation of brucite. As such, the total mass of hydromagnesite precipitated is largely governed by the brucite content of the tailings and the rate of brucite dissolution. Brucite carbonation is primarily driven by the ingress of atmospheric CO₂ into tailings water. Our stable carbon isotopic data indicate that the rate of CO₂ ingress into Mount Keith tailings water is limited by the slow kinetics of diffusion and dissolution of atmospheric CO₂ into saline, moderately high pH waters (i.e., pH < 11). Therefore, increasing the exposure of tailings waters and brucite to CO₂ has the potential to significantly enhance carbon mineralization rates.

Enhanced carbonation of brucite alone could substantially improve the extent of CO₂ emissions offsetting at Mount Keith. Improving the efficiency of brucite carbonation, to ensure

that all the brucite deposited annually within TSF2 were carbonated, would offset the mine's emissions by ~20–60% (Harrison et al., 2013a; Chapter 2). There are several potential options to achieve this.

7.8.1 Tailoring tailings deposition rates to enhance reaction with atmospheric CO₂

Carbonation of Mount Keith tailings via capture of CO₂ from air may be facilitated by altering tailings management practices so that reactive phases such as brucite remain near the tailings surface for a longer period of time. For instance, the duration of deposition from individual risers could be decreased, without changing the overall deposition rate, to extend the duration of exposure of fresh, brucite-rich tailings to the atmosphere prior to burial. This might be accomplished by installing a greater number of risers to distribute thinner, more uniform flows of tailings over the entire surface area of TSF2, which is not currently achieved by the small number of risers concentrated in the interior of the facility. Model calculations suggest that at the average rate of tailings deposition at Mount Keith (i.e., ~50 cm yr⁻¹), approximately 45% of the initial abundance of brucite remains un-carbonated after burial (Fig. 7.10), which is consistent with quantitative mineralogical results. Adoption of a tailings deposition rate of 25 cm yr⁻¹ would allow more than 80% of the brucite to be carbonated prior to burial (Fig. 7.10). Decreasing overall rates of tailings deposition may not be feasible at existing mines, as this would require ore processing rates to be lowered. Deposition of tailings over a larger area could achieve the same effect, and thus the footprint of tailings storage facilities could be an important design consideration in the development of prospective mines with ultramafic tailings.

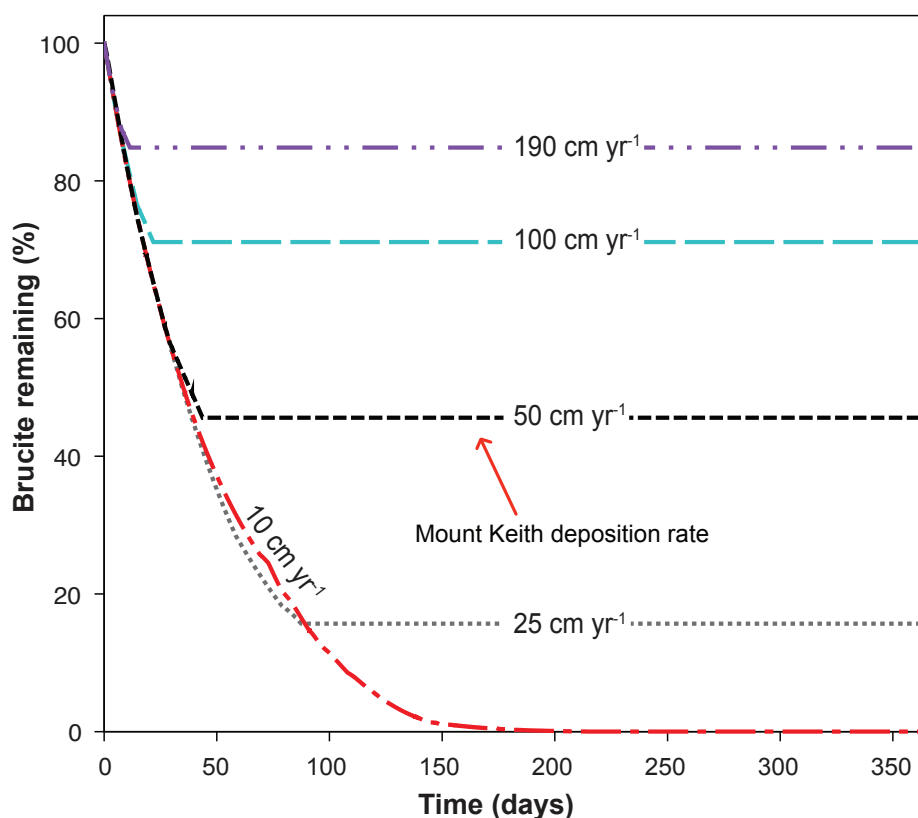


Figure 7.10. Amount of brucite remaining in a 2 cm thick band of tailings versus time at different rates of tailings deposition (brucite burial rate) as estimated using model output.

7.8.2 Direct injection and circulation of CO₂-rich gas streams and DIC-charged waters

Another option for augmenting carbon fixation rates is to circulate air, or CO₂-rich solutions or gases through tailings storage facilities. For example, Harrison et al. (2013a; Chapter 2) reported a ~240-fold increase in brucite carbonation rates in slurry reactors when the concentration of CO₂ was increased from atmospheric levels (~0.04% CO₂) to 10%. The CO₂ concentration used in these experiments is comparable to that of power plant flue gas (~10–20% CO₂; Kikkinides et al., 1993; Uibu et al., 2011). Power generation for mining operations often occurs at mine site power plants, as is the case for Mount Keith. Thus, flue gases from these power plants could be circulated through tailings to directly offset mine

emissions, as has been suggested for carbonation of other alkaline waste types such as cement kiln dust (Arickx et al., 2006). Although reaction rates would be lower, circulation of air rather than flue gas has the advantage that CO₂ leakage would not be a concern. Circulation of air is not an ideal solution because, due to the low CO₂ content in air, the carbonation rate would likely be limited by the rate of gas flow (i.e., CO₂ flux) that could be achieved. Thus, it could be advantageous to cap non-operational tailings storage facilities, such as TSF1, at active mines so that high concentrations of CO₂ could be used to ensure rapid carbonation of brucite while preventing leakage of CO₂ to the atmosphere.

Alternatively, water with elevated DIC concentrations, or at the least, water equilibrated with atmospheric CO₂ could be circulated through tailings. The effectiveness of injecting tailings with DIC-charged water, air or flue gas is more likely to be limited by the flux of CO₂ that can be achieved in low permeability tailings (i.e., flow rate of water or gas; Fig. 7.11) than by the rate of brucite carbonation, which is rapid at elevated $p\text{CO}_2$. Assuming that the rate of CO₂ supply is the limiting factor, and that flow is governed by Darcy's law and driven by the natural elevation gradient at Mount Keith, it is estimated that the maximum CO₂ flux in the aqueous phase would be insufficient to carbonate all the brucite in TSF2 (Fig. 7.11, see Appendix 5 for details on the calculations). Because even minor pressure gradients (e.g., $<1 \text{ Pa m}^{-1}$) can strongly influence rates of gas advection (Thorstenson and Pollock, 1989) the assumption of elevation gradient driven flow was not applied for gas flow, but permeability constraints are expected to be less significant for the gas phase. In addition, in arid conditions, low water content allows high effective permeability for gas flow. These results imply that the use of CO₂-rich gas streams may therefore prove more effective than circulation of DIC-charged waters. In either case, however, the development of preferential flow paths and clogging of injection points will influence the efficiency of CO₂ delivery to all reactive phases.

Tailings permeability and clogging issues could be avoided by carbonating brucite within reactors in the ore processing plants at mine sites prior to deposition. For instance, flue gas from power generation could be supplied to reactors at ambient temperature and pressure.

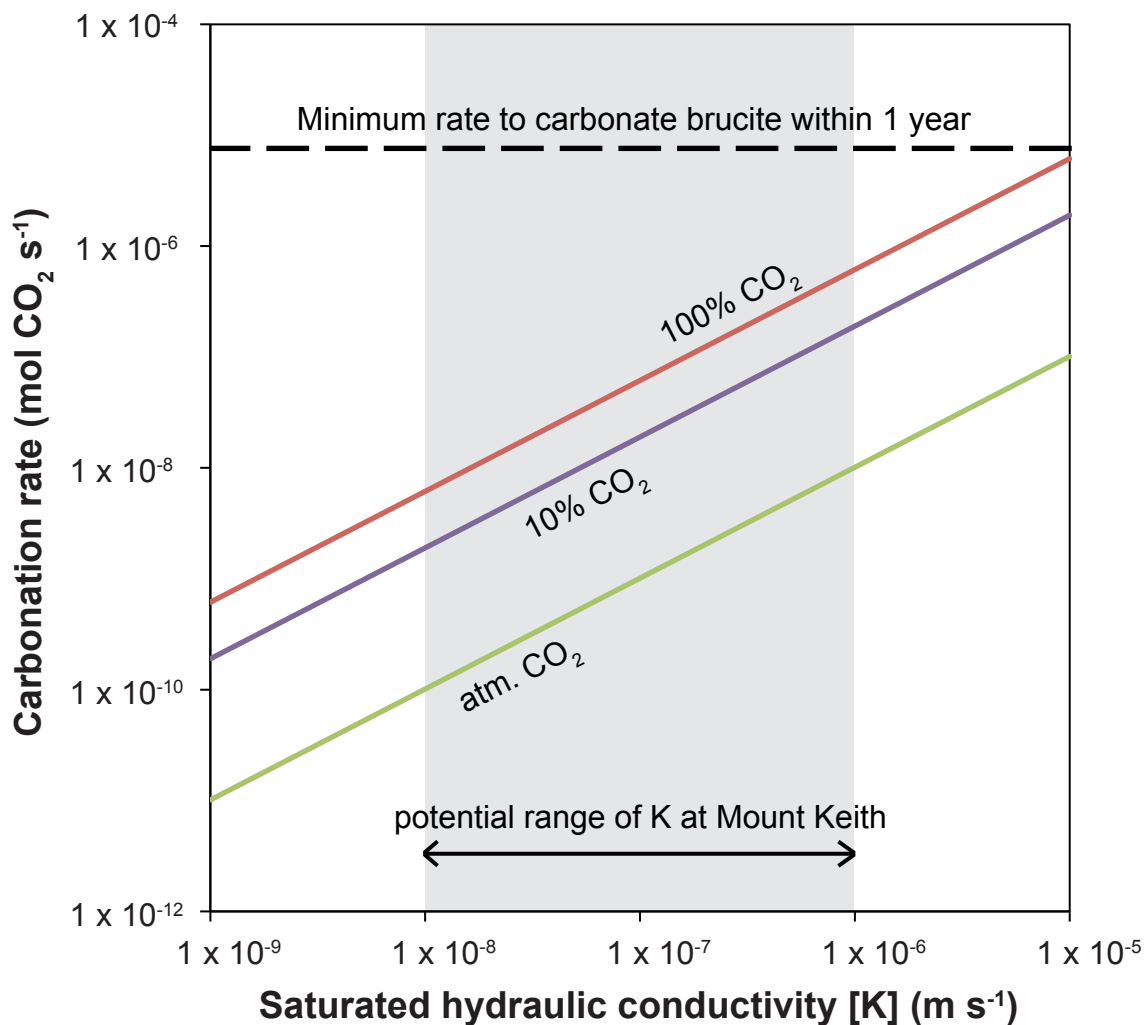


Figure 7.11. Brucite carbonation rate versus saturated hydraulic conductivity. Solid lines represent potential carbonation rates achieved with water equilibrated with atmospheric CO₂ (~0.04% CO₂), 10% CO₂, and 100% CO₂ gas at 1 atm pressure and 25°C. All calculations are for a 50 cm thick tailings deposit representative of 1 year's worth of tailings deposition at the Mount Keith mine. The horizontal dashed line indicates the minimum carbonation rate that would be necessary to carbonate all the brucite (i.e., 2.5 wt.%) in 50 cm of tailings within 1 year. Refer to Appendix 5 for details regarding the calculations.

Given the observed abundance of brucite in ore and tailings, the mill at Mount Keith processes brucite at an average rate of 3.14×10^7 g brucite h⁻¹. Assuming a brucite carbonation rate of 7.78×10^{-3} g CO₂ g brucite⁻¹ h⁻¹ with a 10% CO₂ gas stream (Harrison et al., 2013a; Chapter 2; for carbonation of a brucite slurry), the brucite in Mount Keith tailings could be carbonated at a rate commensurate to the rate at which it is processed at the mill. The disadvantage of this method is that the short reaction time required to carbonate the brucite would be insufficient to carbonate the less reactive phases such as serpentine minerals. In light of this, it may be preferable to continuously expose tailings to CO₂ through circulation of air or CO₂-rich water or gases, as the continued exposure to CO₂ and associated decline in pH could help drive carbonation of less reactive phases to exceed the present rate. Although the rate of serpentine dissolution is promoted at low pH (e.g., Thom et al., 2013), the extent to which CO₂ circulation would enhance Mg-silicate carbonation requires further investigation.

7.9 Tailings management practices for carbon neutral mining

The amount of tailings produced at Mount Keith in one year has the capacity to bind approximately 4 Mt of CO₂ (after Lackner et al., 1995 and estimates from Harrison et al., 2013a; Chapter 2). This exceeds the annual emissions of the mine by more than a factor of ten and represents more than a 100-fold increase of sequestration capacity over the current, passive rate of carbon mineralization (39 800 t yr⁻¹ or approximately 11% of emissions). Importantly, the annual CO₂ sequestration capacity at Mount Keith is comparable to what is currently achieved at the largest demonstration projects for geologic CO₂ sequestration (approximately 1–2.8 Mt CO₂ yr⁻¹; Michael et al., 2009; Whittaker et al., 2011; Harrison et al., 2013a; Chapter 2). Accelerating the rate of mineral carbonation within Mount Keith tailings to make use of 11% of its total capacity to capture and store atmospheric CO₂ would completely offset the greenhouse gas emissions produced by this mine. Further acceleration would provide a greenhouse gas benefit to the mine operator, which, if rigorously quantified, could be used

to offset the cost of carbon credits in a cap-and-trade environment (Hitch and Dipple, 2012).

In the current regulatory climate in Australia, major emitters of greenhouse gases and producers of fossil fuels are liable to pay a carbon tax (i.e., \$25.40 AUD per tonne of CO₂ in 2014–2015). Several major mining companies are currently subject to this tax under the carbon pricing mechanism. Although the Australian Government aims to abolish its current carbon tax from 1 July 2014, the possibilities still remain that (1) the carbon tax may be retained or (2) Australia will move to a market based price for carbon pollution by linking with the European Union Emissions Trading Scheme (EU ETS) in 2015. Enhancing the rate of carbon mineralization at Mount Keith to completely carbonate the brucite within tailings would offset between 20 and 60% of the mine's emissions (i.e., 20–60% of 370 kt yr⁻¹ CO₂ equivalent emissions; Harrison et al., 2013a; Chapter 2). This offsetting represents a non-trivial financial benefit of \$1.9M to \$5.6M (AUD) per year, which translates to a lifetime value of \$56M to \$170M for a mine, such as Mount Keith, that has a 30-year operational lifetime. Furthermore, complete carbonation of brucite (i.e., ~60% offsetting of emissions at Mount Keith) would occur at a rate of 25 t CO₂ h⁻¹, which is approaching the scale at which CO₂ emissions are generated by coal burning energy generation facilities (i.e., ~100–1000 t CO₂ h⁻¹; Power et al., 2013c). Thus, carbon mineralization in mine tailings may be scaled up to a rate commensurate with that attainable by industrial reactors. Our results suggest that this is achievable at Earth surface temperatures, relatively low *p*CO₂ and using standard ore processing procedures.

One of the most significant findings of our study is that most of the 4 Mt CO₂ yr⁻¹ capacity of Mount Keith tailings to store CO₂ is not being accessed due to the slow dissolution kinetics of serpentine minerals. Thus, thermal, chemical or mechanical activation strategies (recently reviewed by Power et al., 2013b) may be required during ore processing in order to enhance reactivity of serpentine minerals in tailings storage facilities. As discussed previously, circulation of CO₂ rich water or gases during ore processing or post-deposition of tailings could also play a role in accelerating dissolution of serpentine minerals.

Our results indicate that greater emissions offsets may be attained through a combination

of changing tailings management practices and redesign of tailings impoundments and ore processing circuits. Three strategies exist for promoting complete carbonation of brucite at Mount Keith and mines with mineralogically similar tailings: (1) tailoring deposition rates to create thinner tailings flows that may react with atmospheric CO₂ on a longer timescale; (2) injecting and circulating CO₂-rich fluids within the TSF to promote carbonation reactions at depth; (3) redirecting the flue gas stream produced by energy generation into carbonation reactors at the end stage of ore processing. The cost associated with optimizing carbonation of brucite through each of these process routes, respectively, will be associated with (1) increasing the footprint of the TSF and construction of additional risers; (2) constructing a network of pipes to permit injection and recirculation of CO₂-rich fluids within tailings as well as engineering controls to limit CO₂ leakage; (3) redesign of the ore processing circuit to include an *ex situ* carbonation reactor. Costing of these process options will be needed to determine which are feasible for implementation given the price of carbon.

Reinvention of tailings storage facilities as geoen지니어ed landscapes and bioreactors may have further potential to enable ultramafic-hosted mines to leverage their full capacity to bind CO₂ within carbonate minerals (Power et al., 2009; Power et al., 2010; Power et al., 2011b). For instance, Power et al. (2011b) estimate that up to 16.7% of annual greenhouse gas emissions at Mount Keith could be offset by implementing coupled acid leaching and microbially mediated carbonate precipitation; this represents an increase over the current rate of emissions offsetting, which is approximately 11%. The tailings at Mount Keith alone provide the mine with the capacity not only to offset its own emissions but those of nine other comparably sized mining operations. Mount Keith is situated in a remote location in Western Australia, approximately 700 km from the nearest regional center at Kalgoorlie. Thus, in the absence of other nearby sources for CO₂, the efficiency of CO₂ capture from air and from flue gas produced by onsite power generation will likely define the maximum amount of CO₂ that can be sequestered at this site. However, ultramafic-hosted mines located closer to regional centers or cities may be able to capitalize on the availability of other CO₂ sources to make full

use of their tailings' capacity to sequester CO₂.

Globally, there is potential to sequester on the order of 400 Mt of CO₂ yr⁻¹ in the mineral waste from mines (Power et al., 2013b). This represents an offsetting of approximately 1.5% of global annual greenhouse gas emissions (Power et al., 2013b) or 16% of one carbon stabilization wedge (after Pacala and Socolow, 2004). Thus, by changing its tailings management practices to promote carbon mineralization, the international minerals industry has the capacity not only to achieve substantial offsetting of its own greenhouse gas emissions, but also to provide a tangible reduction to global CO₂ emissions.

8. Conclusion

8.1 Summary of research outcomes

The primary goals of this thesis were to 1) elucidate the controlling reaction mechanisms during carbon mineralization to help design CO₂ sequestration strategies in near surface environments, namely ultramafic mine tailings, and 2) to contribute to the fundamental understanding of coupled mineral dissolution-precipitation reactions in unsaturated porous media. The main outcomes of this work were: 1) brucite [Mg(OH)₂] carbonation in ultramafic mine tailings could be significantly accelerated by increasing the supply of CO₂ into tailings, thereby providing non-trivial offsets of greenhouse gas emissions from the mining industry, 2) hydrated Mg-carbonates may passivate reactive surfaces depending on the type and morphology of the precipitate formed, 3) water saturation and the dynamics of wetting and drying associated with evaporation and reaction of hydrous minerals has a profound impact on both reaction rates and total reactive capacity of porous media, and 4) a reactive transport model that captures several important, yet previously unrecognized controls on carbonation reactions in unsaturated media was developed and tested. This model provides an important step to permit better prediction of reaction under water-limited conditions, particularly for reactions involving hydrous minerals, and will help guide the design of CO₂ sequestration technologies that employ carbon mineralization.

Batch reactor experiments (Chapter 2) revealed that the rate of carbonation of brucite in water unlimited conditions was governed primarily by the rate of uptake of CO₂ into solution, as typified by anomalously depleted $\delta^{13}\text{C}$ values for dissolved inorganic carbon (DIC) and associated ^{13}C depletion in carbonates precipitated in equilibrium with this DIC (Chapter 2). This is consistent with ^{13}C compositions documented for carbonates formed in the tailings storage facility at the Mount Keith Nickel Mine, wherein carbonation was limited by the relatively slow diffusive ingress of atmospheric CO₂ into tailings pore water (Chapter 7). CO₂

sequestration rates were accelerated linearly with increasing CO₂ concentration in gas streams supplied to brucite slurries (up to ~2400-fold acceleration), but CO₂ uptake into solution remained rate-limiting under these experimental conditions (Chapter 2). CO₂ sequestration technologies that facilitate CO₂ uptake into solution prior to its interaction with the solid phase may help to overcome this limitation. For example, at the CarbFix project in Iceland, gaseous CO₂ is dissolved in water within an injection well prior to its release into a subsurface basalt aquifer (Gislason et al, 2010). In mineral dominated porous media containing fine-grained brucite with high surface area, the overall reaction rate was also CO₂ supply limited (Chapter 5). CO₂ was sequestered as fast as it was supplied to columns, preventing CO₂ leakage. However, the rate-limiting step was demonstrated to transition from CO₂ supply limited to mineral dissolution limited as the brucite grain size was increased. Brucite dissolution was not only decreased due to the lower surface area, but the decreased availability of water and precipitation of carbonates in the restricted pore volume surrounding brucite grains were found to limit reaction in the mineral-dominated columns, as compared to the fluid-dominated batch reactors.

Microfluidic pore scale experiments revealed that the dynamic evolution of the gas-water interface, water content, and mineral surface area to water ratio may significantly alter reaction rates as the volume of water filled pore space changes (Chapter 4). Observed mobility and migration of brucite particles implies that reactivity may be enhanced during evaporation, counter to an inhibitory effect due to water loss. As is consistent with observations at the pore scale, the local water saturation was demonstrated to be a strong control on reaction progress in porous media at larger scale (Chapters 5 and 6). Despite heterogeneous water content in the unsaturated zone of column experiments, sufficient water films were present on the majority of grains such that the effective surface area was not substantially reduced. Yet, at low water saturation, the removal of water via hydrated Mg-carbonate precipitation was self-limiting, effectively reducing the reactive capacity of the material. Although higher water saturation permits extensive carbonate precipitation due to the larger volume of water-filled pores in

which to precipitate, and the greater supply of water to facilitate carbonation, viscous fingering during infiltration of gas into water-filled pores promotes the development of preferential flow paths. These flow paths maintain permeability with respect to the gas phase, despite a nearly three-fold increase in the volume of solids during carbonation. As a consequence, the overall reactive capacity is also decreased at high water saturation, as a large proportion of the porous media is bypassed by the gas phase. These processes have implications for dissolution-precipitation reactions of hydrous minerals in unsaturated porous media, including Mg-carbonates, sulfates, zeolites, and clay minerals. For example, Wilson and Bish (2012), and Bish et al. (2003) demonstrate that smectites and Mg-sulfates can have a considerable impact on water budget in unsaturated media, such as on Mars. Moreover, these experiments confirm that the water budget will be an important consideration for CO₂ sequestration technologies that aim to carbonate hydroxide and silicate minerals. The development of an empirical model for water-limited reaction and inclusion of water as a reactant in MIN3P is an important step towards better prediction of reaction rates under water-limited conditions (Chapter 6). Moreover, this model revealed that simply reducing the reactive surface area to account for heterogeneous exposure to water might not allow reactive transport models to adequately capture reaction progress in unsaturated conditions.

Reactive transport modeling is also complicated by changes in mineral surface features during dissolution, and precipitation of secondary phases that may passivate reactive surfaces. Although numerous studies have endeavored to determine the impact of secondary phase precipitation on mineral dissolution rates, the results are highly variable (c.f., Hodson, 2003; Park and Fan, 2004; Cubillas et al., 2005; Béarat et al., 2006; Lekakh et al., 2008; Andreani et al., 2009; Huntzinger et al., 2009; Daval et al., 2009a; Daval et al., 2009b; Daval et al., 2011; Stockmann et al., 2011; Stockmann et al., 2013). Here, it is demonstrated that Mg-carbonate precipitates have the potential to passivate mineral surfaces, but the passivating effects are strongly dependent on which Mg-carbonate phase forms (Chapters 5 and 6). Precipitation of a flakey, artinite-like carbonate ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot \sim 2\text{H}_2\text{O}$) did not significantly inhibit reaction, but

the transformation from this to highly crystalline, low porosity nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] was associated with a precipitous shutdown in the carbonation reaction. These results have implications for reactions involving other minerals that undergo phase transformations or dehydration/hydration at ambient conditions, such as Mg-sulfates (e.g., Wilson and Bish, 2012). Yet, before the carbonate coatings become sufficiently impermeable such that they passivate reactive surfaces, the roughening and fracturing of brucite surfaces during the early stages of carbonation appeared to maintain reactive surface area at a relatively constant value despite significant consumption of reactive material (Chapter 6).

8.2 Accelerating carbon mineralization in mine tailings

The experimental and modeling work conducted for this thesis provide important insight into the efficacy of carbon mineralization reactions to sequester CO_2 , particularly within ultramafic mine tailings, with implications for carbonation of other industrial wastes and natural rock of similar mineralogical composition. A summary of several of the processes impacting reaction progress during carbonation is illustrated in Figure 8.1. Fieldwork and reactive transport modeling confirmed that the rate of passive carbonation in mine tailings is primarily limited by a lack of exposure to CO_2 (Chapter 7). The most straightforward method to accelerate passive carbonation is therefore to increase the supply of CO_2 , either by altering tailings deposition practices to increase their exposure to atmospheric CO_2 prior to burial under fresh tailings (Chapter 7), or by supplying CO_2 -rich fluids or gases directly into tailings. If reaction rates in the field were limited by the supply of CO_2 , carbonation of highly reactive phases like brucite could occur at a rate commensurate to rates of flue gas CO_2 emissions at some mines (Chapter 3). In this case, the overall sequestration rate would be limited primarily by the abundance of highly reactive phases in tailings, rather than their rate of reaction (Chapter 3). This is consistent with recent observations of Assima et al. (2014a) that demonstrate that the sequestration capacity of various ultramafic mining residues is largely dependent on the

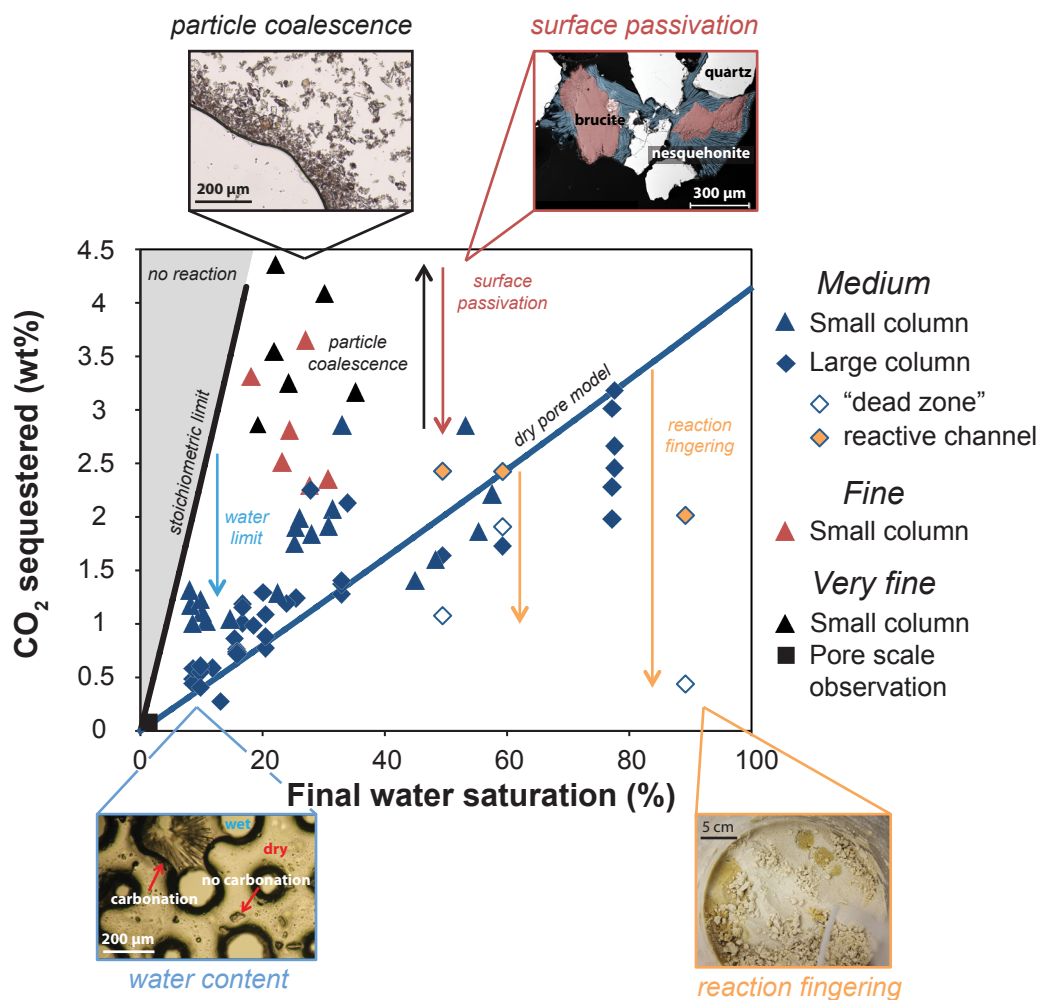


Figure 8.1. Conceptual diagram of some of the processes governing the extent of brucite carbonation.

abundance of brucite. However, the experimental studies conducted for this thesis revealed the importance of considering the water budget to better quantify the CO₂ sequestration capacity of tailings materials. At low water content, reaction is severely limited by a lack of available water to facilitate dissolution and form hydrated Mg-carbonate phases. This effect is also relevant for injection of CO₂ in the subsurface, which displaces water around injection wells (e.g., Loring et al., 2011). Yet, the polydisperse grain size of tailings may encourage the particle movement observed in pore scale experiments, thereby enhancing reactivity by keeping reactive phases exposed to water despite its displacement (Chapter 4). Conversely, at high water saturation, the development of viscous fingers, or heterogeneity-induced fingers, may limit the extent of

reaction by reducing exposure of reactive phases to CO₂. This is likely a significant issue at the field scale in highly heterogeneous tailings. To minimize the development of viscous fingers, the ideal water content is between ~20% and 60% saturation (Chapters 5 and 6), and injection of CO₂-rich gases beneath the water table should be avoided. This saturation range would also lower the injection pressures necessary to maintain higher CO₂ fluxes through tailings, because the relative permeability with respect to the gas phase is increased at low water saturation.

Although surface passivation may also limit reaction, the grain size of mine tailings is similar to that of the very fine and fine brucite used in the column experiments (e.g., Power et al., 2011b), for which passivation effects were negligible (Chapter 5). This implies that accelerated carbonation of brucite in tailings is likely to be controlled by the availability of CO₂. However, the transition from CO₂ supply limited to mineral dissolution limited conditions due to a decrease in brucite surface area is conceptually similar to carbonation of Mg-silicate minerals in tailings (Chapter 5). These minerals have much slower dissolution rates than brucite under similar conditions (c.f., Pokrovsky and Schott, 2000; Pokrovsky and Schott, 2004; Assima et al., 2013a; Thom et al., 2013; Assima et al., 2014a), but comprise the majority of ultramafic mine tailings (e.g., Wilson et al., 2011; Bea et al., 2012; Wilson et al. 2014; Chapter 7). Thus, in order to capture the full reactive capacity of tailings, acceleration strategies that directly target enhanced silicate dissolution may be necessary, in addition to increasing the CO₂ supply (e.g., Power et al., 2010; Power et al., 2014a).

8.3 Suggestions for future research

This thesis tested the efficacy of accelerating CO₂ sequestration rates in mine tailings by supplying CO₂-rich gases into tailings, and delineated several limitations on reaction progress. The range of experimental apparatus used in this thesis highlighted the importance of scale on reaction rate and quantification of reactive capacity. The microfluidics experiments, for example, revealed that overlooking pore scale phenomena could result in order of magnitude

differences in the prediction of reaction rates, and viscous fingering became more problematic in the larger scale columns. Consequently, the next step in the development of accelerated carbonation strategies in mine tailings should be the deployment of field to pilot scale studies (e.g., Power et al., 2014a).

While the threshold model developed to capture surface passivation effects and water-limited reaction produced excellent agreement between modeled and experimental results, a mechanistic model remains elusive. Detailed studies of the reaction mechanisms at the mineral-water interface would provide valuable insight into the mechanisms behind the observed reaction behavior. Moreover, conventional geometric models alone do not adequately reproduce reaction progress during brucite carbonation. The development of a mechanistic model to capture these effects would improve the ability to predict the fate of CO₂ injected in the subsurface or alkaline waste (e.g., mine tailings) storage facilities. This also has implications for modeling of reaction progress during coupled dissolution-precipitation reactions in the shallow subsurface in general, as the reactive surface area may not evolve in a straightforward manner. Finally, although the microfluidic experiments revealed previously unrecognized processes with potential order of magnitude impacts on reaction rates in the Earth's shallow subsurface, a pore scale model capturing these effects was not developed. Further study into the impacts of particle transport and water limited reaction for various minerals and the development of a pore scale model would significantly improve prediction of reaction rate and distribution in the subsurface, with relevance to many issues of environmental importance (e.g., toxic metal release and transport).

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Appendices

Appendix 1: Appendix to Chapter 2⁸

Accelerated carbonation of brucite in mine tailings for carbon sequestration

A1.1 Detailed methods

A1.1.1 Brucite carbonation procedure

To investigate the effect of elevated $p\text{CO}_2$ on brucite carbonation rate, batch systems consisting of brucite slurries in 3.0 L of deionized water were prepared in 4.0 L side arm flasks (Fig. A1.1). The solution composition mimicked that of pore water at the Mount Keith Nickel Mine (MKM), Western Australia (Stolberg, 2005). One day prior to the start of each experiment, 175.3 g NaCl, and 61.0 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added to solution (1 M NaCl, 0.1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Chemical reagents were supplied by Fisher Scientific® and were of 99.9% purity. Pulverized brucite ore (150.0 g) from Brucite Mine, Gabbs District, Nye County, Nevada was added to each saline solution just prior to supplying CO_2 gas. Rietveld refinement of X-ray diffraction (XRD) data indicated the brucite ore was between 89-95% pure, with the remainder consisting primarily of dolomite with trace lizardite. Initial grain size and surface area of pulverized brucite ore were 2-40 μm diameter, and 6.6 $\text{m}^2 \text{g}^{-1}$, respectively. Slurries were stirred continuously at ~300 rpm using Fisher Scientific® magnetic stir plates. Each flask was sealed with a rubber stopper, with a re-sealable glass sampling port and a glass sparge tube (~8 mm outer diameter) inserted through the stopper (Fig. A1.1). Sparge tubes with coarse porosity (40-60 μm) from Canadian Scientific Glass® were employed to bubble mixtures of CO_2 and N_2 gas into the slurries. Gases were blended using a Series 150 two tube

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gas blender from Matheson® with high accuracy metering valves and Model E401 tubes, with an accuracy of $\pm 5\%$ of the full 150 mm scale. Gaseous CO₂ and N₂ were drawn from liquid CO₂ and N₂ tanks with single stage 316L stainless steel diaphragm liquid cylinder regulators from Matheson® using a delivery pressure of 10 PSIG. CO₂ concentration in the supplied gas stream was varied between experiments for values of 10%, 50%, and 100% CO₂ at a total flow rate of 540 mL min⁻¹, which was divided evenly between duplicate experiments that were run simultaneously. Duplicate experiments are henceforth referred to as ‘X% CO₂ 1 and 2.’ Three experiments were run using laboratory air ($p\text{CO}_2 \approx 0.04\%$) supplied at ~ 270 mL min⁻¹ using a Cole-Parmer Masterflex® L/S precision® standard pump system fitted with a L/S Easy-Load II® pump head operated at 100 rpm, to act as experimental controls and establish background carbonation rates.

Flasks were vented through the side arm to maintain atmospheric pressure. The exhaust stream from high $p\text{CO}_2$ experiments was directed into a Los Gatos Research (LGR)® off-axis integrated cavity output laser spectrometer for continuous measurement of CO₂ concentration (Barker et al., 2011). All gas composition data represent the combination of exhaust from duplicate, simultaneous high $p\text{CO}_2$ reactors. Particulates and water vapor were removed from the gas stream before entering the instrument, using a Swagelok® filter and a Perma Pure Nafion® gas dryer with a Drierite® laboratory air and gas drying unit, respectively.

Slurry temperature and pH were measured routinely using a thermometer with $\pm 0.5^\circ\text{C}$ precision and a portable Thermo Scientific® Orion 4-Star pH/ISE probe, respectively. The pH probe was calibrated daily using three standard buffer solutions at pH 4, 7, and 10. The reactors were not insulated, allowing heat exchange with the surroundings. Water samples for dissolved inorganic carbon (DIC) and Mg concentrations ($[\text{Mg}]$), and $\delta^{13}\text{C}_{\text{DIC}}$ were collected routinely. Water samples were filtered into 2 mL borosilicate glass vials using 0.22 μm Millipore Millex® GP sterile syringe filters. Vials were wrapped with Parafilm M® to prevent evaporative loss and stored in a refrigerator at $\sim 4^\circ\text{C}$ to inhibit precipitation of solids. Samples for cation analysis were preserved with 2% HNO₃. Solid samples were taken at the same time for mineralogical

analysis using XRD, $\delta^{13}\text{C}$ and carbon abundance (%C) analysis, and imaging using scanning electron microscopy (SEM). Solids were separated from water samples by centrifugation using a VWR® Clinical 100 centrifuge run for 2 minutes at 6500 rpm, or by filtering with Whatman® 1 filter paper. System mass before and after sampling and the mass of each sample were measured.

The experimental durations were 198, 56, and 72 h for the 10%, 50%, and 100% CO_2 experiments, respectively. Two short-term experiments using atmospheric CO_2 were run for 56 and 72 h to serve as experimental controls (i.e., systems with negligible carbonation). A single atmospheric CO_2 experiment was conducted for 2856 h to establish background carbonation rates. Experimental duration of the high $p\text{CO}_2$ experiments was determined based on the time of achievement of steady-state conditions, i.e., when pH stabilized, system mass ceased increasing, the temperature difference between the control and high $p\text{CO}_2$ systems was minimal, and, when applicable, CO_2 concentration of the exhaust equaled that of the incoming gas supply.

At the end of each experiment, the entire contents of each reactor were filtered through Whatman® 1 qualitative filter paper. Solids and flasks were then dried for a minimum of 7 days in a fume hood at room temperature. Dry flasks were weighed to provide an estimate of the mass of solid residue remaining in the flask. Dried solid samples were weighed to determine the total solid mass.

A1.1.2 Analyses

A1.1.2.1 Particle size distribution analysis and surface area analysis

The initial surface area of pulverized brucite ore used in experiments was determined by multipoint BET with N_2 adsorption using a Quantachrome® Autosorb-1 surface area analyzer. Particle size distribution analysis was performed using a Malvern® Mastersizer 2000 Laser Diffraction Particle Size Analyzer.

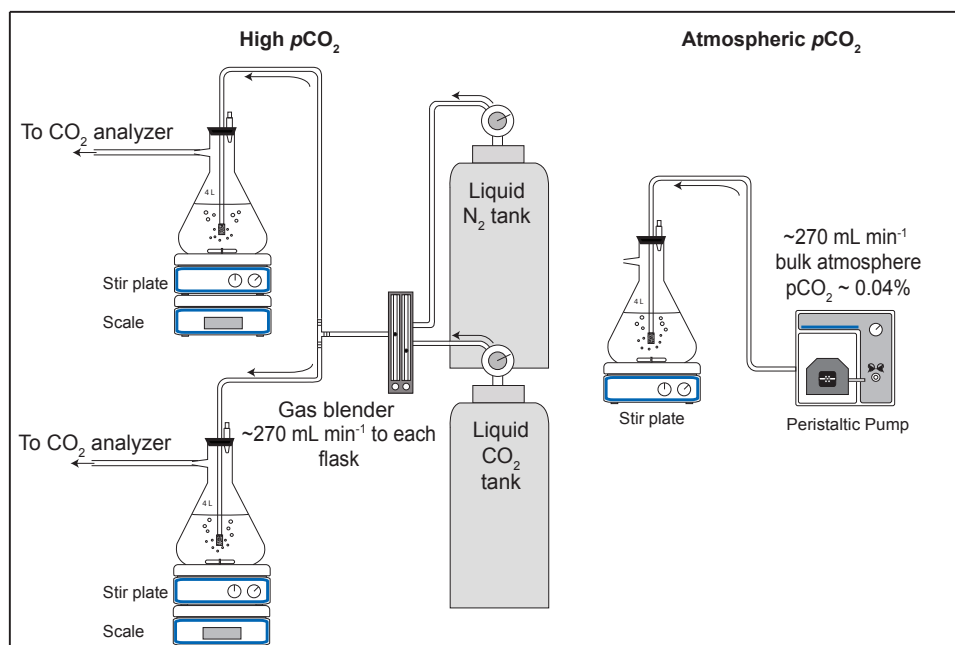


Figure A1.1. Schematic of brucite carbonation setup.

A1.1.2.2 *X-ray powder diffraction methods*

Synthetic and natural mineral phases in all solid samples were identified using X-ray powder diffraction methods (XRPD). Aliquots of precipitates were ground under ethanol using a corundum mortar and pestle. The resulting slurry was mounted on a glass plate and allowed to dry at room temperature. Quantitative phase analysis using Rietveld refinement was performed on aliquots of the initial natural brucite ore. Aliquots were ground under ethanol for three minutes using a McCrone[®] micronizing mill and agate grinding elements. Micronized aliquots were dried for ~24 h and gently disaggregated with an agate mortar and pestle. Powder mounts were prepared against ground glass to minimize preferred orientation (Raudsepp and Pani, 2003).

All XRPD data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with $\text{CoK}\alpha$ radiation and a step size of 0.04° over a range of $3\text{--}80^\circ 2\theta$ at 0.2s/step . Fe monochromator foil, 0.6 mm divergence slit, incident and diffracted beam soller slits, and a Lynx Eye detector were used. A long fine focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6° . A rotation speed of 50 rpm was utilized for collection of qualitative

data. Search-match software by Bruker (DIFFRACplus EVA 14; Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement for quantitative phase analysis was completed using Topas Version 3 (Bruker AXS, 2004) refinement software. Sources of crystal structure data used in refinements are provided in Table A1.1.

Table A1.1. Sources of crystal structure data for Rietveld refinement.

Mineral	Source
Brucite	Catti et al. (1995)
Halite	Nickels et al. (1949)
Dolomite	Ross and Reeder (1992)
Lizardite	Mellini and Viti (1994)

A1.1.2.3 Aqueous chemistry

Total aqueous Mg concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 725-ES Optical Emission Spectrometer, with a detection limit of 0.2 mg L⁻¹. Reproducibility was better than 12 mg L⁻¹ based on repeated analysis of standards. DIC concentration was determined using a Lachat IL550 TOC-TN analyzer. Aliquots (100 µL) of sample are added to a 10% H₃PO₄ solution to release CO_{2(g)}, which was measured with an infrared detector. The detection limit on this instrument is 0.5 mg L⁻¹. Both DIC and [Mg] samples were diluted to fall within the calibrated concentration range of the instruments; standards were matrix-matched for ICP-OES analysis.

A1.1.2.4 Carbon abundance analysis

The inorganic carbon abundance (%C) in all solid samples was determined using a CM5130 acidification module with a Model 5014 CO₂ Coulometer from UIC Inc. Pulverized solid samples were acidified to release CO_{2(g)}, which is quantified using a photodetector to monitor the color change of a colorimetric pH indicator. Repeated analysis of calcium carbonate standards and replicate samples indicated measurements were accurate within ± 0.05% by mass. This method has a detection limit of 0.10% C.

A1.1.2.5 Stable isotope analyses

The stable carbon isotopic composition of the initial CO_{2(g)} gases were analyzed using an LGR® off-axis integrated cavity output laser spectrometer as per the method of Barker et al. (2011). The $\delta^{13}\text{C}$ of solids and $\delta^{13}\text{C}_{\text{DIC}}$ were determined at the Department of Earth and Planetary Sciences, the University of New Mexico. $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}$ of solids samples were analyzed using continuous flow isotope ratio mass spectrometry with a gas bench attached to a Thermo Finnigan DeltaPlus and a Finnigan Mat Delta Plus isotope ratio mass spectrometer, respectively (Spotl and Vennemann, 2003; Torres et al., 2005). All $\delta^{13}\text{C}$ results are reported relative to Vienna Pee Dee Belemnite (VPDB) in units of per mil (‰), with $\delta^{13}\text{C}$ defined as follows (Eq. A1.1; Craig, 1957):

$$\delta(\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (\text{Eq. A1.1})$$

Where R_{sample} and R_{standard} are equal to the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample and a standard, respectively (Craig, 1957).

A1.1.2.6 Scanning electron microscopy

SEM was performed at The University of Western Ontario. Images were collected using a LEO (Zeiss) 1540 XB field emission - scanning electron microscope (FE-SEM), equipped with a secondary electron detector at an operating voltage of 1.0 kV.

A1.2 Detailed results

A1.2.1 Analytical results

The Mg concentration in the atmospheric experiment, exhaust gas composition, temperature, and carbon abundance in all experiments are shown in Figures A1.2-A1.5 below. Representative XRD patterns and SEM images from all experiments are shown in Figures A1.6-A1.8. A comparison between brucite dissolution rates versus pH and HCO₃⁻ concentration

in this study and previously published data is shown in Figure A1.9, and the nesquehonite saturation index with time in high $p\text{CO}_2$ experiments is shown in Figure A1.10. Raw stable isotope data are detailed in Table A1.2.

A1.2.2 Gas composition

CO_2 concentration in the exhaust gas from duplicate reactors in the 10% CO_2 and 50% CO_2 experiments was reduced by up to 45% and 44%, respectively at the onset of each experiment, implying carbonation began immediately (Fig. A1.3). No change in gas composition was measurable in the 100% CO_2 experiment as the entire volume of gas consisted of CO_2 . In both the 10% and 50% CO_2 experiments, CO_2 concentration increased with time until steady state was reached at ~120 h in the 10% CO_2 experiment and at ~33 h in the 50% CO_2 experiment (Fig. A1.3). There is a discrepancy in reaction completion time inferred from gas composition data, and from aqueous chemistry and solids data. This is attributed to the time required to flush the headspace of the flask.

A1.2.3 Rate laws used in geochemical models

To discern the effect of elevated $p\text{CO}_2$ on brucite dissolution rate, experimental conditions were modeled with PHREEQC (Parkhurst and Appelo, 1999) using the Pitzer database. Experimentally determined, steady state, far from equilibrium rate laws dependent on pH (Pokrovsky and Schott, 2004) and ligand (HCO_3^-) concentration (Pokrovsky et al., 2005b) were used. The pH-dependent rate law is shown (Eq. A1.2; Pokrovsky and Schott, 2004):

$$\text{Rate} = k_b A \{ \text{H}^+ \}^{0.2} (1 - \Omega^2) \quad (\text{Eq. A1.2})$$

Where k_b is the kinetic rate constant equal to $10^{-6.38} \text{ mol m}^{-2} \text{ s}^{-1}$, A is the surface area in contact with 1 L of water in m^2 , and Ω is the saturation ratio of brucite as described by Equation A1.3:

$$\Omega = \text{IAP}/K \quad (\text{Eq. A1.3})$$

Where IAP is the ion activity product and K is the equilibrium constant for brucite dissolution.

The HCO_3^- concentration dependent rate law used is described by Equation A1.4 (Pokrovsky et al., 2005b):

$$\text{Rate} = A \left\{ k_{\text{Mg}} \left(1 - \left(K_{\text{Mg-HCO}_3^-} [\text{HCO}_3^-] / 1 + K_{\text{Mg-HCO}_3^-} [\text{HCO}_3^-] \right) \right)^{1.9} + k_{\text{HCO}_3^-} \left(K_{\text{Mg-HCO}_3^-} [\text{HCO}_3^-] / 1 + K_{\text{Mg-HCO}_3^-} [\text{HCO}_3^-] \right) \right\} \times (1 - \Omega^2) \quad (\text{Eq. A1.4})$$

Where k_{Mg} is the rate constant in the absence of ligands at pH 8.5 and is equal to $8.0 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$, $K_{\text{Mg-HCO}_3^-}$ is the adsorption constant of HCO_3^- on brucite surface sites equal to 50, and $k_{\text{HCO}_3^-}$ is the rate constant in the presence of HCO_3^- equal to $2.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ at pH 8.5 (Pokrovsky et al., 2005b). Equilibrium between the $p\text{CO}_2$ of the supplied gas was maintained throughout carbonation in models. Nesquehonite precipitation and homogeneous aqueous reactions were modeled as equilibrium processes.

Table A1.2. Raw $\delta^{13}\text{C}$ values of dissolved inorganic carbon and carbonate solids.

Experiment	Time (h)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	$\delta^{13}\text{C}$ solids (‰ VPDB)
10% CO_2 1	0	nd ^a	-4.53
	2	-34.46	-3.89
	4	-35.99	-6.42
	6	nd	-8.52
	8	-36.99	-12.80
	12	-36.61	-26.27
	21	-39.09	-29.36
	29	-40.53	-30.76
	36	-40.13	-28.28
	46	-34.40	-29.63
	102	-35.17	-30.12
	126	-29.33	-30.24
	175	-26.62	-29.29
	194	-27.79	-30.75
10% CO_2 2	0	nd	-3.94
	2	-36.46	-8.26
	4	-36.88	-11.83
	6	-36.22	-22.28
	8	-37.43	-30.22
	12	-38.46	-30.47
	21	-39.52	-31.15
	29	-34.61	-31.41
	36	-38.18	-29.61
	46	-33.06	-30.79
	102	-28.32	-31.71
	126	nd	-30.44
	175	-28.02	-31.52
	194	-27.70	-32.58
50% CO_2 1	0	nd	-5.03
	2	nd	-11.88
	4	-40.09	-29.61
	6	-40.29	-31.74
	8	-41.49	-35.50
	12	-41.61	-36.74
	22	-37.18	-35.85
	34	-32.82	-32.56
	52	-32.09	-36.23
	56	-31.01	-33.28

^and = no data

Table A1.2 (continued). Raw $\delta^{13}\text{C}$ values of dissolved inorganic carbon and carbonate solids.

Experiment	Time (h)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	$\delta^{13}\text{C}$ solids (VPDB‰)
50% CO_2 2	0	nd	-6.32
	2	-39.34	-10.39
	4	-39.22	nd
	6	-38.73	-33.48
	8	-39.36	-35.72
	12	-37.95	-36.06
	22	-33.28	-33.61
	34	-33.42	-32.54
	52	-31.40	-32.37
	56	-31.38	-31.25
100% CO_2 1	0	nd	-4.41
	2	-34.38	-23.15
	4	-31.81	-28.43
	6	-32.13	-30.11
	10	-31.45	-29.90
	18	-26.96	-28.97
	28	-22.75	-25.03
	44	-25.92	-28.90
	52	-25.81	-29.96
	68	-24.66	-29.02
	72	-25.80	-29.60
100% CO_2 2	0	nd	-4.43
	2	-34.07	-22.99
	4	-35.24	-29.01
	6	-31.04	-30.49
	10	-29.22	-31.04
	18	-18.36	nd
	28	-20.78	-30.11
	44	-24.87	-25.58
	52	-26.47	-29.79
	68	-25.38	-30.97
	72	-25.56	-30.04

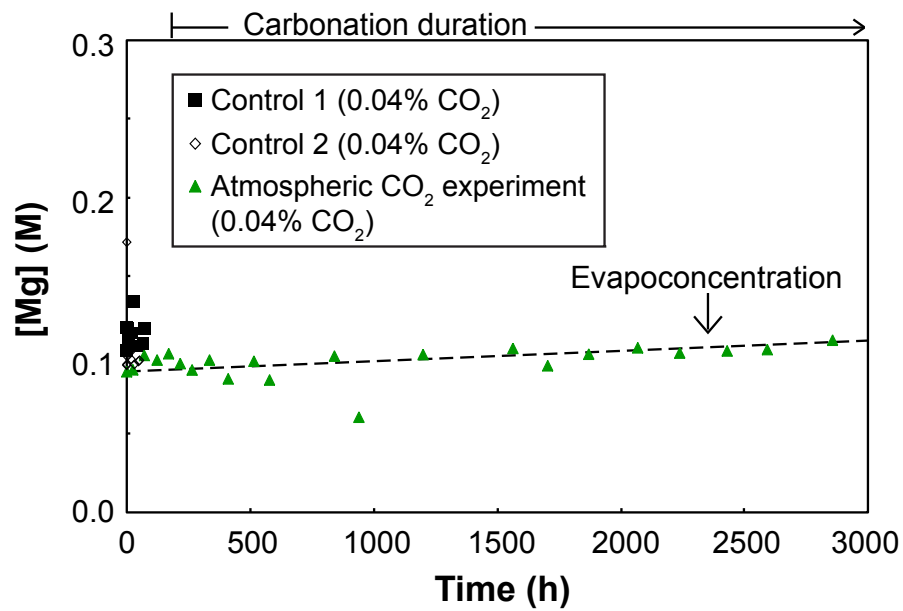


Figure A1.2. Mg concentration ([Mg]) versus time in the long term atmospheric CO₂ experiment and experimental controls. Dashed line indicates calculated increase in Mg concentration in the long term atmospheric CO₂ experiment due to evaporation.

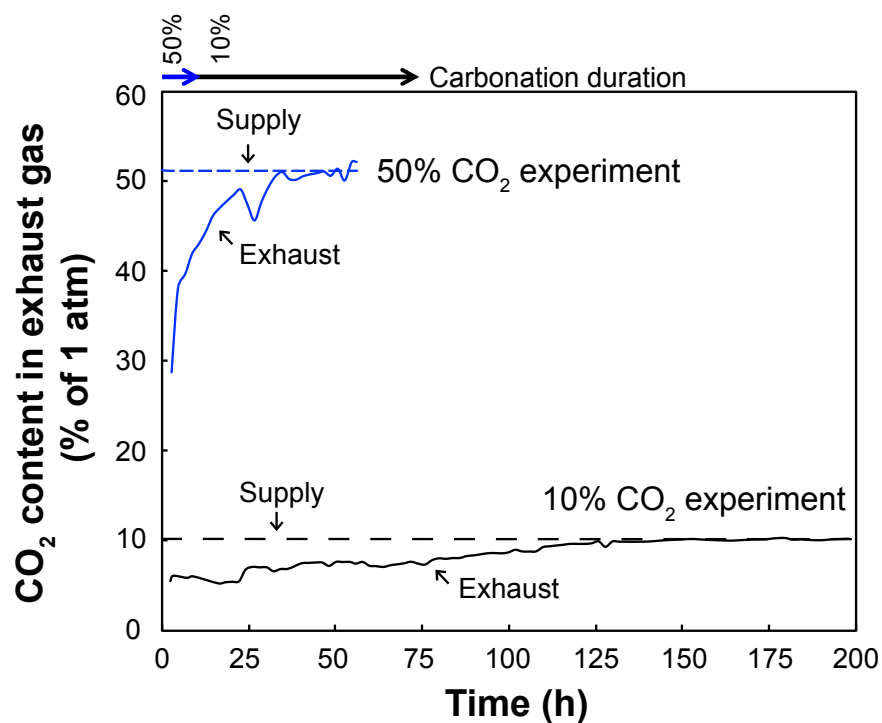


Figure A1.3. CO_{2(g)} content (balance N_{2(g)}) of combined exhaust from duplicate, simultaneous, high $p\text{CO}_2$ reactors in the 50% CO₂ and 10% CO₂ experiments versus time. Solid lines represent exhaust composition and dashed lines indicate composition of supplied gas. Arrows above the graph represent the duration of the carbonation reaction in the 50% and 10% CO₂ experiments, respectively.

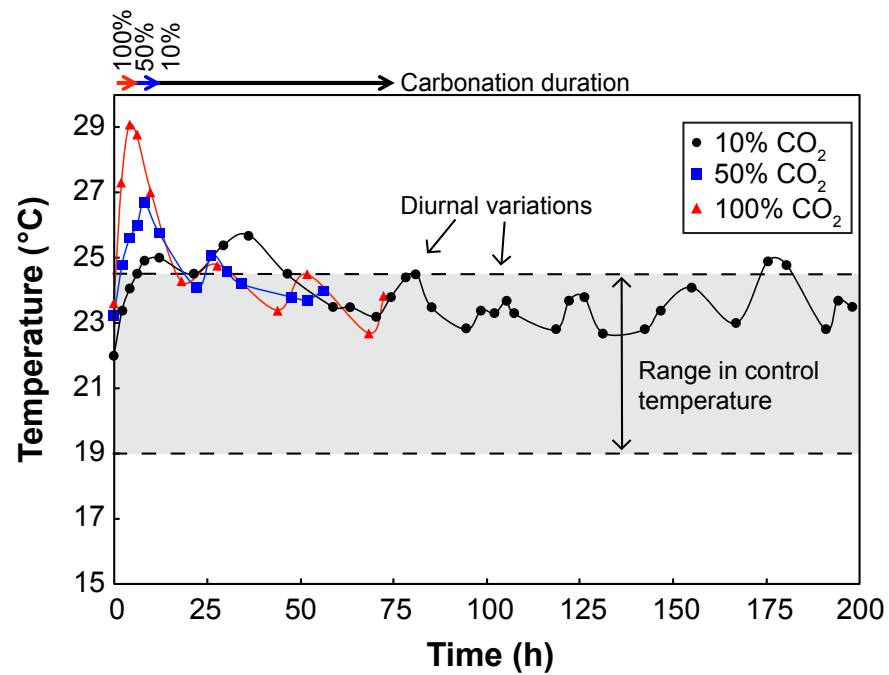


Figure A1.4. Temperature in high $p\text{CO}_2$ experiments versus time. The range of temperature in the experimental controls is indicated by the shaded area. Arrows above the graph represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

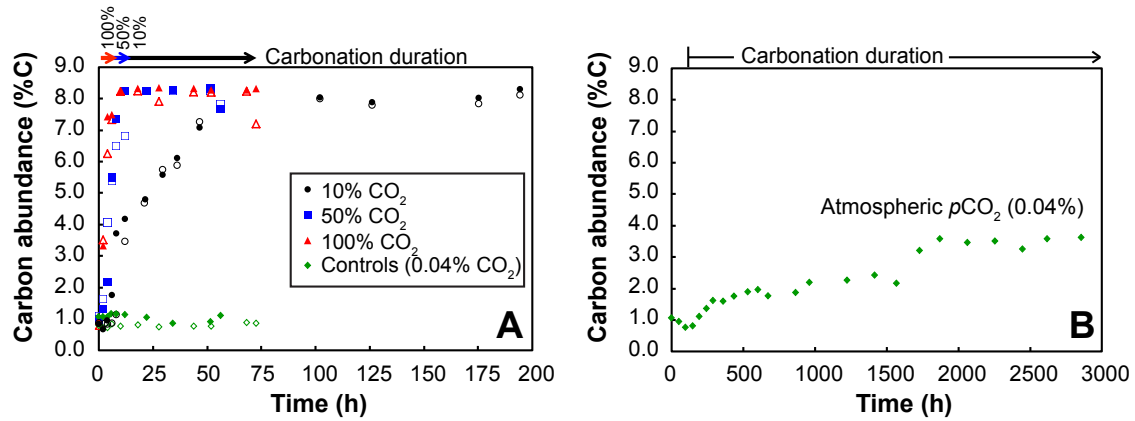


Figure A1.5. Carbon abundance (%C) versus time in high $p\text{CO}_2$ experiments and experimental controls (A) and the long term atmospheric $p\text{CO}_2$ experiment (B). Open and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graph represent the duration of the carbonation reaction in the 100%, 50% and 10% CO₂ experiments, respectively in (A).

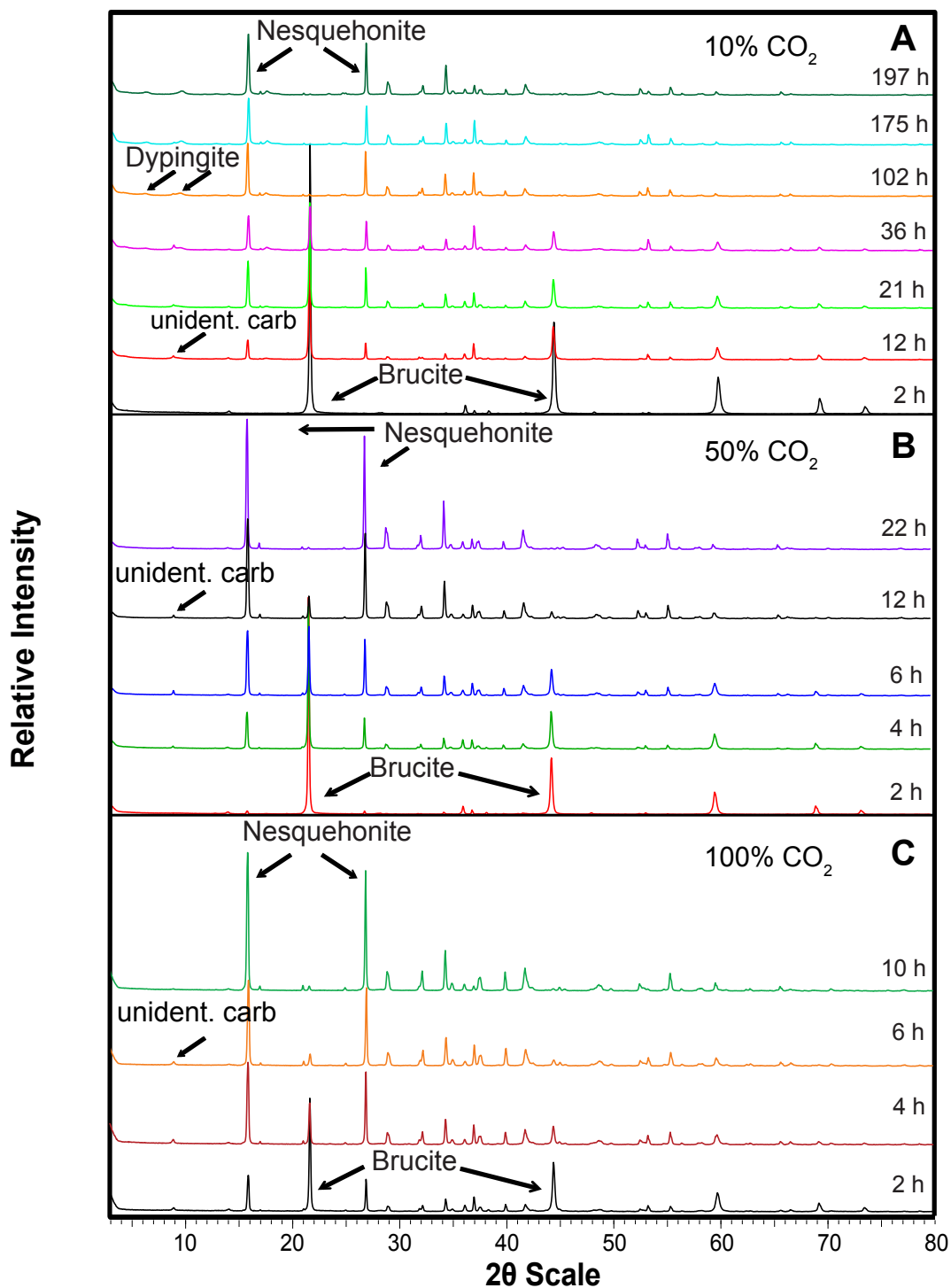


Figure A1.6. X-ray diffraction patterns of solids in the 10% CO₂ (A), 50% CO₂ (B), and 100% CO₂ (C) experiments with time. The most intense peaks of the relevant phases are indicated with arrows. 'Unident. carb' refers to unidentified carbonate phases.

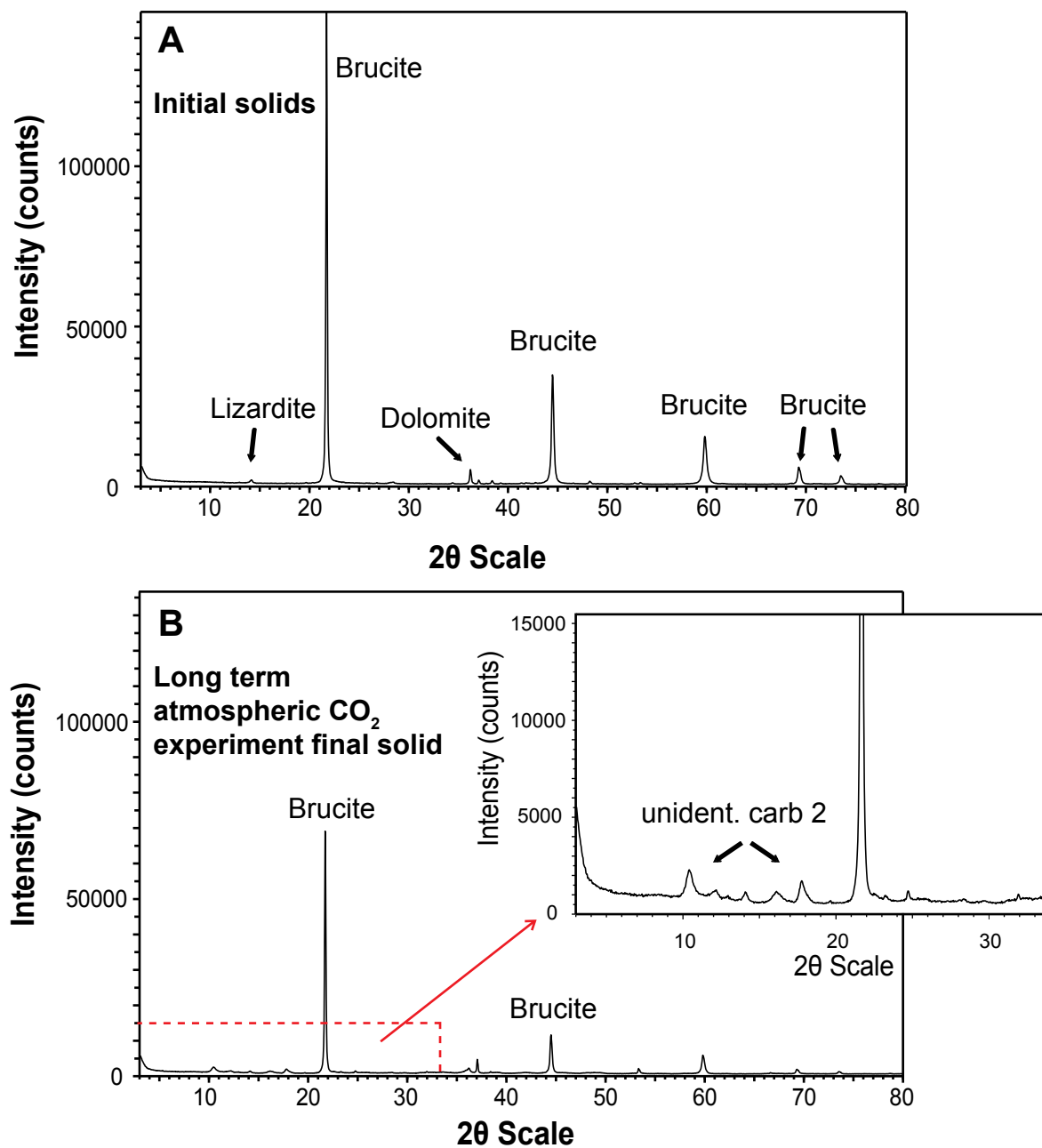


Figure A1.7. X-ray diffraction patterns of initial solids in all experiments (A) and final solids in the long-term atmospheric CO₂ experiment (B). “Unident. Carb 2” refers to an unidentified carbonate phase different than that documented in high $p\text{CO}_2$ experiments.

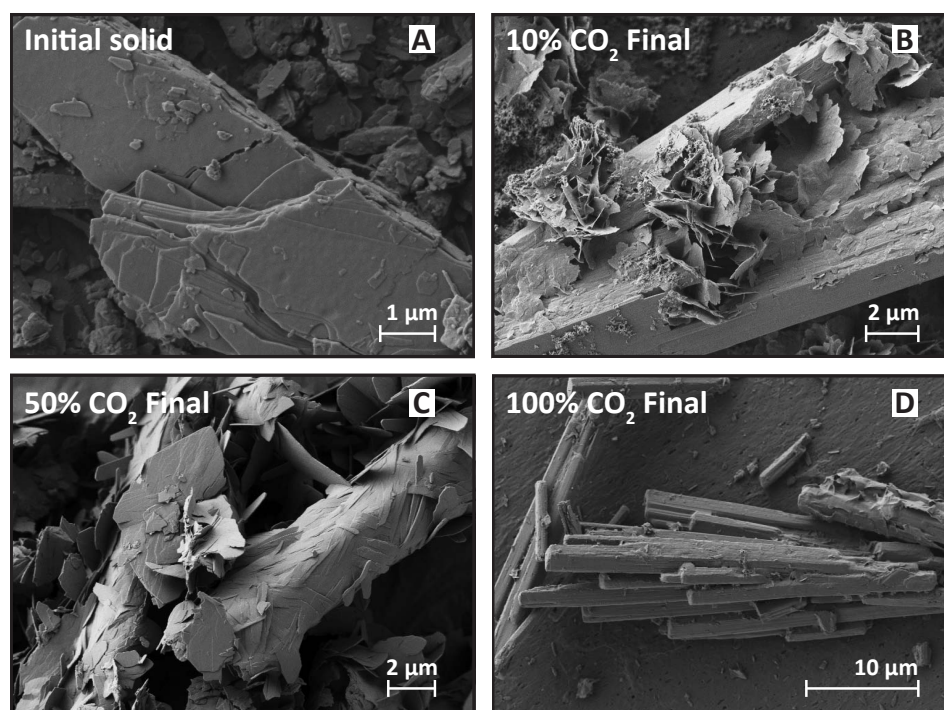


Figure A1.8. Scanning electron micrographs of initial solids in all experiments (A), and final solids in the 10% CO₂ (B), 50% CO₂ (C), and 100% CO₂ (D) experiments. Images depict pulverized brucite (A), elongate nesquehonite crystals armored by poorly crystalline rosettes and flakes (B, C), and elongate nesquehonite crystals with minor flaky texture (D).

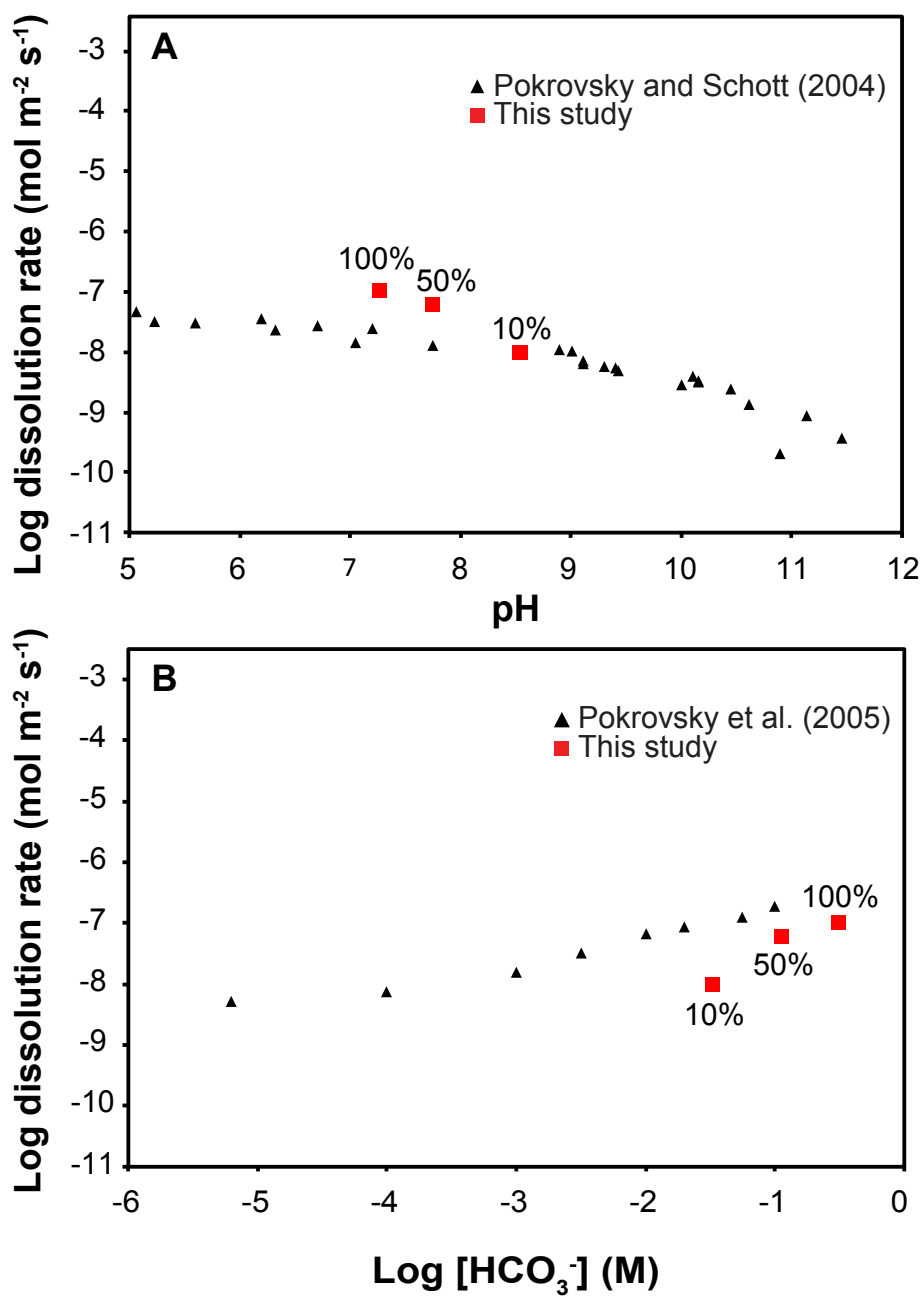


Figure A1.9. Comparison of brucite dissolution rate versus pH recorded in this study and by Pokrovsky and Schott (2004) (A), and comparison of brucite dissolution rate versus log $[\text{HCO}_3^-]$ in this study and recorded by Pokrovsky et al. (2005b) (B). For this study, plotted pH and HCO_3^- values are the average recorded during the carbonation reaction.

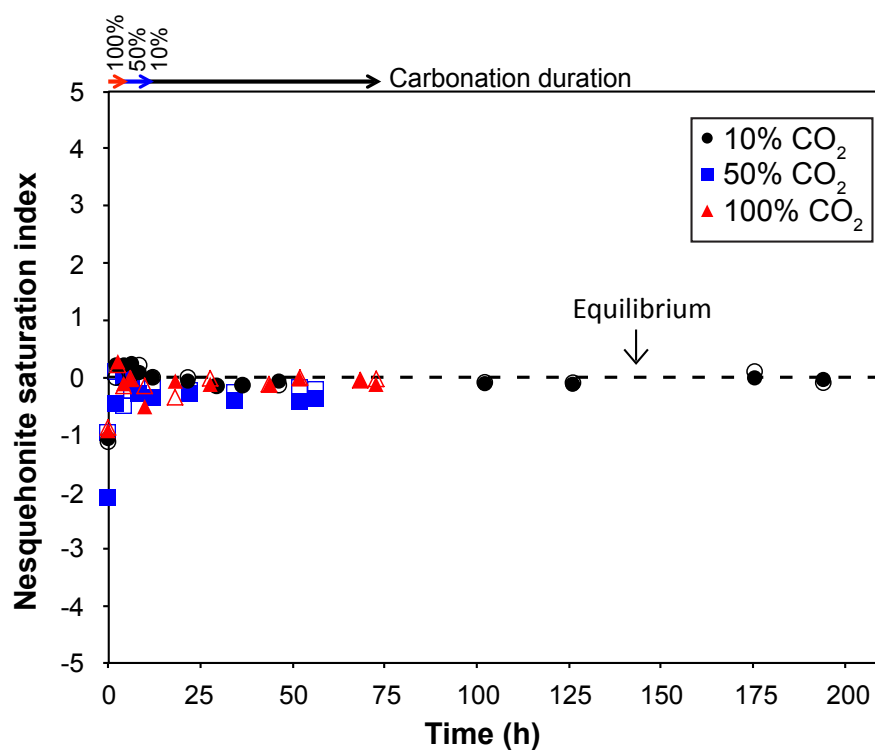


Figure A1.10. Nesquehonite saturation index versus time in all high $p\text{CO}_2$ experiments calculated using PHREEQC (Parkhurst and Appelo, 1999) and measured experimental pH, dissolved inorganic carbon, and Mg concentration. Dashed line indicates nesquehonite equilibrium (saturation index = 0). Open and solid symbols represent duplicates 1 and 2, respectively. Arrows above the graph represent the duration of the carbonation reaction in the 100%, 50% and 10% CO_2 experiments, respectively.

Appendix 2: Appendix to Chapter 4⁹

Enhanced mineral reactivity driven by pore fluid mobility in partially wetted porous media

A2.1 Supplementary methods

A2.1.1 Micromodel

The micromodel employed had a pore network that was 5.0 cm long by 1.5 cm wide with cylindrical glass pillars representative of quartz [SiO₂] grains (Fig. A2.1).

A2.1.2 Characterization of initial brucite

The brucite was obtained from Premier Magnesia LLC, and was pulverized using a hammermill and subsequently sieved to ≤ 53 μm in diameter. The particle size distribution was determined using a Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer, which indicated that the mean particle radius was 12 μm . The initial surface area of duplicate samples was determined by multipoint BET with N₂ adsorption using a Quantachrome Autosorb-1 surface area analyzer. It was equal to 5.2 ± 0.2 m² g⁻¹.

Rietveld refinement of X-ray diffraction (XRD) data was used to quantify the initial mineralogical composition of the brucite. Triplicate samples were spiked with 10 wt.% highly crystalline CaF₂ to allow quantification of the amorphous (non-crystalline) content (Gualtieri, 2000; Wilson et al., 2006). Samples were ground under ethanol for five minutes using a McCrone micronizing mill and agate grinding elements to reduce the mean particle size. Micronized samples were gently disaggregated with an agate mortar and pestle when dry. The samples were placed in back loaded cavity mounts against sandpaper to minimize preferred orientation (Raudsepp and Pani, 2003). A Bruker D8 Focus Bragg-Brentano diffractometer with CoK α

⁹A version of this appendix will be submitted as the Supporting Information for the verison of Chapter 4 that is submitted for publication.

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radiation and a step size of 0.04° over a range of $3\text{--}80^\circ 2\theta$ at 0.09 s/step was employed. The long fine focus Co X-ray tube was operated using a take-off angle of 6° at 35 kV and 40 mA. *DIFFRACplus* EVA 14 software (Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement was performed using Topas Version 3 refinement software (Bruker AXS, 2004). Crystal structure data for brucite (Catti et al., 1995), fluorite (Batchelder and Simmons, 1964), magnesite (Markgraf and Reeder, 1985), lizardite-1T (Mellini and Viti, 1994), hydromagnesite (Akao and Iwai, 1977), dolomite (Ross and Reeder, 1992), and pyroaurite (Olowe, 1995) were used in refinements. Analysis of triplicate samples of the brucite ore indicated it contained $78.8 \pm 3.8\text{ wt.}\%$ brucite, $5.5 \pm 0.4\text{ wt.}\%$ dolomite, $1.9 \pm 0.3\text{ wt.}\%$ magnesite, $7.4 \pm 1.0\text{ wt.}\%$ hydromagnesite, $5.9 \pm 3.3\text{ wt.}\%$ amorphous content, and $<0.5\text{ wt.}\%$ lizardite and pyroaurite.

A2.1.3 Videos

Time lapse greyscale brightfield images were taken at 5 minute intervals during the experiment using an inverted Olympus CKX41 transmitted light microscope and an Orca-ER (1344×1024 pixels) Hamamatsu camera. ImageJ (Abràmoff et al., 2004) software was used to compile these images into video format (Accompanying Materials (AM) Videos AM.1-AM.2) at 2 frames per second. Videos AM.1 and AM.2 are a compilation of images collected

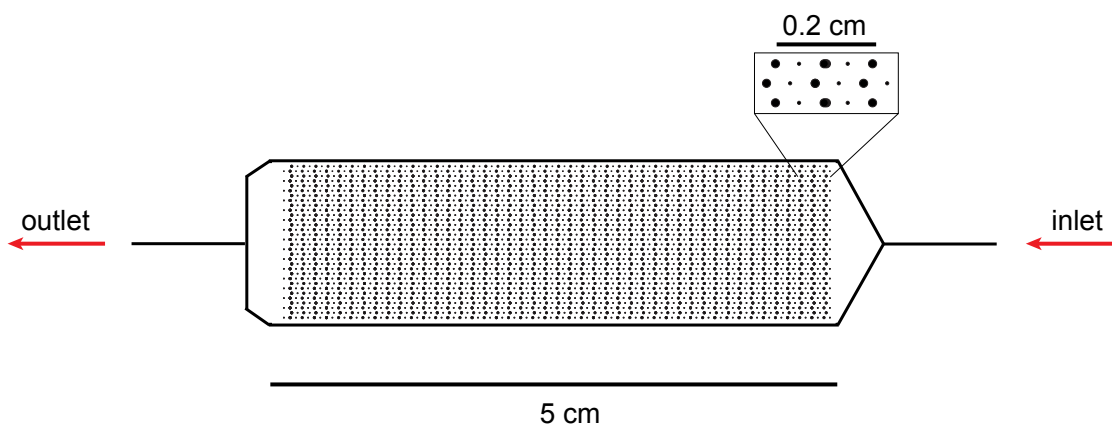


Figure A2.1. Schematic of the micromodel pore network.

during the 8 h and 18 h experiment, respectively. The field of view in Videos AM.1 and AM.2 are $3.4 \text{ mm} \times 2.2 \text{ mm}$ and $1.9 \text{ mm} \times 1.3 \text{ mm}$, respectively. The first ~ 10 h of the latter are included only, as little change was observed for the remainder of the experiment. The videos are available in the Accompanying Materials.

A2.1.4 Geochemical modeling

Geochemical modeling was conducted using PHREEQC (Parkhurst and Appelo, 2013) to assess the saturation state of carbonate phases, pH changes, and carbonation rate with varying mineral-water interfacial area (MWI). The Pitzer database was used with mineral solubility data from the LLNL database. Kinetic brucite dissolution was simulated according to a $[\text{HCO}_3^-]$ -dependent kinetic brucite dissolution rate law (Pokrovsky et al., 2005b), assuming equilibrium with pure CO_2 was maintained throughout the reaction. This was justified by the high flushing rate of the gas-filled pore volume in the micromodel with CO_2 . Nesquehonite and lansfordite $[\text{MgCO}_3 \cdot 5\text{H}_2\text{O}]$ precipitation was simulated at equilibrium, and precipitation of other Mg-carbonate minerals (e.g., magnesite) was suppressed to be consistent with experimental results. The models simulated 10 h of reaction, which is generally consistent with the cessation of reaction due to near complete evaporation of water (estimated between 8 and 12 hours based on time lapse images). Kinetic dissolution of calcite, anorthite (Ca-endmember), and quartz was modeled using the LLNL database. A specific surface area of $0.04 \text{ m}^2 \text{ g}^{-1}$ (Pokrovsky et al., 2005a), $0.09 \text{ m}^2 \text{ g}^{-1}$ (Gudbrandsson et al., 2014), and $0.11 \text{ m}^2 \text{ g}^{-1}$ (Brady and Walther, 1990) was used for calcite, anorthite, and quartz, respectively. Calcite, anorthite, and quartz dissolution were simulated according to kinetic dissolution rate laws from Chou et al. (1989), Gudbrandsson et al. (2014), and Brady and Walther (1990) at room temperature. For calcite, quartz, and anorthite, the dependence of the reaction rate on reaction affinity was assumed to follow a linear transition state theory rate law of the form proposed by Aagaard and Helgeson (1982).

A2.2 Supplementary discussion

A2.2.1 Raman spectroscopy

Raman spectroscopy indicated that a large portion of the precipitates were the hydrated Mg-carbonate, nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$], typified by a prismatic habit consistent with previous studies (Power et al., 2009) (AM Video AM.1; Fig. A2.2). Dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$] was also detected (Fig. A2.2), and was likely a dehydration product of pseudo-rhombohedral crystals interpreted to be lansfordite [$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$] that disappeared prior to analysis via Raman spectroscopy (Figs. A2.2 and A2.3; AM Video AM.2). The pseudo-rhombohedral crystals were consistent with the morphology of lansfordite synthesized in our laboratory from natural water collected from a Mg- and CO_2 -rich wetland pond in Atlin, British Columbia (Fig. A2.3).

A2.2.2 Geochemical modeling

Geochemical modeling using PHREEQC (Parkhurst and Appelo, 2013) and a HCO_3^- concentration dependent kinetic brucite dissolution rate law (Pokrovsky et al., 2005b) confirmed that without brucite dissolution, hydrated carbonate minerals would not become saturated in the experimental solutions (Fig. A2.4). The development of saturated conditions with respect to carbonate phases is facilitated with increasing mineral-water interfacial area per unit volume of water (Fig. A2.4).

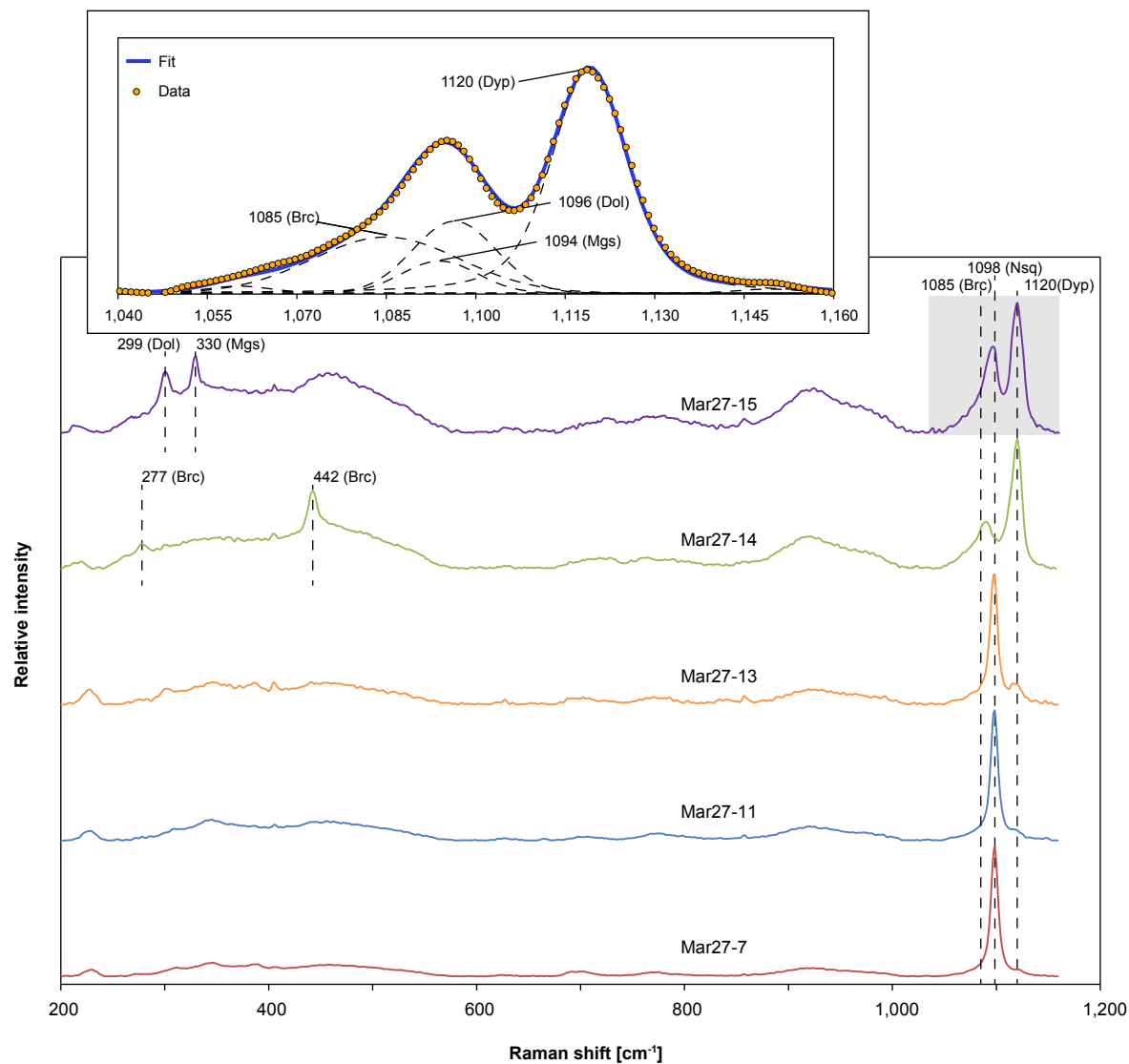


Figure A2.2. Raman spectra of reaction products from five locations within the micromodel following the second (8 h) experiment. Characteristic peaks of brucite (Brc), nesquehonite (Nsq), dolomite (Dol), dypingite (Dyp), and magnesite (Mgs) are identified. The inset figure shows a close up of the grey shaded region of spectrum ‘Mar27-15.’

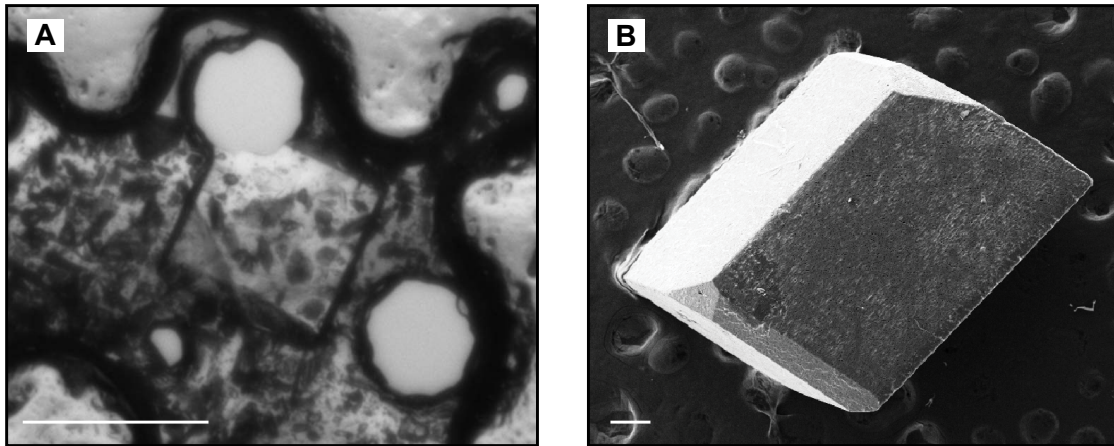


Figure A2.3. Brightfield light and scanning electron micrographs of lansfordite crystals [$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$]. A) Brightfield image of rhombohedral crystal formed during the first micromodel experiment in a water filled zone. B) Scanning electron micrograph of a lansfordite crystal synthesized in our laboratory from natural water collected from a Mg- and CO_2 -rich wetland pond in Atlin, British Columbia. Scale bars are 200 μm .

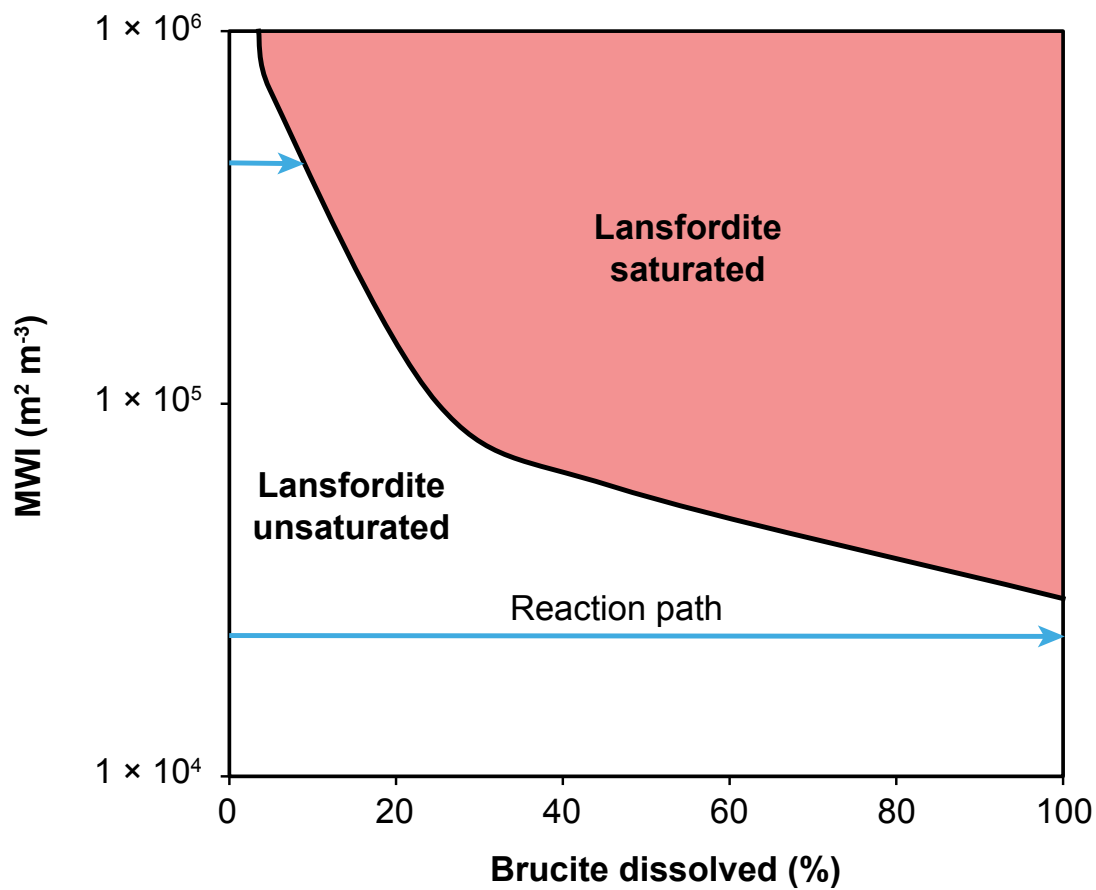


Figure A2.4. Lansfordite saturation as a function of mineral-water interfacial area (MWI) and brucite dissolution. Values were calculated using PHREEQC (Parkhurst and Appelo, 2013) and a HCO_3^- concentration-dependent kinetic brucite dissolution rate law (Pokrovsky et al., 2005b).

Appendix 3: Appendix to Chapter 5¹⁰

Influence of surface passivation and water content on mineral reactions in unsaturated porous media: Implications for brucite carbonation and CO₂ sequestration

A3.1 Detailed experimental design

A3.1.1 Initial solution composition and volume

Solutions were prepared by dissolving MgCl₂·6H₂O (from Fisher Scientific; assayed at 99.9%) in nanopure de-ionized water to provide a concentration of 0.1 M Mg. Initial solutions contained $<4 \times 10^{-4}$ M dissolved inorganic carbon. A volume of 58 mL was added to both the very fine and fine columns (35% saturation), whereas 29, 71, and 97 mL of solution was added to the 15%, 35%, and 50% saturated medium brucite columns, respectively. The solution was applied slowly and distributed evenly across the sediment surface using a dropper to minimize surface disturbance, and infiltrated the columns under the force of gravity. Once the wetting front was observed to reach the base of the column, the gas supply was initiated.

A3.1.2 Gas supply

The columns were equipped with stainless steel hose barbs at their base for gas input, and stainless steel compression fittings with 0.32 cm outer diameter Tygon tubing as gas exits. Gas was introduced to the base of the sediment through a stainless steel grate covered with fabric mesh (300 mesh). Gaseous CO₂ and N₂ were drawn from liquid CO₂ and N₂ tanks with single stage 316L stainless steel diaphragm liquid cylinder regulators from Matheson using a delivery pressure of 10 psig. The CO₂ and N₂ streams were blended to create a 10.0 vol.% CO₂

¹⁰A version of this Appendix is published as the Supplementary Material to Harrison et al. (2015). It is reprinted with permission from *Geochimica et Cosmochimica Acta*, 148, Harrison, A. L., Dipple, G.M., Power, I.M. and Mayer, K. U., Influence of surface passivation and water content on mineral reactions in unsaturated porous media: Implications for brucite carbonation and CO₂ sequestration, 477-495, Copyright (2014), with permission from Elsevier.

stream using a Series 150 two tube gas blender from Matheson equipped with high accuracy metering valves and Model E100(B) tubes, with an accuracy of $\pm 5\%$ of the full scale. A Cole-Parmer Masterflex® L/S precision® standard pump system fitted with an L/S Easy-Load II® pump head with four Tygon tubing lines was used to draw the 10.0 vol.% CO₂ gas from a 4 L reservoir to supply $\sim 15 \text{ mL min}^{-1}$ ($\sim 2.7 \times 10^{-3} \text{ g CO}_2 \text{ min}^{-1}$) to each column. With this flow rate, the pressure at the base of the column remained close to ambient atmospheric pressure. The CO₂ supply rate to the reservoir always exceeded the rate of withdrawal by at least 4 times ($\sim 280 \text{ mL min}^{-1}$).

The initial gas composition was verified and the CO₂ content of the gas outflow from the columns was monitored continuously using Vaisala® GMT221 CO₂ concentration sensors. The sensor output was recorded at five minute intervals using National Instruments® LabVIEW™8.6 software (National Instruments, 2008) interfaced with a LabJack® U3-HV. The accuracy of the sensor measurements varied between $\pm 0.5\%$ to $\pm 2.0\%$ depending on the experimental apparatus; at times the measurement reservoir was contaminated with ambient laboratory air, resulting in greater measurement error.

A3.2 Detailed analytical methods

A3.2.1 Characterization of solids

A3.2.1.1 *Particle size distribution and surface area analysis*

The initial surface area of each size fraction of the brucite ore used in the experiments was determined by multipoint BET with N₂ adsorption using a Quantachrome Autosorb-1 surface area analyzer. Particle size distribution analysis was performed using a Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer for brucite particles less than 250 μm (i.e., very fine and fine size fractions), and sieves were used to determine the size distribution of brucite particles in the 250-500 μm medium brucite size range.

A3.2.1.2 X-ray fluorescence spectroscopy

The major oxide composition of the initial solids was determined using X-ray fluorescence (XRF) spectroscopy with a Philips PW-1480 wavelength dispersive XRF spectrometer at The University of Western Ontario. Solids were powdered using a ring-mill for 30 s prior to analysis.

A3.2.1.3 X-ray powder diffraction methods

Synthetic and natural mineral phases in all solid samples were identified using X-ray diffraction (XRD) methods. Rietveld refinement of XRD data was used to quantify the weight percent (wt.%) abundance of all phases. Solid samples from each depth interval (2 cm) were homogenized and split in two; half of the material was ring-milled for 30 s to form a powder and the remainder was set aside for imaging. Aliquots of the ring-milled material were spiked with either 10 wt.% highly crystalline CaF_2 or Al_2O_3 (NIST standard 676A) to allow quantification of the amorphous (non-crystalline) content (e.g., Gualtieri, 2000). All spiked aliquots were ground under ethanol for 5 min using a McCrone micronizing mill and agate grinding elements to ensure homogenization and reduce the mean particle size. Micronized aliquots were dried for ~24 h then gently disaggregated with an agate mortar and pestle. Powder mounts were prepared in back loaded cavity mounts against sandpaper to minimize preferred orientation (Raudsepp and Pani, 2003).

All XRD data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with $\text{CoK}\alpha$ radiation and a step size of 0.04° over a range of $3\text{--}80^\circ 2\theta$ at 0.09 s/step. Fe monochromator foil, 0.6 mm divergence slit, incident and diffracted beam soler slits, and a Lynx Eye detector were used. A long fine focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6° . Search-match software by Bruker (DIFFRACplus EVA 14; Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement was completed using Topas Version 3 refinement software (Bruker AXS, 2004). The sources of crystal structure data used

in refinements are provided in Table A3.1.

A3.2.1.4 Inorganic carbon content

The inorganic carbon content in all solid samples was determined using a CM5130 acidification module with a Model 5014 CO₂ Coulometer from UIC Inc. Aliquots of the ring-milled solid samples were acidified to release CO_{2(g)}, which was quantified using a photodetector that monitors the color change of a colorimetric pH indicator. Analysis of replicate samples indicated measurements were reproducible within $\pm 0.11\%$ CO₂ by mass. This method has a detection limit of 0.37% CO₂. Carbon content values are expressed as %CO₂ by mass.

A3.2.1.5 Scanning electron microscopy

Samples were prepared for scanning electron microscopy (SEM) both as disaggregated powders on carbon adhesive tabs on aluminum specimen mounts and as polished epoxy-embedded mounts. The epoxy-embedded mounts were polished using sandpaper and 1 μm diamond paste to provide cross-sectional views of reacted grains. Images of disaggregated powders were collected using a LEO (Zeiss) 1540 XB field emission - scanning electron microscope (FE-SEM), equipped with a backscattered electron detector at an operating voltage of 10.0 kV. Elemental analysis was conducted using an Oxford Instruments' INCAx-sight energy dispersive spectrophotometer (EDS) at 10.0 kV. Images of epoxy-embedded mounts were collected using a Philips XL30 electron microscope and backscattered electron detector at an operating voltage of 15.0 kV. High resolution images of epoxy-embedded mounts were collected using an FEI Helios NanoLab 650 SEM operating at 10.0 kV or 3.0 kV. Disaggregated powders were coated with Os and epoxy-embedded mounts were coated with either Au or C.

A3.2.2 Initial aqueous chemistry

The total aqueous Mg concentration of the initial solutions was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) employing a Varian 725-ES Optical Emission Spectrometer, with a detection limit of 0.2 mg L⁻¹. Reproducibility was

better than 5.1 mg L^{-1} based on repeated analysis of standards and duplicate samples. Cation samples were acidified to 2% ultrapure HNO_3 immediately following sampling. The dissolved inorganic carbon concentration of the initial solutions was determined using a Lachat IL550 TOC-TN analyzer. Aliquots ($100 \mu\text{L}$) of sample were added to a 10% H_3PO_4 solution to release $\text{CO}_{2(\text{g})}$, which was measured with an infrared detector. The detection limit for this instrument is 0.5 mg L^{-1} .

A3.2.3 Soil water characteristic curves and gravimetric moisture content

The soil water characteristic curves of two representative medium brucite/quartz mixtures were determined using Tempe cell tests (e.g., Fredlund and Rahardjo, 1993). A Tempe cell test is used to determine the water content at different applied suction values. The applied suction was varied by changing the elevation difference between the base of each Tempe cell and a hydraulically connected drainage bottle. All tests were conducted at atmospheric pressure. The head gradient was maintained for at least 24 h until equilibrium was reached; at which point the masses of the Tempe cells were recorded to determine the equilibrium water content of the porous media at each value of applied suction. These data were used to construct a soil water retention curve, which was fit using the van Genuchten function (van Genuchten, 1980) with SoilVision software (Fredlund, 2004), providing a measurement of the residual moisture content of the porous material and soil hydraulic function parameters.

In order to estimate the water content profile of the columns following completion of the experiments, solids were sampled by removing the entirety of solid material in 2 cm intervals. Samples were weighed immediately following the experiment, and then were dried at room temperature for approximately one week until a constant weight was recorded. This provided a gravimetric estimate of water content with depth following reaction. Because the bulk volume of each sample was known ($2 \text{ cm thick} \times 2.95 \text{ cm radius}$), the gravimetric moisture content could be converted to volumetric moisture content (ratio of water volume to total volume),

Table A3.1. Sources of crystal structure data for Rietveld refinement.

Mineral	Source
Quartz	Glinnemann et al. (1992)
Brucite	Catti et al. (1995)
Nesquehonite	Giester et al. (2000)
Fluorite	Batchelder and Simmons (1964)
Corundum	Finger and Hazen (1978)
Magnesite	Markgraf and Reeder (1985)
Muscovite-2M ₁	Liang and Hawthorne (1996)
Lizardite-1T	Mellini and Viti (1994)
Hydromagnesite	Akao and Iwai (1977)
Dolomite	Ross and Reeder (1992)
Pyroaurite	Olowe (1995)

A3.3 Transport parameters and initial conditions employed in reactive transport models

Initial conditions including water chemistry, water saturation, initial and final brucite volume fractions and effective reactive surface areas employed in MIN3P-DUSTY (Molins and Mayer, 2007) simulations are provided in Tables A3.2 and A3.3. Transport parameters used in MIN3P-DUSTY simulations are given in Table A3.4.

Table A3.2. Initial conditions applied in MIN3P-DUSTY simulations.

Experiment	Mg concentration (M)	pH
very fine	0.1	9.2
fine	0.1	9.2
medium	0.1	9.2

Table A3.3. Brucite volume fractions and surface areas in experiments compared to models.

Experiment	Model	Experiment				Model			SA ^e (%)	r_{carb} ^a
		r_{carb} ^a	ϕ^0 ^b	ϕ^f ^c	SA ^d (m ² g ⁻¹)	ϕ^0 ^b	ϕ^f ^c	SA ^d (m ² g ⁻¹)		
v fine brc	geometric	1.5	0.041	0.003	5.23	0.029	0	1.09	21	1.6
v fine brc	threshold	1.5	0.041	0.003	5.23	0.029	0.002	0.86	16	1.6
fine brc	geometric	1.7	0.041	0.008	3.70	0.029	0	0.77	21	1.5
fine brc	threshold	1.7	0.041	0.008	3.70	0.029	0.005	0.59	16	1.5
med brc, 35% sat	geometric	1.8	0.041	0.017	2.40	0.022	2.6×10^{-4}	0.50	21	2.1
med brc, 35% sat	threshold	1.8	0.041	0.017	2.40	0.022	0.008	0.37	15	2.1

^a r_{carb} = ratio of moles of Mg consumed to CO₂ captured in the solid phase during carbonation

^b ϕ^0 = initial brucite volume fraction

^c ϕ^f = final brucite volume fraction, which is equivalent to ϕ^p in the passivation models

^dSA = brucite surface area

^eSA(%) = (SA_{model}/SA_{experiment}) × 100%

assuming the density of water was ~1 g cm⁻³.

Table A3.4. Physical and transport parameters employed for simulations using MIN3P-DUSTY.^a

Parameter	Value	Reference
Saturated hydraulic conductivity (m s^{-1})	1.00×10^{-3}	estimated
Porosity	0.53	this study
Soil-water retention curve		
α (m^{-1})	4.0	this study
n	5.0	this study
S_{rl}	0.10	this study
Aqueous phase diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	1.00×10^{-9}	Molins and Mayer (2007)
Gas phase binary diffusion coefficients ($\text{m}^2 \text{s}^{-1}$)		
$\text{N}_2\text{--O}_2$	2.083×10^{-5}	Molins and Mayer (2007)
$\text{CO}_2\text{--O}_2$	1.635×10^{-5}	Molins and Mayer (2007)
$\text{CO}_2\text{--N}_2$	1.649×10^{-5}	Molins and Mayer (2007)
Gas phase viscosity ($\text{Pa}\cdot\text{s}$)		
O_2	2.05×10^{-5}	Molins and Mayer (2007)
CO_2	1.46×10^{-5}	Molins and Mayer (2007)
N_2	1.75×10^{-5}	Molins and Mayer (2007)

^aTemperature is 298 K.

A3.4 Detailed results

A3.4.1 Particle size distribution

The particle size distribution of each of the initial brucite size fractions is shown in Figure A3.1.

A3.4.2 CO_2 breakthrough

The gas effluent composition data used to construct the CO_2 breakthrough curves are provided in Tables A3.5-A3.7.

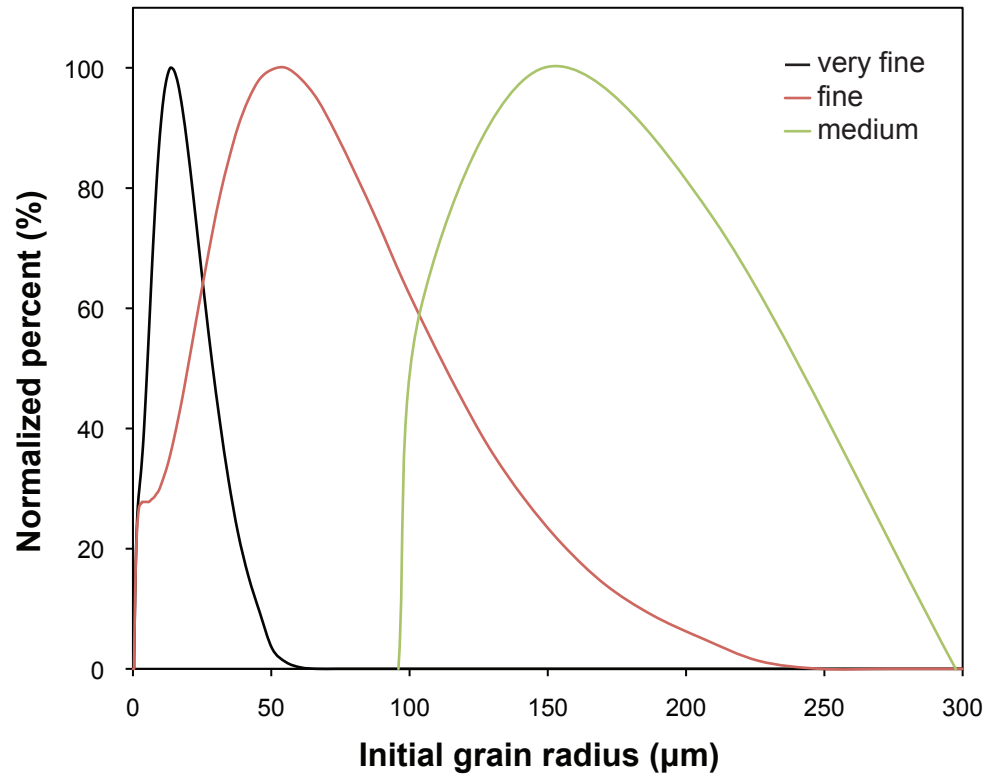


Figure A3.1. Particle size distribution of initial very fine, fine, and medium brucite ore.

Table A3.5. Gas effluent composition in the very fine and fine brucite columns.

Experiment	Gas outflow composition (% CO ₂)	
	Very fine, 35% saturated	Fine, 35% saturated
Time (h)		
0	0.0	0.0
2.4	0.0	0.0
4.9	0.0	0.0
7.4	0.0	0.0
9.9	0.0	0.0
12.4	0.0	0.2
14.9	0.0	0.2
17.4	0.0	0.2
19.9	0.0	0.2
22.5	0.0	0.2
25.0	0.0	0.1
27.5	0.0	0.1
30.0	0.0	0.1
32.5	0.0	0.0
35.0	0.0	0.2
37.5	0.0	0.2
40.0	0.0	0.2
42.5	0.0	0.3
45.0	0.0	0.3
47.5	0.0	0.4
50.0	0.1	0.5
52.5	0.1	0.6
55.0	0.2	0.7
57.5	0.3	0.8
60.0	0.5	1.1
62.5	0.7	1.4
65.0	1.0	1.6
67.5	1.3	2.0
70.0	1.3	2.3
72.5	1.6	2.6
75.0	2.1	2.8
77.5	1.9	3.1
80.0	2.3	3.5
82.5	2.9	3.9
85.0	3.3	4.2
87.5	3.5	4.6
90.0	3.8	4.9
92.5	4.2	5.3
95.0	3.9	5.6
97.5	4.5	5.8
100.0	4.7	6.1
102.5	4.6	6.3
105.0	4.9	6.6
107.5	5.2	6.8
110.0	5.3	6.9
112.5	5.7	7.1
115.0	5.7	7.2

Table A3.5 (continued). Gas effluent composition in the very fine and fine brucite columns.

Experiment	Gas outflow composition (% CO ₂)	
	Very fine, 35% saturated	Fine, 35% saturated
Time (h)		
117.5		7.4
120.2	6.1	7.5
122.7	6.5	7.5
125.2	6.2	7.5
127.7		
130.2	6.3	7.7
132.7	7.0	7.8
135.2	6.9	7.9
137.7	6.9	7.9
140.2	7.0	7.9
142.8	7.6	8.0
145.3	6.7	8.0
147.8	6.8	8.1
150.3	6.6	8.0
152.8	6.7	8.1
155.3	6.6	8.0
157.8	6.7	8.1
160.3	6.7	8.0
162.8	6.6	8.2
165.3	6.6	8.2
167.8	7.0	8.1
170.3	6.7	8.1
172.8	7.1	8.2
175.3	7.0	8.2
177.8	7.2	8.2
180.3	7.0	8.2
182.8	7.1	8.3
185.3	7.1	8.2
187.8	7.1	8.2
190.5	7.2	8.2
193.0	7.0	8.3
195.5	7.2	8.3
198.0	7.4	8.3
200.5	7.7	8.3
203.0	7.5	8.3
205.5	7.3	8.2
208.0	7.3	8.2
210.5	7.6	8.3
213.0	7.7	
215.5	8.1	8.3
218.0	8.1	8.3
220.5	7.7	8.3
223.0	7.8	8.3
225.5	7.5	8.2
228.0	7.7	8.3

Table A3.5 (continued). Gas effluent composition in the very fine and fine brucite columns.

Experiment	Gas outflow composition (% CO ₂)	
	Very fine, 35% saturated	Fine, 35% saturated
Time (h)		
230.5	7.5	8.3
233.0	7.5	8.3
235.5	7.5	8.4
238.4	7.2	8.3
240.9	7.4	8.3
243.4	8.3	8.3
245.9	8.3	8.4
248.4	7.7	8.3
250.9	7.5	8.3
253.4	7.4	8.2
255.9	7.2	8.2
258.4	7.5	8.2
260.9	7.5	8.3

Table A3.6. Gas effluent composition in the 35% and 50% saturated medium brucite columns.

Experiment	Gas outflow composition (% CO ₂)	
	medium, 35% saturated 1	medium, 50% saturated 1
Time (h)		
0.2	0.0	
2.6	0.0	1.4
5.1	2.3	3.7
7.6		4.8
10.1	4.8	5.1
12.6	4.4	5.1
15.1	4.4	5.1
17.6	4.3	5.1
20.1	4.3	5.1
22.6	4.2	4.9
25.1	4.2	4.8
27.6	4.1	4.7
30.1	3.9	4.6
32.6	3.8	4.6
35.1	3.9	4.6
37.6	3.9	4.6
40.1	4.0	4.5
42.6	3.7	4.3
45.1	3.7	4.3
47.6	3.7	4.4
50.1	3.7	4.2
52.6	3.8	4.3
55.1	4.0	4.5
57.6	4.2	4.7
60.1	4.4	4.8
62.6	4.6	5.0
65.1	4.9	5.1
67.7	5.1	5.3
70.2	5.4	5.5
72.7	5.6	5.5
75.2	6.0	5.9
77.7	6.2	6.0
80.2	6.4	6.2
82.7	6.7	6.4
85.2	7.0	6.5
87.7	7.2	6.7
90.3	7.2	6.7
92.8	7.5	6.8
95.3	7.7	7.0
97.8	7.7	6.9
100.3	8.1	7.2
102.8	8.1	7.4
105.3	8.4	7.4
107.8	8.4	7.6

Table A3.6 (continued). Gas effluent composition in the 35% and 50% saturated medium brucite columns.

Experiment	Gas outflow composition (% CO ₂)	
	medium, 35% saturated 1	medium, 50% saturated 1
Time (h)		
110.3	8.6	7.6
112.8	8.7	7.7
115.3	8.8	7.7
117.8	8.6	7.8
120.3	8.8	8.0
122.8		8.0
125.3	9.1	8.2
127.8	9.0	8.2
130.3	9.2	8.2
132.8	9.2	8.2
135.3	9.3	8.3
137.8	9.3	8.3
140.3	9.4	8.4
142.8	9.2	8.4
145.3	9.4	8.5
147.8	9.4	8.5
150.3	9.5	8.4
152.8	9.5	8.6
155.3	9.5	8.5
157.8	9.3	8.4
160.3	9.5	8.5
162.8	9.6	8.6
165.4	9.4	8.6
167.9	9.5	8.7
170.4	9.4	8.6
172.9	9.5	8.6
175.4	9.4	8.6
177.9	9.4	8.6
180.4	9.6	8.6
182.9	9.6	8.6
185.4	9.5	8.6
187.9	9.5	8.6
190.4	9.4	8.6
192.9	9.4	8.6
195.4	9.5	8.7
197.9	9.5	8.6
200.4	9.4	8.5
202.9	9.4	8.6
205.4	9.2	
207.9	9.4	
210.5	9.4	8.3
213.0	9.4	8.4
215.5	9.3	8.4
217.8	9.3	8.6

Table A3.7. Gas effluent composition in the 35% and 50% saturated medium brucite duplicate columns.

Experiment	Gas outflow composition (% CO ₂)	
	medium, 35% saturated 2	medium, 50% saturated 2
Time (h)		
0.0	0.0	0.0
2.4	0.2	1.2
4.9	3.0	3.7
7.4	4.7	4.5
9.9	4.7	4.5
12.4	4.4	4.5
14.9	4.1	4.6
17.4	4.1	4.6
20.2	4.4	5.0
22.7	4.9	5.5
25.2	4.8	5.5
27.7	4.8	5.4
30.2	4.7	5.1
32.7	4.5	4.9
35.2	4.5	4.8
37.7	4.4	4.7
40.2	4.2	4.6
42.8	3.9	4.5
45.3	3.9	4.4
47.8		
50.3	4.0	4.3
52.8	3.9	4.4
55.3	4.1	4.4
57.8	4.2	4.5
60.3	4.4	4.6
62.8	4.6	4.8
65.3	4.8	4.9
68.0	5.1	5.0
70.5	5.2	5.1
73.0	5.5	
75.5	5.7	5.5
78.0	6.1	5.7
80.5	6.4	5.9
83.0	6.6	6.1
85.5	7.0	6.3
88.0	7.2	6.5
90.7	7.2	6.6
93.2	7.7	6.9
95.7	7.8	7.2
98.2	8.1	7.3
100.7		
103.2	8.6	7.6
105.7	8.8	7.8
108.2	8.7	7.9
110.7	9.0	8.0
113.3	9.0	8.0

Table A3.7 (continued). Gas effluent composition in the 35% and 50% saturated medium brucite duplicate columns.

Experiment	Gas outflow composition (% CO ₂)	
	medium, 35% saturated 2	medium, 50% saturated 2
Time (h)		
115.8	9.2	8.1
118.3	9.2	8.3
120.8	9.3	8.4
123.3	9.2	8.5
125.8	9.7	8.5
128.3	9.7	8.6
130.8	9.6	8.5
133.3	9.6	8.6
135.8	9.8	8.6
138.4	9.5	8.7
140.9		
143.4	9.8	8.8
145.9	9.6	
148.4	9.9	8.9
150.9	9.9	9.0
153.4	9.8	9.0
155.9	9.8	9.1
158.4	9.7	9.0
160.9	10.1	9.0
163.5	9.9	9.1
166.0	10.3	9.2
168.5	9.8	9.2
171.0	9.2	9.3
173.5	10.2	9.2
176.0	10.0	9.2
178.5	10.0	9.2
181.0	10.2	9.2
183.5	10.2	9.3
187.3	10.0	9.2
189.8	10.2	9.3
192.3	9.9	9.3
194.8	10.1	9.2
197.3	9.4	8.9
199.8	9.5	9.0
202.3	9.7	8.9
204.8	9.6	9.1
204.9	9.6	9.4

A3.4.3 Extent of carbonation and water content

The abundance and distribution of nesquehonite, the poorly crystalline phase, and total CO₂ sequestered varied significantly between experiments of different grain size. The greatest mass of CO₂ sequestered was measured in the very fine brucite column (up to 4.4% CO₂), followed by the fine brucite column (up to 3.7% CO₂). Both of these columns exhibited similar %CO₂ trends, with the greatest CO₂ content near the column inlet. The extent of brucite removal calculated using Rietveld refinement of the XRD data is consistent with these results, with the least brucite remaining in the very fine brucite column, followed by the fine brucite column. In these columns, brucite abundance increased along the flow-path, whereas nesquehonite abundance tended to decrease. All columns with medium brucite were less carbonated than columns with finer-grained brucite. The 15% saturated column captured the lowest mass of CO₂, with only 0.27-0.36% CO₂ and 0.9-1.5 wt.% nesquehonite. A similar extent of carbonation was achieved in both the rinsed and unrinsed medium brucite columns that were 35% saturated as well as the 50% saturated column, with total CO₂ abundance between 1.1-3.0 wt.%. However, the distribution of CO₂ and brucite differed; in the 35% saturated column, total CO₂ and nesquehonite abundance decreased along the flow-path, whereas nesquehonite, brucite, and total CO₂ were more evenly distributed throughout the 50% saturated column. The 35% saturated column with rinsed medium brucite showed a nearly indistinguishable %CO₂ trend compared to the column with the unrinsed material. In the 35% saturated columns of all grain sizes, the poorly crystalline phase increased in abundance along the flow path. Conversely, the highest abundance of the poorly crystalline phase occurred at the base of the 50% saturated medium brucite column. It was fairly evenly distributed in the 15% saturated column.

Based on the Rietveld refinement results, the mass of CO₂ stored in nesquehonite in the very fine, fine, and medium 35% saturated columns was 4.0 g, 3.7 g, and 2.1 g, respectively. Approximately 4.7 g, 2.1 g, and 0.7 g CO₂ were stored in nesquehonite in the 50%, 35%, and 15% saturated medium brucite columns, respectively. However, the total mass of CO₂ sequestered in each column calculated using the %CO₂ data and the total column mass gain

was significantly greater than can be attributed to the measured abundance of nesquehonite. The %CO₂ data indicated that 16.8 g, 13.1 g, and 9.0 g CO₂ were sequestered in the very fine, fine, and medium brucite columns, respectively. In the medium brucite columns 5.2 g, 9.0 g, and 8.6 g CO₂ were sequestered in the 15%, 35%, and 50% saturated columns, respectively. Similarly, 9.3 g CO₂ were sequestered in the 35% saturated column with rinsed medium brucite.

The %CO₂, Rietveld refinement, gravimetric, and water content results are summarized in Tables A3.8-A3.14. An example of a typical X-ray diffraction pattern collected from reacted material is shown in Figure A3.2. The final volumetric water content profiles are shown in Figure A3.3.

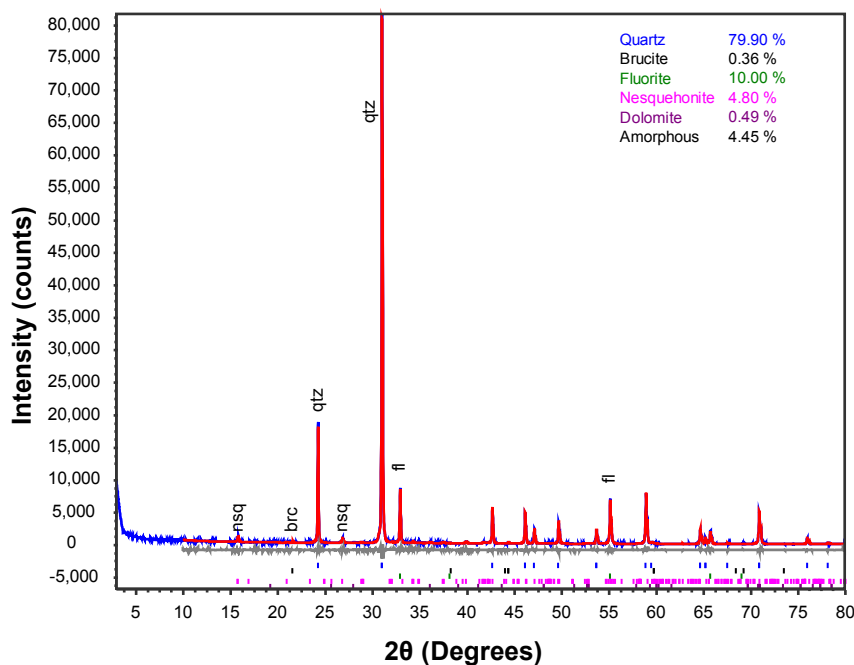


Figure A3.2. Representative X-ray diffraction pattern and Rietveld refinement plot of reacted solids from the bottom 2 cm of the fine brucite column. The blue line represents the observed data that is overlain by the calculated pattern (red line). The grey line shows the residual pattern, and the vertical lines below show the positions of the Bragg reflections for each phase. Blue, black, green, pink, and purple vertical lines indicate quartz, brucite, fluorite, nesquehonite, and dolomite, respectively. The fluorite was added to experimental samples to allow calculation of the amorphous or nano-crystalline content in each sample.

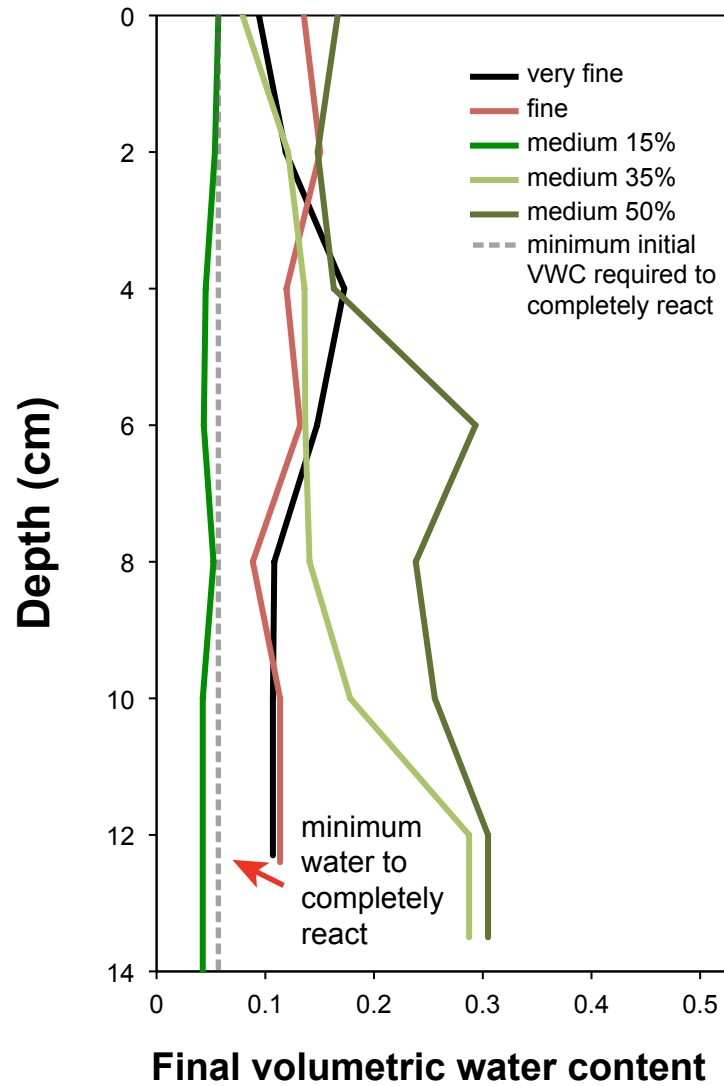


Figure A3.3. Final volumetric water content versus depth measured at the conclusion of the experiments. Grey line indicates the minimum initial volumetric water content that would be required to allow complete carbonation of the brucite given stoichiometric conversion to nesquehonite.

Table A3.8. Rietveld refinement and carbon content results with depth from the very fine and fine brucite columns.

Experiment	Mineral abundance (wt.%)						Carbon content (wt.%)	
	Brucite		Nesquehonite		Flakey phase		%CO ₂	
	very fine, 35% saturated	fine, 35% saturated	very fine, 35% saturated	fine, 35% saturated	very fine, 35% saturated	fine, 35% saturated	very fine, 35% saturated	fine, 35% saturated
Depth interval^a								
0-2 cm	0.8	3.4	0.0	0.0	5.5	8.0	2.86	2.29
2-4 cm	0.7	2.7	0.0	0.0	7.8	8.9	3.25	2.35
4-6 cm	1.1	1.8	0.0	0.0	3.9	5.7	3.17	2.81
6-8 cm	0.2	0.6	1.7	3.9	8.2	3.5	4.09	3.65
8-10 cm	0.0	0.4	6.7	4.3	6.0	4.4	4.36	3.31
10-12 cm ^b	0.0	0.4	6.5	5.3	2.4	4.9	3.55	2.51

^aDepth = 0 cm represents the top of the sediment column

^bbottom interval is 10-12.3 cm for the very fine brucite column, and 10-12.4 cm for the fine brucite column

Table A3.9. Rietveld refinement and carbon content results with depth from the medium brucite columns with different water saturations.

Experiment	Mineral abundance (wt.%)									Carbon content (wt.%)			
	Brucite			Nesquehonite			Flakey phase			%CO ₂			
	medium, 15% saturated	medium, 35% saturated	medium, 50% saturated	medium, 15% saturated	medium, 35% saturated	medium, 50% saturated	medium, 15% saturated	medium, 35% saturated	medium, 50% saturated	medium, 15% saturated	medium, 35% saturated	rinsed medium, 35% saturated	medium, 50% saturated
Depth interval^a													
0-2 cm	6.1	4.1	3.4	0.0	0.0	2.7	1.9	4.1	7.3	1.02	1.05	1.30	2.07
2-4 cm	5.5	3.7	3.2	0.0	0.0	3.9	1.8	6.9	3.6	1.11	1.29	1.38	1.84
4-6 cm	5.1	3.2	2.9	0.0	0.4	5.2	1.9	6.9	4.6	1.01	1.75	1.85	1.92
6-8 cm	4.7	3.0	2.3	0.0	0.6	2.9	2.4	8.2	2.7	1.18	1.90	1.99	1.86
8-10 cm	4.4	2.8	3.5	0.9	1.8	2.0	0.0	4.5	5.6	1.23	1.99	2.34	1.41
10-12 cm ^b	5.0	2.6	4.2	1.5	3.5	1.4	2.7	6.1	8.5	1.32	2.86	2.97	1.60
12-13.5 cm		2.2	3.7		4.3	4.2		3.5	8.4		2.86		2.21

^aDepth = 0 cm represents the top of the sediment column

^bbottom interval is 10-14 cm and 10-13 cm for the 15% saturated column and the rinsed medium brucite 35% saturated column, respectively.

Table A3.10. Total mass of solids and water at the end of the experiment in the very fine and fine brucite columns.

Experiment	Total mass of solids (g)		Total mass of water (g)	
	Mass		Mass	
	very fine, 35% saturated	fine, 35% saturated	very fine, 35% saturated	fine, 35% saturated
Depth interval^a				
0-2 cm	70.06	73.35	5.15	7.41
2-4 cm	72.31	77.84	6.49	8.23
4-6 cm	76.58	62.71	9.44	6.53
6-8 cm	84.91	84.17	8.07	7.23
8-10 cm	81.23	69.17	5.92	4.84
10-12 cm ^b	85.09	97.17	6.73	7.45

^aDepth = 0 cm represents the top of the sediment column^bbottom interval is 10-12.3 cm for the very fine brucite column, and 10-12.4 cm for the fine brucite**Table A3.11.** Total mass of solids and water at the end of the experiment in the medium brucite columns with different water saturations.

Experiment	Total mass of solids (g)			Total mass of water (g)		
	Mass			Mass		
	medium, 35% saturated	medium, 50% saturated	medium, 15% saturated	medium, 35% saturated	medium, 50% saturated	medium, 15% saturated
Depth interval^a						
0-2 cm	56.43	82.17	75.75	4.28	9.03	3.11
2-4 cm	80.88	69.41	67.53	6.56	8.01	2.93
4-6 cm	78.90	64.62	59.04	7.35	8.82	2.47
6-8 cm	69.20	84.48	60.86	7.39	15.85	2.37
8-10 cm	61.24	56.46	72.08	7.56	12.8	2.86
10-12 cm ^b	61.53	57.02	112.33	9.61	13.75	4.64
12-13.5 cm	58.60	49.09		11.37	12.2	

^aDepth = 0 cm represents the top of the sediment column^bbottom interval is 10-14 cm for the 15% saturated column

Table A3.12. Mass of CO₂ gained through time in the very fine and fine 35% saturated columns and the rinsed 35% saturated and 15% saturated medium brucite columns.

Experiment	Mass gain (g) ^a			
	Very fine, 35% saturated 1	Fine, 35% saturated 1	Medium, 15% saturated 1	Rinsed Medium 35% saturated
Time (h)				
0.0	0.00	0.00	0.00	0.00
3.7	0.59	0.60	0.46	0.51
7.5	1.19	1.19	0.82	0.83
10.7	1.70	1.68	1.11	1.02
20.7	3.23	3.16	1.87	1.52
24.4	3.80	3.71	2.13	1.75
28.5	4.40	4.32	2.40	2.00
32.1	4.95	4.84	2.62	2.25
44.8	6.92	6.73	3.33	3.21
47.8	7.37	7.18	3.47	3.45
52.0	7.99	7.76	3.65	3.79
55.9	8.55	8.29	3.78	4.12
68.8	10.36	9.99	4.14	5.23
73.1	10.89	10.48	4.23	5.60
77.3	11.37	10.91	4.29	5.93
80.4	11.70	11.21	4.32	6.18
93.5	12.95	12.25	4.45	7.10
96.9	13.20	12.43	4.47	7.29
100.4	13.45	12.60	4.47	7.46
103.9	13.68	12.76	4.48	7.63
117.8	14.42	13.20	4.51	8.13
120.9	14.55	13.27	4.53	8.22
124.5	14.68	13.34	4.54	8.31
127.8	14.80	13.39	4.53	8.37
141.1	15.19	13.60	4.56	8.59
144.9	15.29	13.66	4.57	8.65
148.4	15.35	13.67	4.53	8.67
151.9	15.42	13.71	4.54	8.71
164.9	15.65	13.84	4.55	8.82
168.9	15.71	13.88	4.60	8.85
172.4	15.76	13.89	4.55	8.88
176.4	15.80	13.91	4.54	8.88
188.7	15.95	14.01	4.54	8.96
193.5	16.00	14.05	4.54	8.98
199.4	16.03	14.06	4.52	9.00
212.9	16.14	14.12	4.51	9.05
218.5	16.19	14.16	4.51	9.08
223.4	16.19	14.15	4.49	9.07
237.1	16.28	14.22	4.48	9.11
241.5	16.30	14.23	4.47	9.12
247.2	16.32	14.25	4.46	9.13
261.4	16.40	14.31	4.45	9.19

^aCorrection applied for evaporative mass loss according to evaporation rate of 0.01 g h⁻¹

Table A3.13. Mass of CO₂ gained through time in the 35% and 50% saturated medium brucite columns.

Experiment	Mass gain (g) ^a	
	medium 35% saturated 1	medium, 50% saturated 1
Time (h)		
0.0	0.00	0.00
3.5	0.57	0.52
7.5	1.02	0.89
18.0	1.90	1.64
21.9	2.26	1.92
25.5	2.56	2.21
29.0	2.90	2.47
42.5	4.16	3.55
46.1	4.51	3.88
49.7	4.86	4.18
51.7	5.05	4.36
66.0	6.31	5.47
69.0	6.52	5.66
72.4	6.74	5.86
76.3	6.96	6.09
89.8	7.58	6.75
92.8	7.70	6.82
95.8	7.76	6.93
99.1	7.83	7.03
114.3	8.07	7.41
117.3	8.11	7.46
120.5	8.13	7.52
122.7	8.15	7.55
138.3	8.24	7.79
141.4	8.25	7.83
144.5	8.26	7.87
162.9	8.30	8.07
166.0	8.31	8.10
169.9	8.31	8.13
185.7	8.30	8.28
190.0	8.32	8.31
194.5	8.30	8.32
199.4	8.29	8.34
210.3	8.27	8.39
214.5	8.27	8.43
217.8	8.23	8.42
219.2	8.26	8.44

^aCorrection applied for evaporative mass loss according to evaporation rate of 0.01 g h⁻¹

Table A3.14. Mass of CO₂ gained through time in the 15%, 35%, and 50% saturated medium brucite column duplicate experiments.

Experiment	Mass gain (g) ^a		
	medium, 15% saturated 2	medium 35% saturated 2	medium, 50% saturated 2
Time (h)			
0.0	0.00	0.00	0.00
3.0	0.43	0.47	0.45
7.1	0.90	0.97	0.89
18.2	1.87	1.83	1.71
21.5	2.13	2.12	1.97
25.0	2.40	2.45	2.24
28.9	2.69	2.82	2.54
42.0	3.46	4.08	3.71
45.0	3.62	4.41	4.01
48.1	3.75	4.74	4.31
52.6	3.92	5.23	4.76
66.4	4.29	6.61	6.06
70.0	4.35	6.92	6.40
73.2	4.35	7.18	6.63
76.9	4.40	7.45	6.92
90.0	4.49	8.18	7.79
94.0	4.51	8.34	8.01
97.3	4.52	8.46	8.17
101.0	4.52	8.53	8.30
113.5	4.52	8.76	8.73
118.3	4.53	8.82	8.85
121.5	4.55	8.86	8.94
125.1	4.49	8.85	8.98
138.3	4.50	8.97	9.27
141.2	4.51	8.96	9.32
146.1	4.49	8.96	9.38
149.0	4.45	8.94	9.40
162.7	4.42	8.97	9.58
166.7	4.42	8.96	9.62
171.5	4.40	8.97	9.66
186.3	4.36	8.97	9.81
190.7	4.36	8.97	9.85
194.6	4.35	8.97	9.87

^aCorrection applied for evaporative mass loss according to evaporation rate of 0.01 g h⁻¹

A3.4.4 Energy dispersive spectroscopy results

Representative examples of energy dispersive spectra collected from the flakey carbonate phase and nesquehonite are shown in Figure A3.4. Both phases consist of Mg, C, and O; both samples were coated with Os.

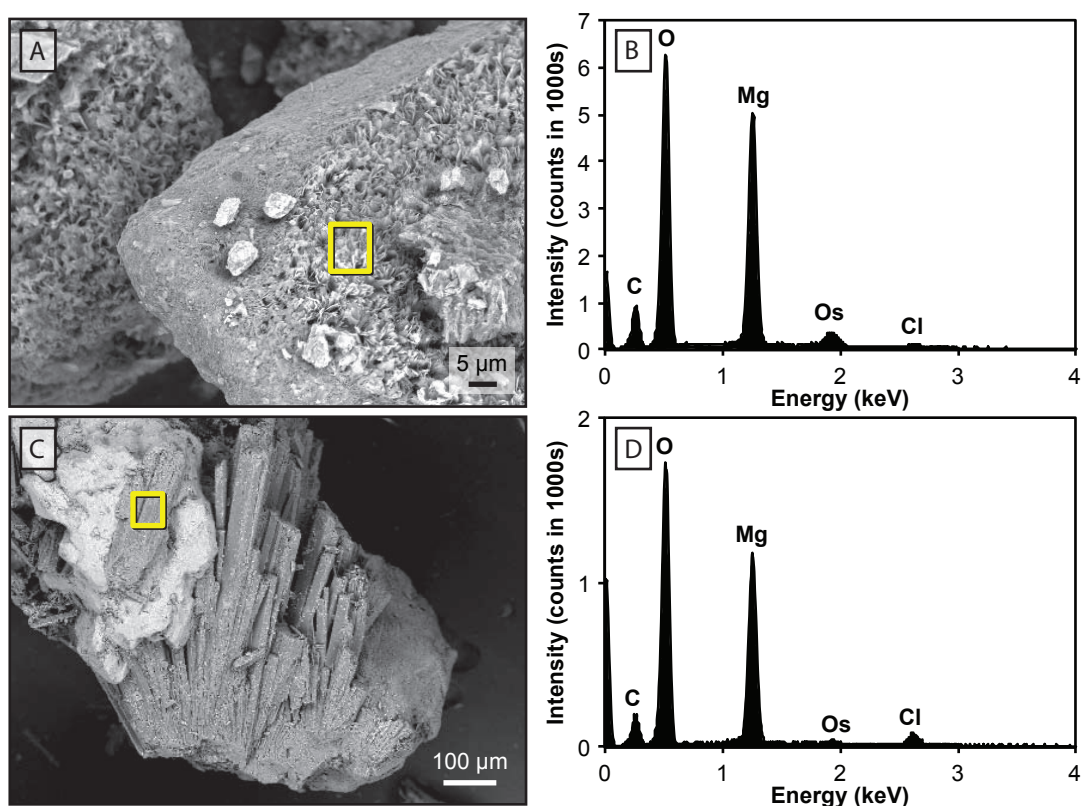


Figure A3.4. Scanning electron micrographs and energy dispersive spectra (EDS) of representative reaction products. Micrograph of flakey carbonate coating a brucite grain (A) and the associated EDS spectrum (B). Micrograph of nesquehonite (C) and the associated EDS spectrum (D). Yellow outlines indicate the area from which the EDS spectrum was collected.

A3.5 Discussion

A3.5.1 Threshold model functional form

An example of the evolution of reaction rate and extent of brucite reaction as dictated by the geometric versus threshold models is shown in Figure A3.5.

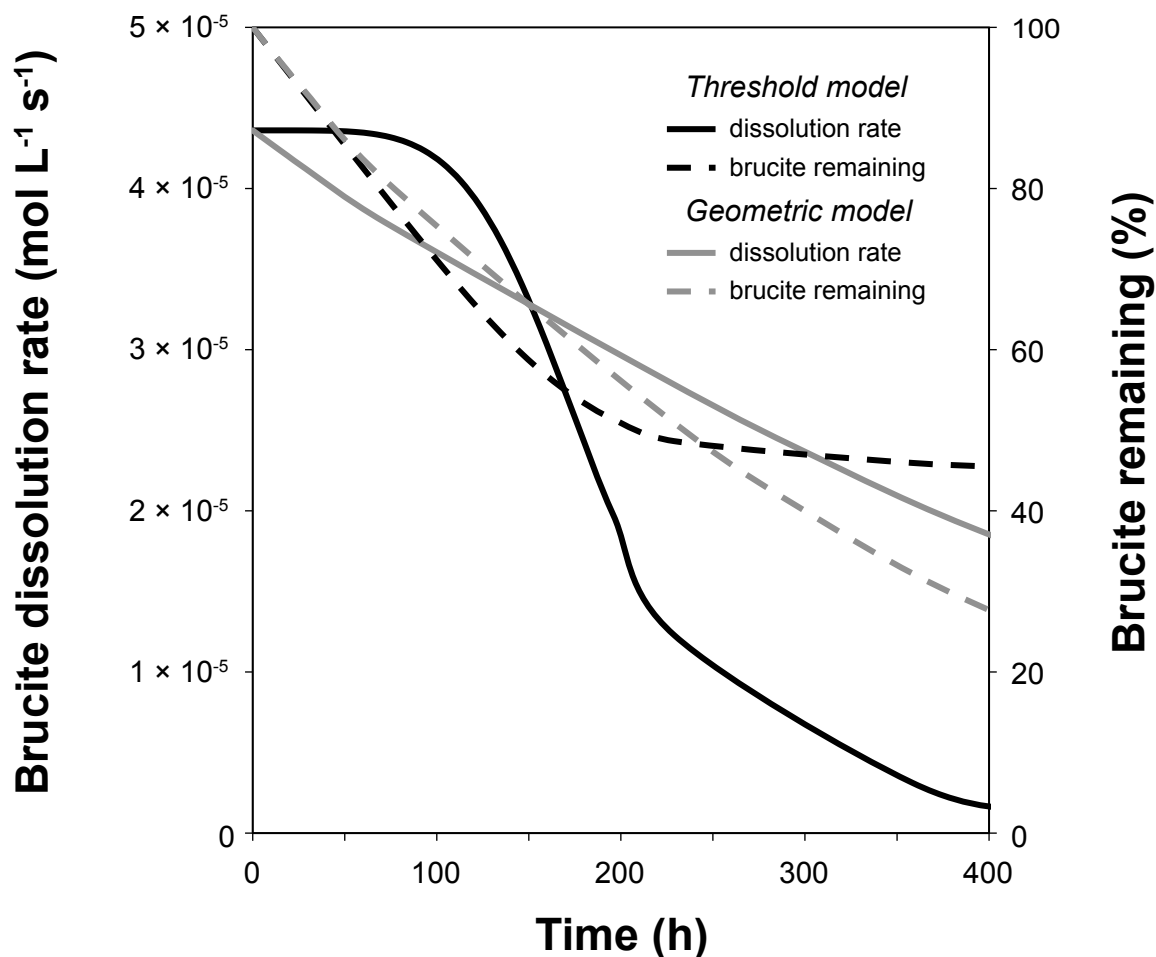


Figure A3.5. Calculated brucite dissolution rate and percent brucite remaining versus time in a hypothetical column containing 10 wt.% brucite ore. Black lines were calculated using the threshold model, whereas grey lines were calculated using the geometric model. Solid and dashed lines represent the brucite dissolution rate and percent brucite remaining, respectively.

A3.5.2 CO₂ injection pressure calculations

Darcy's law (Eq. A3.1; Molins and Mayer, 2007) was used to calculate the decrease in gas flow associated with increased water saturation at a constant pressure.

$$q_g = -\frac{k_{rg}\mathbf{k}}{\mu_g}(\nabla p_g + \rho_g g \nabla z) \quad (\text{Eq. A3.1})$$

where q_g is the Darcy flux (m s^{-1}), k_{rg} is the relative permeability with respect to the gaseous phase, μ_g is the viscosity of the gaseous phase ($\text{kg m}^{-1} \text{s}^{-1}$), $\mathbf{k}$ is the intrinsic permeability of the porous medium (m^2), p_g is the total gaseous phase pressure (Pa), ρ_g is the density of the gas phase (kg m^{-3}), g is the acceleration due to gravity (m s^{-2}), and z is a vertical distance (m). An intrinsic permeability representative of fine grained mine tailings equal to $5 \times 10^{-15} \text{ m}^2$ was utilized for the calculation (e.g., Wilson et al., 2014; Chapter 7). For illustrative purposes, the change in Darcy flux was assumed to correlate to relative permeability, assuming ∇p_g and ∇z remained constant. The gaseous phase viscosity and density were calculated utilizing a 90% N₂ and 10% CO₂ gaseous phase according to Molins and Mayer (2007), and were equal to $1.7 \times 10^{-5} \text{ kg m}^{-1} \text{s}^{-1}$, and 1.22 kg m^{-3} , respectively. The relative permeability was calculated according to the following equation (Eq. A3.2):

$$k_{rg} = (1 - S_{ea})^{1/2} \left(1 - S_{ea}^{1/m}\right)^{2m} \quad (\text{Eq. A3.2})$$

where m is a soil hydraulic function parameter equal to 0.29 in this case, and S_{ea} is the effective saturation defined by Equation A3.3:

$$S_{ea} = \frac{S_w - S_{rl}}{1 - S_{rl}} \quad (\text{Eq. A3.3})$$

where S_w is the water saturation, and S_{rl} is the residual saturation of water.

In order to calculate the curve shown in Figure 5.9, the value of S_a was varied. The

percent reduction in gas flux (Eq. A3.4) was determined compared to an initial water saturation of 0.001, which was considered the residual saturation.

$$\% \text{ reduction in gas flux} = \frac{q_g}{q_{g_0}} \times 100\% \quad (\text{Eq. A3.4})$$

where q_g is the Darcy flux at a given value of S_w and q_{g_0} is the initial Darcy flux at residual saturation ($S_a = 0.001$).

Appendix 4: Appendix to Chapter 6¹¹

Physical and chemical influences of water on mineral carbonation in variably saturated porous media: Implications for CO₂ sequestration

A4.1 Detailed methods

A4.1.1 Detailed experimental methods

Solutions were prepared by dissolving MgCl₂·6H₂O (from Fisher Scientific; assayed at 99.9%) in deionized water to provide a concentration of 0.1 M Mg. Initial solutions contained $<9.0 \times 10^{-9}$ M dissolved inorganic carbon (DIC). A volume of 7.2 L was added to both 35% saturated columns, whereas 11.2 L of solution was added to the 60% saturated column.

A4.1.2 Sampling techniques

Solid samples were removed from 10 cm intervals along the depth of the columns immediately following each experiment. Discrete triplicate samples were collected from at least three depth intervals to assess spatial heterogeneity in mineral distribution. From all other intervals the entirety of material was removed and mechanically homogenized, and aliquots were removed for subsequent analysis. A portion of the sampled material was ring-milled for 30 s to form a powder for X-ray fluorescence spectroscopy, X-ray diffraction, and %CO₂ analysis, and the remainder was set aside for scanning electron microscopy.

Water samples for DIC concentration and $\delta^{13}\text{C}_{\text{DIC}}$ analyses from 35% 2 and the 60% saturated experiments were diluted with deionized water ($<9.0 \times 10^{-9}$ M DIC) immediately

¹¹A version of this appendix will be submitted as the Supplementary Material for the version of Chapter 6 that is submitted for publication in a peer-reviewed international journal. It is reproduced here with the permission of all authors. The submitted manuscript will be authored and titled as: Harrison, A. L., Dipple, G.M., Mayer, K. U. and Power, I.M. Physical and chemical influences of water on mineral carbonation in variably saturated porous media: Implications for CO₂ sequestration.

following sampling to prevent precipitation of solids prior to analysis. Cation samples were acidified to 2% ultrapure HNO_3 immediately following sampling. All water samples were stored at $\sim 4^\circ\text{C}$ prior to analysis in vials with no headspace to prevent gas exchange.

Gas samples were extracted using 60 mL syringes connected to tubing that extended into the center of the columns at each of the three sampling ports. Tubes were capped with fabric mesh to prevent contamination of samples by solid materials. Syringes were flushed three times to obtain representative samples. Gas samples were stored in previously evacuated 100 mL glass vials with rubber septa and crimped aluminum seals. Vials were capped with silicone during storage to prevent leakage.

A4.1.3 Characterization of solids

A4.1.3.1 Particle size distribution and surface area analysis

The particle size distribution of the brucite ore used in the experiments was determined by sieving. The initial surface area of the brucite ore was determined by multipoint BET with N_2 adsorption using a Quantachrome Autosorb-1 surface area analyzer.

A4.1.3.2 X-ray fluorescence spectroscopy

The major oxide composition of the initial solids and solid experimental reaction products from 35% 1 and the 60% saturated experiments were determined using X-ray fluorescence (XRF) spectroscopy with a Philips PW-1480 wavelength dispersive XRF spectrometer at The University of Western Ontario.

A4.1.3.3 X-ray powder diffraction methods

Synthetic and natural mineral phases in all solid samples were identified using X-ray diffraction (XRD) methods. Rietveld refinement of XRD data was used to quantify the weight percent (wt.%) abundance of all phases. Aliquots of powdered samples were spiked with 10 wt.% highly crystalline CaF_2 to allow quantification of the X-ray amorphous (or non-

crystalline) content (e.g., Gualtieri, 2000). All spiked aliquots were ground further under ethanol for 5 min using a McCrone[®] micronizing mill and agate grinding elements to ensure homogenization and reduce the mean particle size. Micronized aliquots were dried for ~24 h then gently disaggregated with an agate mortar and pestle. Back loaded powder mounts were prepared on sandpaper to minimize preferred orientation (Raudsepp and Pani, 2003).

The XRD data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with CoK α radiation and a step size of 0.04° over a range of 3-80°2 θ at 0.09 s/step. Incident and diffracted beam soler slits, 0.6 mm divergence slit, a Lynx Eye detector, and Fe monochromator foil were used. A long fine focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6°. Search-match software by Bruker (DIFFRACplus EVA 14; Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement was completed using Topas Version 3 refinement software (Bruker AXS, 2004). The sources of crystal structure data used in refinements are provided in Table A4.1.

A4.1.3.4 Inorganic carbon content

The inorganic carbon content in all pulverized solid samples was determined using a CM5130 acidification module with a Model 5014 CO₂ Coulometer from UIC Inc. Aliquots of the ring-milled solid samples were acidified to release CO_{2(g)}, which was quantified using a photodetector that monitors the color change of a colorimetric pH indicator. Analysis of replicate samples indicated measurements were reproducible within 0.18% CO₂ by mass. This method has a detection limit of 0.37% CO₂. Inorganic carbon content values are expressed as %CO₂ by mass.

A4.1.3.5 Scanning electron microscopy

Samples were prepared for scanning electron microscopy (SEM) both as thin sections of partially cemented reaction products and disaggregated powders on carbon adhesive tabs

on aluminum specimen mounts. Images were collected using a LEO (Zeiss) 1540 XB field emission - scanning electron microscope (FE-SEM), equipped with a backscattered electron detector at an operating voltage of 10.0 kV, and an FEI Helios NanoLab 650 SEM operating at 10.0 kV or 3.0 kV. Samples were coated either with Os or Ir.

A4.1.4 Aqueous chemistry

The DIC concentration of water samples was analyzed using a Lachat IL550 TOC-TN analyzer. Aliquots of sample were added to a 10% H_3PO_4 solution to release $\text{CO}_{2(g)}$, which was measured with an infrared detector with a detection limit of 0.5 mg L^{-1} . The total aqueous Mg concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian 725-ES Optical Emission Spectrometer. This method had a detection limit of 0.2 mg L^{-1} .

A4.1.5 Stable carbon isotopic composition

The stable carbon isotopic composition of the gas and solid phase CO_2 was analyzed with an LGR[®] off-axis integrated cavity output laser spectrometer using the method of Barker et al. (2011). Solids were acidified with 85% H_3PO_4 at $\sim 70^\circ\text{C}$ for approximately 1 h in sealed vials to release CO_2 which was then drawn directly into the instrument for analysis. The error on these measurements was equal to or better than $\pm 0.4\text{‰}$ (1σ). The stable carbon isotopic composition of the DIC was measured by continuous flow using a Finnigan Mat DeltaPlus isotope ratio mass spectrometer with an analytical precision of $\pm 0.2\text{‰}$ (2σ) (St-Jean, 2003). All $\delta^{13}\text{C}$ values are reported relative to Vienna Pee Dee Belemnite (VPDB) in units of per mil (‰), with $\delta^{13}\text{C}$ defined as follows (Eq. A4.1; Craig, 1957):

$$\delta(\text{‰}) = \left[\left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \right] \times 1000 \quad (\text{Eq. A4.1})$$

where R_{sample} and R_{standard} are equal to the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample and a standard,

respectively.

A4.1.6 Soil water characteristic curves and volumetric moisture content

The soil water characteristic curves of two LM50 quartz samples were determined using Tempe cell tests (Fredlund and Rahardjo, 1993). Samples were initially water saturated, and the applied suction was varied by changing the elevation difference between the base of each Tempe cell and a hydraulically connected drainage bottle. All tests were conducted at atmospheric pressure. The elevation head gradient was maintained for at least 24 h or until equilibrium was reached; at which point the masses of the Tempe cells were recorded to determine the equilibrium water content of the porous media at each value of applied suction. These data were used to construct a soil water retention curve, which was fit using the van Genuchten function (van Genuchten, 1980) with SoilVision software (Fredlund, 2004), providing an estimate of the residual moisture content of the porous media and soil hydraulic function parameters. The parameters obtained from the Tempe cells were then adjusted using MIN3P-DUSTY (Mayer et al., 2002; Molins and Mayer, 2007) to match observed water saturation distributions in columns prior to reaction.

To provide higher resolution measurement of the water saturation profile at the end of each experiment than was provided by the three sensors, water saturation was estimated gravimetrically using two aliquots from each 10 cm depth interval at the end the experiment. Aliquots were removed using a graduated cylinder so that their volume could be measured and were weighed while wet. They were then placed in an oven at 70°C for ~24 h to dry, at which point they were reweighed. The gravimetric moisture content was converted to volumetric moisture content (ratio of water volume to total volume) using the measured bulk volume and the assumption that the density of water was 1 g cm⁻³. An average of the measurements from the duplicate aliquots was used to represent the volumetric water content at a given depth interval.

Table A4.1. Sources of crystal structure data for Rietveld refinement.

Mineral	Source
Quartz	Glinnemann et al. (1992)
Brucite	Catti et al. (1995)
Nesquehonite	Giester et al. (2000)
Fluorite	Batchelder and Simmons (1964)
Corundum	Finger and Hazen (1978)
Magnesite	Markgraf and Reeder (1985)
Muscovite-2M ₁	Liang and Hawthorne (1996)
Lizardite-1T	Mellini and Viti (1994)
Hydromagnesite	Akao and Iwai (1977)
Dolomite	Ross and Reeder (1992)
Pyroaurite	Olowe (1995)

A4.2 Transport parameters and initial conditions employed in reactive transport models

The reactive transport parameters and variables employed in the MIN3P-DUSTY simulations are summarized in Tables A4.2 and A4.3. No flow boundary conditions were applied to both the top and bottom of the column for the water phase. An initial hydraulic head of -0.23 m was applied throughout the column, which corresponded to the approximate initial water content of 35% 1.

Table A4.2. Initial brucite volume fractions and surface areas employed in the MIN3P-DUSTY simulations and experimental brucite volume fractions and surface areas.

	Initial volume fraction (ϕ^b)	Threshold volume fraction (ϕ^p)	Initial SA (m^2g^{-1})
Experiment	0.037	n/a ^a	2.4
Base case model	0.037	0.0167	0.16
Dry pore model	$0.037 \times S_w^c$	$0.0167 \times S_w$	$0.16 \times S_w$
Water film model	0.037	$0.037 - (0.102 \times S_w)$	0.16

^an/a = not applicable^c S_w = water saturation**Table A4.3.** Physical and transport parameters employed for simulations using MIN3P-DUSTY.^a

Parameter	Value	Reference
Saturated hydraulic conductivity (m s^{-1})	1.00×10^{-3}	estimated
Porosity	0.52	this study
Soil-water retention curve		
α (m^{-1})	4.0	this study
n	4.5	this study
S_{ri}	0.08	this study
air entry pressure (m)	-0.18	this study
Aqueous phase diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	1.00×10^{-9}	Molins and Mayer (2007)
Gas phase binary diffusion coefficient ($\text{CO}_2\text{-N}_2$) ($\text{m}^2 \text{s}^{-1}$)	1.649×10^{-5}	Molins and Mayer (2007)
Gas phase viscosity ($\text{Pa}\cdot\text{s}$)		
CO_2	1.46×10^{-5}	Molins and Mayer (2007)
N_2	1.75×10^{-5}	Molins and Mayer (2007)

^aTemperature is 298 K.

A4.3 Detailed results

A4.3.1 Particle size distribution of the brucite ore

The particle size distribution of the brucite ore is shown in Figure A4.1.

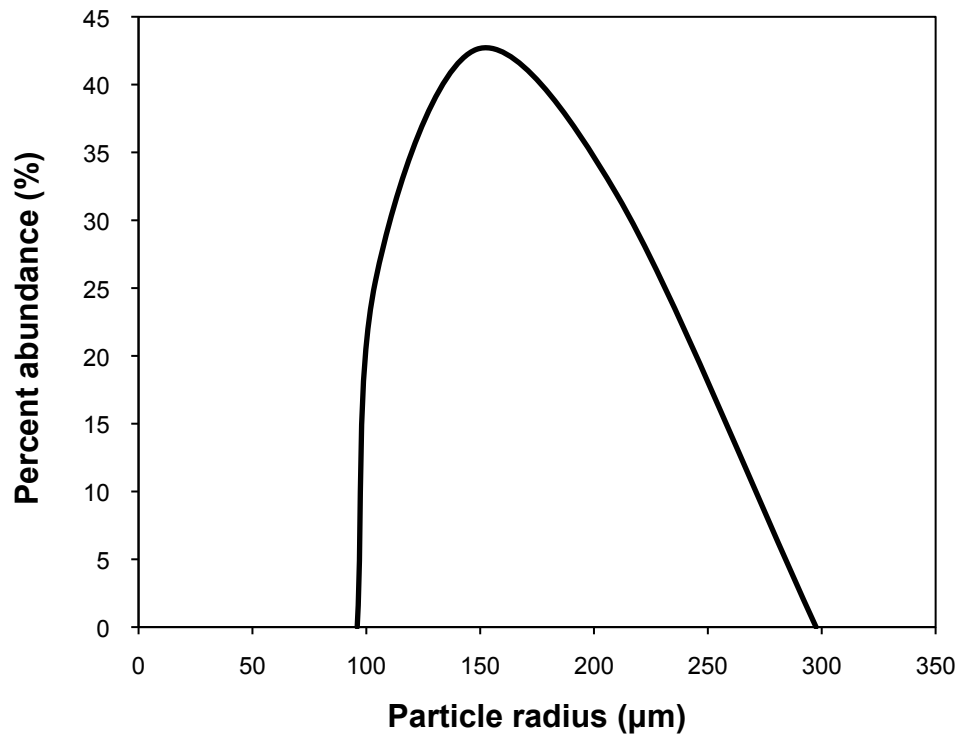


Figure A4.1. Particle size distribution of the brucite ore.

A4.3.2 Soil-water characteristic curve

The soil-water characteristic curves measured from two samples of the quartz sand are shown in Figure A4.2.

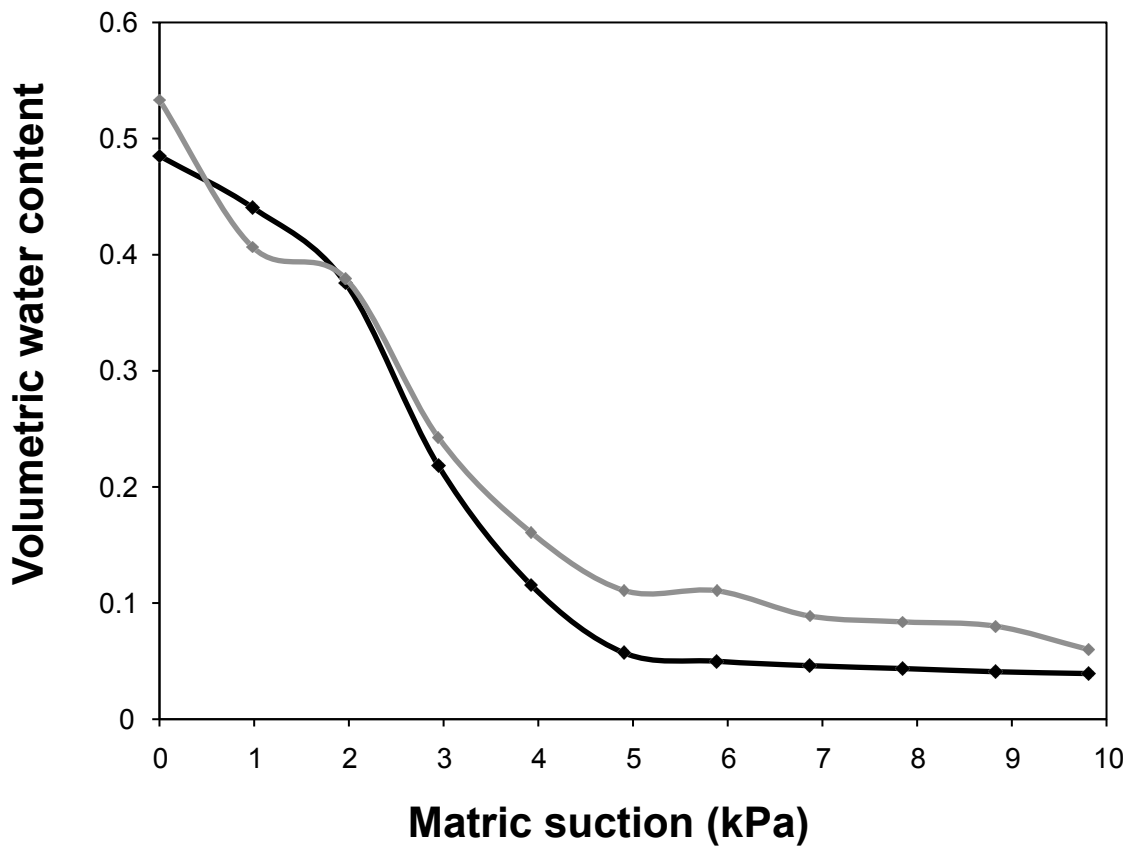


Figure A4.2. Volumetric water content versus matric suction from the Tempe pressure cell tests of duplicate initial LM50 quartz samples.

A4.3.3 Qualitative characterization of initial material

Scanning electron micrographs of the initial brucite ore and LM50 quartz sand are shown in Figure A4.3.

A4.3.4 Water saturation and temperature

Changes in water saturation and temperature with time in each experiment are shown in Figure A4.4.

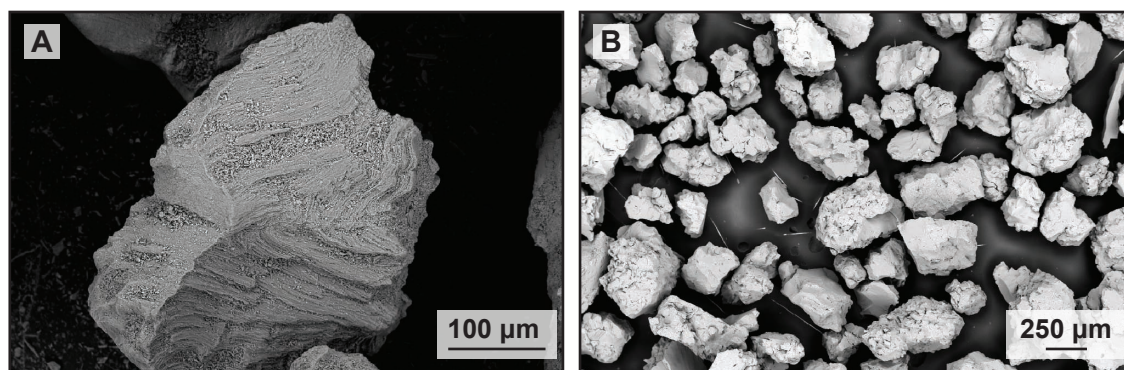


Figure A4.3. Representative scanning electron micrographs of initial solids. Initial pulverized brucite ore with fine powder on the surface of a larger brucite grain (A) and initial quartz particles (B). The large grain in (A) is representative of the bulk of the brucite.

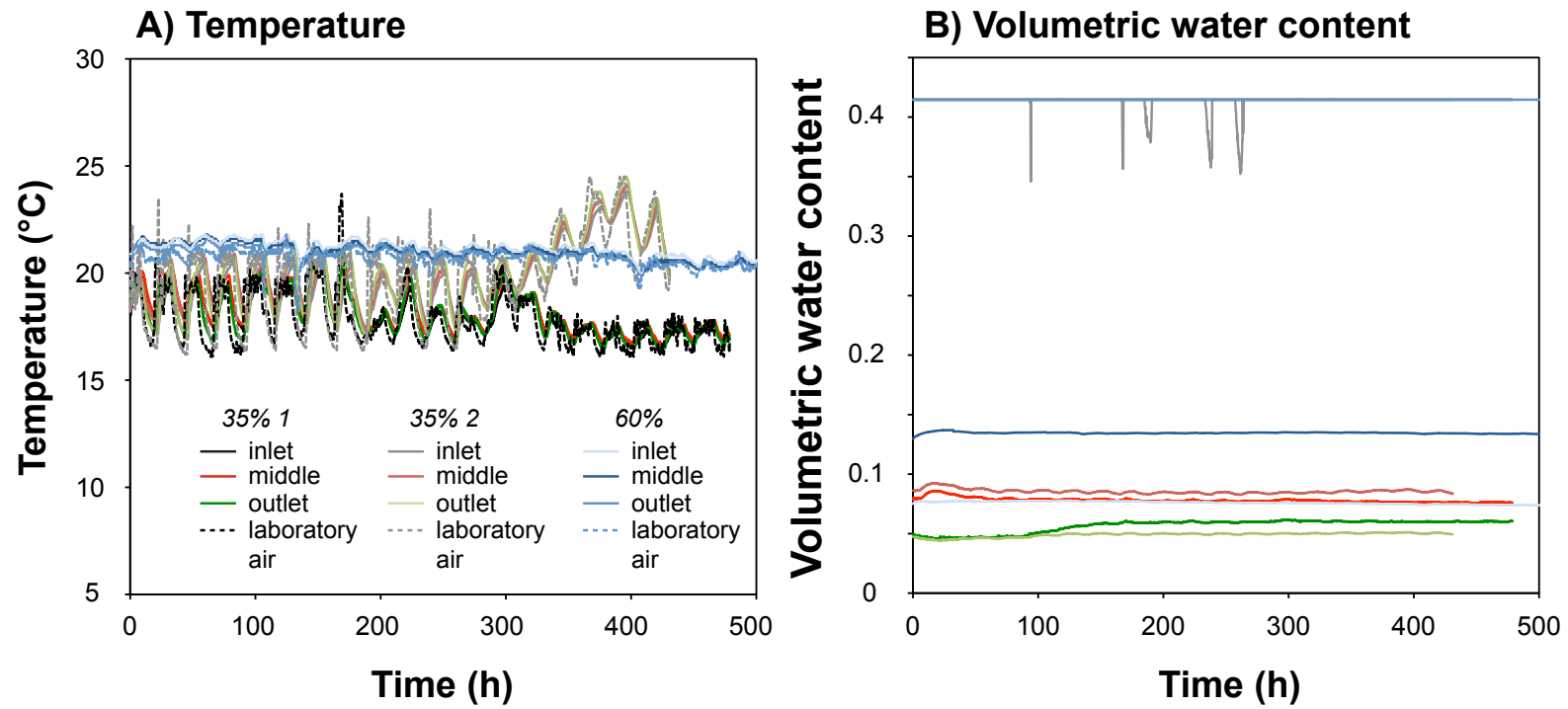


Figure A4.4. Temperature (A) and volumetric water content (B) versus time in all experiments as measured with 5TM sensors.

A4.3.5 Reaction stoichiometry, mineralogy, and carbonation extent

The %CO₂ and Rietveld refinement results are summarized in Tables A4.4-A4.6. The CO₂, Mg, and H₂O mass balance and reaction stoichiometry calculations are summarized in Tables A4.7-A4.14. An example of a typical X-ray diffraction pattern collected from experimental run products is shown in Figure A4.5. The typical orange coloration of reaction products and its relationship to solid %CO₂ is demonstrated in Figure A4.6.

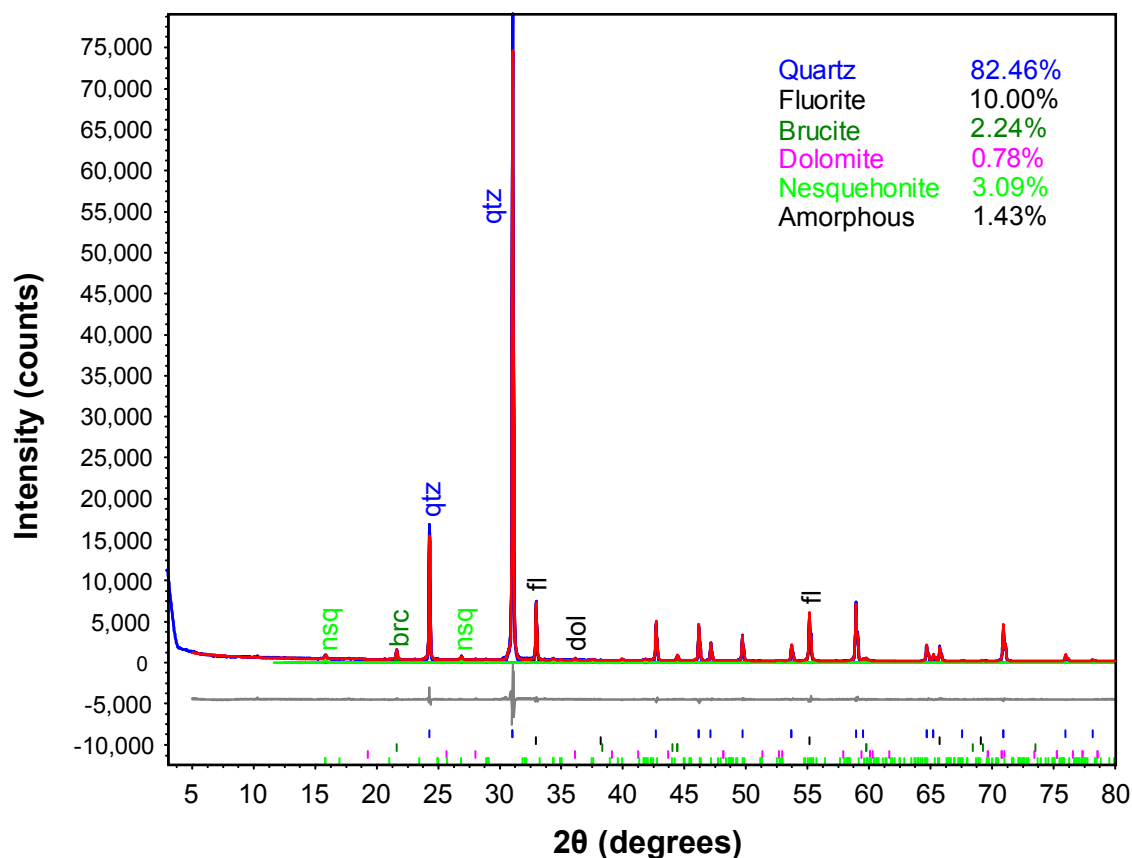


Figure A4.5. Representative X-ray diffraction pattern and Rietveld refinement plot of reacted solids from the 40-50 cm depth interval in the 60% saturated column. The blue line represents the observed data that is overlain by the calculated Rietveld refinement pattern (red line). The grey line shows the residual pattern, and the vertical lines below show the positions of the Bragg reflections for each phase. Blue, black, dark green, pink, and bright green lines indicate calculated Rietveld refinement patterns for quartz, fluorite, brucite, dolomite, and nesquehonite, respectively. Bragg reflections for each mineral are indicated by these same colors. The fluorite was added to experimental samples to allow calculation of the X-ray amorphous or nano-crystalline content in each sample.

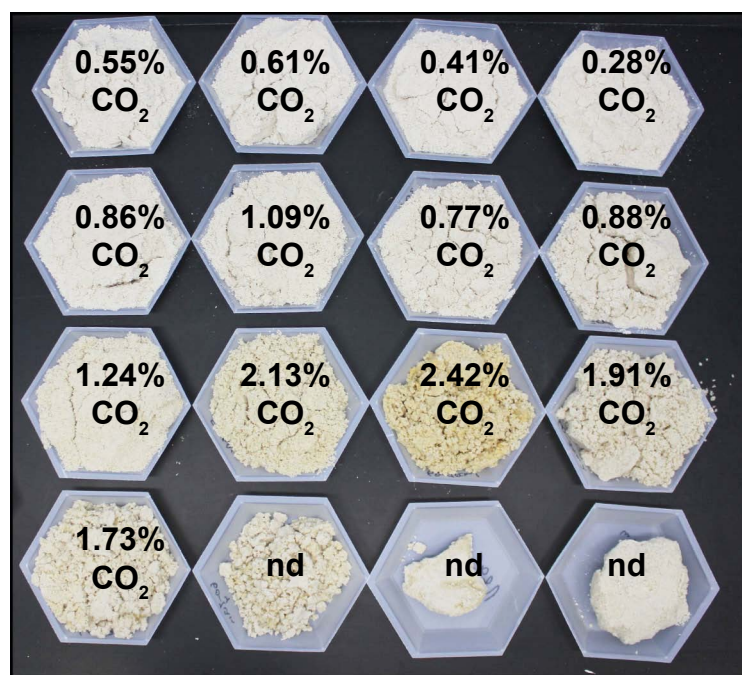


Figure A4.6. Color of experimental end products from 35% 2 and its correspondence to the extent of carbonation (nd = no data).

Table A4.4. Rietveld refinement and total solid phase CO₂ (%CO₂) data for 35% 1.

Depth midpoint (cm)	Quartz (wt.%)	Brucite (wt.%)	Dolomite (wt.%)	Mica ^a (wt.%)	Nesquehonite (wt.%)	Lansfordite (wt.%)	Amorphous (wt.%)	CO ₂ secondary (wt.%)
5	93.4	5.0	0.7	0.9	0.0	0.0	0.0	0.5
5	93.4	5.1	0.5	1.0	0.0	0.0	0.0	0.4
5	91.1	6.3	0.6	0.7	0.0	0.0	1.3	0.6
15	93.6	4.8	0.7	0.9	0.0	0.0	0.0	0.6
25	93.3	5.0	0.7	0.0	0.0	0.0	1.0	0.8
35	93.1	4.9	0.7	0.6	0.0	0.0	0.1	1.0
35	93.6	5.1	0.7	0.0	0.0	0.0	0.6	1.2
35	92.9	5.5	0.7	0.8	0.0	0.0	0.0	1.2
45	93.1	3.7	0.6	0.7	0.7	1.2	0.0	1.3
55	88.0	4.6	0.8	0.7	2.9	1.6	1.4	2.3
65	88.5	2.7	0.6	0.9	6.4	0.5	0.5	2.7
65	90.5	2.5	0.7	0.9	5.0	0.5	0.0	2.5
65	90.5	2.6	0.6	0.9	4.2	0.0	1.2	3.2

^aMica was fit with muscovite during Rietveld refinement.

Table A4.5. Rietveld refinement and total solid phase CO₂ (%CO₂) data for 35% 2.

Depth midpoint (cm)	Quartz (wt.%)	Brucite (wt.%)	Dolomite (wt.%)	Mica ^a (wt.%)	Nesquehonite (wt.%)	Lansfordite (wt.%)	Amorphous (wt.%)	CO ₂ secondary (wt.%)
5	92.6	6.7	0.7	0.0	0.0	0.0	0.0	0.6
5	91.8	6.2	0.8	0.0	0.0	0.0	1.2	0.6
5	93.4	6.0	0.6	0.0	0.0	0.0	0.0	0.4
15	93.7	5.7	0.7	0.0	0.0	0.0	0.0	0.3
25	92.2	6.6	0.9	0.0	0.0	0.0	0.3	0.9
35	93.2	4.9	0.6	0.0	0.0	0.0	1.3	1.1
35	93.5	4.5	0.7	0.0	0.0	0.0	1.3	0.8
35	90.9	5.3	0.7	0.0	0.0	0.0	3.0	0.9
45	93.7	4.0	0.6	0.0	0.0	0.0	1.6	1.2
55	90.8	4.0	0.7	0.0	0.9	0.0	3.6	2.1
65 ^b	88.4	1.8	0.7	0.0	2.2	0.0	6.9	2.4
65 ^c	91.0	3.5	0.8	0.0	0.0	0.0	4.8	1.9
65	93.7	3.3	0.9	0.0	0.0	0.0	2.2	1.7

^aMica was fit with muscovite during Rietveld refinement.^bSample was taken from a visible reaction finger.^cSample was taken from a visible dead-zone.

Table A4.6. Rietveld refinement and total solid phase CO₂ (%CO₂) data for the 60% saturated experiment.

Depth midpoint (cm)	Quartz (wt.%)	Brucite (wt.%)	Dolomite (wt.%)	Mica ^a (wt.%)	Nesquehonite (wt.%)	Lansfordite (wt.%)	Amorphous (wt.%)	CO ₂ secondary (wt.%)
5	93.9	4.7	0.7	0.7	0.0	0.0	0.0	0.7
5	93.6	5.6	0.8	0.0	0.0	0.0	0.0	0.7
5	93.4	5.0	0.6	0.0	0.0	0.0	1.0	0.7
15	93.2	5.1	0.7	0.6	0.0	0.0	0.4	1.0
25	93.4	5.0	0.6	0.0	0.0	0.0	1.0	1.2
35	92.3	4.5	0.6	0.8	0.0	0.0	1.8	1.3
35	93.1	4.2	0.8	0.0	0.0	0.0	1.9	1.4
35	93.2	5.1	0.7	0.6	0.0	0.0	0.4	1.4
45 ^b	94.6	4.8	0.7	0.0	0.0	0.0	0.0	1.1
45 ^c	91.6	2.5	0.9	0.0	3.4	0.0	1.6	2.4
45								1.6
55 ^c	93.4	1.3	0.7	0.0	3.1	0.0	1.5	2.0
55 ^b	94.3	5.0	0.6	0.0	0.0	0.0	0.1	0.4
65	92.9	4.2	1.1	0.9	0.0	0.0	0.8	2.0
65	92.4	4.2	0.0	0.0	0.0	0.0	3.4	2.3
65	84.3	3.1	0.8	1.0	4.0	0.0	6.8	3.0

^aMica was fit with biotite during Rietveld refinement.^bSample was taken from a visible reaction finger.^cSample was taken from a visible dead-zone.

Table A4.7. Solid phase CO₂ mass balance for 35% 1.

Depth (cm)	Total sample mass (g)	CO₂ total (%)	CO₂ in secondary carbonates (%)	Total mass CO₂ in sample (g)	Dolomite abundance (wt.%)	Dolomite mass (g)	Mass of CO₂ in dolomite (g)
5	128.31	1.12	0.49	1.44	0.65	0.84	0.40
5	145.08	1.08	0.44	1.57	0.54	0.79	0.38
5	107.08	1.22	0.58	1.30	0.63	0.68	0.32
15	121.65	1.22	0.59	1.49	0.66	0.81	0.39
25	128.91	1.40	0.77	1.81	0.73	0.94	0.45
35	143.65	1.64	1.01	2.36	0.71	1.02	0.48
45 ^a	128.53	1.93	1.29	2.48	0.62	0.80	0.38
55 ^a	129.61	2.89	2.25	3.74	0.79	1.02	0.49
65 ^a	129.79	3.30	2.66	4.28	0.56	0.73	0.35

^aNesquehonite-bearing samples

Table A4.7 (continued). Solid phase CO₂ mass balance for 35% 1.

Depth (cm)	Nesquehonite abundance (wt.%)	Nesquehonite mass (g)	Mass of CO ₂ in nesquehonite (g)	Lansfordite abundance (wt.%)	Lansfordite mass (g)	Mass of CO ₂ in lansfordite (g)	Mass of CO ₂ in nesquehonite + lansfordite (g)	Mass of CO ₂ in flakey carbonate (g)	Moles of CO ₂ in flakey carbonate
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.04	0.02
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.19	0.03
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.98	0.02
15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.10	0.03
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.35	0.03
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.88	0.04
45 ^a	0.72	0.93	0.30	1.20	1.54	0.39	0.69	1.41	0.03
55 ^a	2.93	3.80	1.21	1.61	2.08	0.53	1.75	1.51	0.03
65 ^a	6.35	8.24	2.63	0.51	0.66	0.17	2.80	1.13	0.03

^aNesquehonite-bearing samples

Table A4.8. Solid phase Mg mass balance for 35% 1.

Depth (cm)	Total sample mass (g)	MgO (%)	Brucite abundance (wt.%)	Total mass MgO in sample (g)	Total moles Mg in sample	Moles Mg in dolomite	Moles Mg in brucite	Moles Mg in secondary carbonates	Moles Mg in nesquehonite	Moles Mg in lansfordite	Moles Mg in flakey carbonate	Mass Mg in flakey carbonate (g)
5	128.31	5.42	5.02	6.96	0.17	4.55×10^{-3}	0.11	0.06	0.00	0.00	0.06	1.38
5	145.08	5.27	5.10	7.65	0.19	4.28×10^{-3}	0.13	0.06	0.00	0.00	0.06	1.41
5	107.08	6.27	6.28	6.71	0.17	3.67×10^{-3}	0.12	0.05	0.00	0.00	0.05	1.14
15	121.65	5.45	4.84	6.63	0.16	4.38×10^{-3}	0.10	0.06	0.00	0.00	0.06	1.42
25	128.91	5.63	5.00	7.26	0.18	5.12×10^{-3}	0.11	0.06	0.00	0.00	0.06	1.55
35	143.65	6.12	4.87	8.79	0.22	5.51×10^{-3}	0.12	0.09	0.00	0.00	0.09	2.22
45 ^a	128.53	5.10	3.65	6.56	0.16	4.33×10^{-3}	0.08	0.08	0.01	0.01	0.06	1.49
55 ^a	129.61	6.58	4.63	8.53	0.21	5.54×10^{-3}	0.10	0.10	0.03	0.01	0.06	1.52
65 ^a	129.79	5.86	2.75	7.61	0.19	3.95×10^{-3}	0.06	0.12	0.06	0.00	0.06	1.44

^aNesquehonite-bearing samples

Table A4.9. Solid phase H₂O mass balance for 35% 1.

Depth (cm)	Total sample mass (g)	Volatile ^b (%)	Total volatile mass in sample (g)	Volatile mass in brucite (g)	Volatile mass contributed by CO ₂ (g)	Volatile mass contributed by water in carbonates (g)	Moles water in carbonates	Moles water in nesquehonite	Moles water in lansfordite	Moles water in flakey carbonate	Mass water in flakey carbonate (g)
5	128.31	3.85	4.94	2.16	1.44	1.34	0.07	0.00	0.00	0.07	1.34
5	145.08	3.81	5.53	2.48	1.57	1.48	0.08	0.00	0.00	0.08	1.48
5	107.08	4.28	4.58	2.25	1.30	1.02	0.06	0.00	0.00	0.06	1.02
15	121.65	4.00	4.87	1.97	1.49	1.40	0.08	0.00	0.00	0.08	1.40
25	128.91	4.40	5.67	2.16	1.81	1.71	0.09	0.00	0.00	0.09	1.70
35	143.65	5.24	7.53	2.35	2.36	2.82	0.16	0.00	0.00	0.16	2.82
45 ^a	128.53	4.95	6.36	1.57	2.48	2.31	0.13	0.02	0.04	0.06	1.14
55 ^a	129.61	6.09	7.89	2.01	3.74	2.14	0.12	0.08	0.06	>0	n/a
65 ^a	129.79	7.55	9.80	1.20	4.28	4.32	0.24	0.18	0.02	0.04	0.75

^aNesquehonite-bearing samples^bDetermined by Loss-on-ignition

Table A4.10. Overall reaction stoichiometry and stoichiometry of flakey carbonate phase in 35% 1.

Depth (cm)	Overall reaction stoichiometry			Flakey carbonate phase stoichiometry		
	Mg:C	H ₂ O:C	H ₂ O:Mg	Mg:C	H ₂ O:C	H ₂ O:Mg
5	1.8	2.3	1.3	2.4	3.2	1.3
5	1.6	2.3	1.4	2.2	3.0	1.4
5	1.6	1.9	1.2	2.1	2.5	1.2
15	1.8	2.3	1.3	2.4	3.1	1.3
25	1.6	2.3	1.5	2.1	3.1	1.5
35	1.7	2.9	1.7	2.2	3.7	1.7
45 ^a	1.4	2.3	1.6	1.9	2.0	1.0
55 ^a	1.2	1.4	1.2	1.9	n/a	n/a
65 ^a	1.3	2.5	1.9	2.3	1.6	0.7
Average ^b :	1.5	2.2	1.5	2.2	3.1	1.4

^aNesquehonite-bearing samples
^bNesquehonite-bearing samples not included in calculation of average stoichiometry of the flakey carbonate phase.

Table A4.11. Solid phase CO₂ mass balance for the 60% saturated column.

Depth (cm)	Total sample mass (g)	CO ₂ total (%)	CO ₂ in secondary carbonates (%)	Total mass CO ₂ in sample (g)	Dolomite abundance (wt.%)	Dolomite mass (g)	Mass of CO ₂ in dolomite (g)
5	141.97	1.44	0.74	2.05	0.71	1.01	0.48
5	144.76	1.44	0.74	2.09	0.81	1.17	0.56
5	146.49	1.42	0.72	2.08	0.61	0.90	0.43
15	136.26	1.69	0.99	2.30	0.70	0.95	0.45
25	153.51	1.89	1.19	2.91	0.61	0.94	0.45
35	157.71	1.98	1.28	3.12	0.65	1.02	0.49
35	140.45	2.08	1.37	2.91	0.78	1.10	0.52
35	155.37	2.11	1.41	3.28	0.69	1.08	0.52
45	161.10	1.78	1.08	2.86	0.68	1.09	0.52
45 ^a	174.30	3.13	2.43	5.45	0.87	1.52	0.73
55 ^a	189.19	2.72	2.01	5.14	0.66	1.25	0.60
55	229.43	1.14	0.44	2.62	0.61	1.41	0.67
65	151.47	2.68	1.98	4.06	1.10	1.67	0.80
65	180.70	2.98	2.28	5.38	0.00	0.00	0.00
65 ^a	152.32	3.71	3.01	5.66	0.78	1.19	0.57

^aNesquehonite-bearing samples

Table A4.11 (continued). Solid phase CO₂ mass balance for the 60% saturated column.

Depth (cm)	Total sample mass (g)	Nesquehonite abundance (wt.%)	Nesquehonite mass (g)	Mass of CO ₂ in nesquehonite (g)	Mass of CO ₂ in flakey carbonate (g)	Moles of CO ₂ in flakey carbonate
5	141.97	0.00	0.00	0.00	1.57	0.04
5	144.76	0.00	0.00	0.00	1.53	0.03
5	146.49	0.00	0.00	0.00	1.65	0.04
15	136.26	0.00	0.00	0.00	1.85	0.04
25	153.51	0.00	0.00	0.00	2.46	0.06
35	157.71	0.00	0.00	0.00	2.64	0.06
35	140.45	0.00	0.00	0.00	2.39	0.05
35	155.37	0.00	0.00	0.00	2.76	0.06
45	161.10	0.00	0.00	0.00	2.34	0.05
45 ^a	174.30	3.43	5.98	1.91	2.82	0.06
55 ^a	189.19	3.11	5.89	1.88	2.66	0.06
55	229.43	0.00	0.00	0.00	1.94	0.04
65	151.47	0.00	0.00	0.00	3.26	0.07
65	180.70	0.00	0.00	0.00	5.38	0.12
65 ^a	152.32	3.96	6.03	1.92	3.17	0.07

^aNesquehonite-bearing samples

Table A4.12. Solid phase Mg mass balance for the 60% saturated column.

Depth (cm)	Total sample mass (g)	MgO (%)	Brucite abundance (wt.%)	Total mass MgO in sample (g)	Total moles Mg in sample	Moles Mg in dolomite	Moles Mg in brucite	Moles Mg in secondary carbonates	Moles Mg in nesquehonite	Moles Mg in flakey carbonate	Mass Mg in flakey carbonate (g)
5	141.97	5.45	4.72	7.74	0.19	0.01	0.11	0.07	0.00	0.07	1.72
5	144.76	6.21	5.64	8.99	0.22	0.01	0.14	0.08	0.00	0.08	1.84
5	146.49	5.76	4.97	8.44	0.21	0.00	0.12	0.08	0.00	0.08	1.91
15	136.26	6.25	5.13	8.52	0.21	0.01	0.12	0.09	0.00	0.09	2.07
25	153.51	5.93	4.97	9.10	0.23	0.01	0.13	0.09	0.00	0.09	2.16
35	157.71	5.92	4.47	9.34	0.23	0.01	0.12	0.11	0.00	0.11	2.53
35	140.45	5.80	4.20	8.15	0.20	0.01	0.10	0.10	0.00	0.10	2.28
35	155.37	6.06	5.13	9.42	0.23	0.01	0.14	0.09	0.00	0.09	2.19
45	161.10	5.79	4.76	9.33	0.23	0.01	0.13	0.09	0.00	0.09	2.26
45 ^a	174.30	5.54	2.49	9.65	0.24	0.01	0.07	0.16	0.04	0.11	2.72
55 ^a	189.19	6.06	1.35	11.47	0.28	0.01	0.04	0.23	0.04	0.19	4.60
55	229.43	5.78	5.02	13.27	0.33	0.01	0.20	0.12	0.00	0.12	2.98
65	151.47	6.64	4.24	10.06	0.25	0.01	0.11	0.13	0.00	0.13	3.13
65	180.70	6.99	4.18	12.63	0.31	0.00	0.13	0.18	0.00	0.18	4.41
65 ^a	152.32	6.44	3.11	9.81	0.24	0.01	0.08	0.16	0.04	0.11	2.69

^aNesquehonite-bearing samples

Table A4.13. Solid phase H₂O mass balance for the 60% saturated column..

Depth (cm)	Total sample mass (g)	Volatile ^b (%)	Total volatile mass in sample (g)	Volatile mass in brucite (g)	Volatile mass contributed by CO ₂ (g)	Volatile mass contributed by water in carbonates (g)	Moles water in carbonates	Moles water in nesquehonite	Moles water in flakey carbonate	Mass water in flakey carbonate (g)
5	141.97	4.32	6.13	2.24	2.05	1.84	0.10	0.00	0.10	1.84
5	144.76	4.49	6.50	2.74	2.09	1.68	0.09	0.00	0.09	1.67
5	146.49	4.22	6.18	2.44	2.08	1.66	0.09	0.00	0.09	1.66
15	136.26	4.98	6.79	2.34	2.30	2.14	0.12	0.00	0.12	2.14
25	153.51	5.06	7.77	2.56	2.91	2.30	0.13	0.00	0.13	2.30
35	157.71	5.38	8.48	2.36	3.12	3.00	0.17	0.00	0.17	3.00
35	140.45	5.43	7.63	1.98	2.91	2.73	0.15	0.00	0.15	2.73
35	155.37	5.75	8.93	2.67	3.28	2.98	0.17	0.00	0.17	2.98
45	161.1	5.08	8.18	2.57	2.86	2.75	0.15	0.00	0.15	2.75
45 ^a	174.3	8.66	15.09	1.46	5.45	8.19	0.45	0.13	0.32	5.84
55 ^a	189.19	5.75	10.87	0.85	5.14	4.88	0.27	0.13	0.14	2.57
55	229.43	4.54	10.42	3.86	2.62	3.94	0.22	0.00	0.22	3.94
65	151.47	7.02	10.63	2.15	4.06	4.42	0.25	0.00	0.25	4.41
65	180.7	8.00	14.46	2.53	5.38	6.54	0.36	0.00	0.36	6.53
65 ^a	152.32	11.79	17.96	1.59	5.66	10.71	0.59	0.13	0.46	8.34

^aNesquehonite-bearing samples

^bDetermined by Loss-on-ignition

Table A4.14. Overall reaction stoichiometry and stoichiometry of flakey carbonate phase in the 60% saturated column.

Depth (cm)	Overall reaction stoichiometry			Flakey carbonate phase stoichiometry		
	Mg:C	H ₂ O:C	H ₂ O:Mg	Mg:C	H ₂ O:C	H ₂ O:Mg
5	1.5	2.2	1.4	2.0	2.9	1.4
5	1.6	2.0	1.2	2.2	2.7	1.2
5	1.7	2.0	1.2	2.1	2.5	1.2
15	1.7	2.3	1.4	2.1	2.8	1.4
25	1.4	1.9	1.4	1.6	2.3	1.4
35	1.5	2.3	1.6	1.8	2.8	1.6
35	1.4	2.3	1.6	1.7	2.8	1.6
35	1.2	2.2	1.8	1.5	2.6	1.8
45	1.4	2.3	1.6	1.8	2.9	1.6
45 ^a	1.3	3.7	2.9	1.8	5.1	2.9
55 ^a	2.0	2.3	1.2	3.2	2.4	0.7
55	2.1	3.7	1.8	2.8	5.0	1.8
65	1.4	2.7	1.9	1.8	3.3	1.9
65	1.5	3.0	2.0	1.5	3.0	2.0
65 ^a	1.2	4.6	3.8	1.6	6.4	4.1
Average^b:	1.5	2.6	1.8	1.9	3.0	1.6

^aNesquehonite-bearing samples^bNesquehonite-bearing samples not included in calculation of average stoichiometry of the flakey carbonate phase.

A4.3.6 Energy dispersive spectroscopy results

Representative energy dispersive spectra (EDS) collected from reaction products are presented in Figure A4.7.

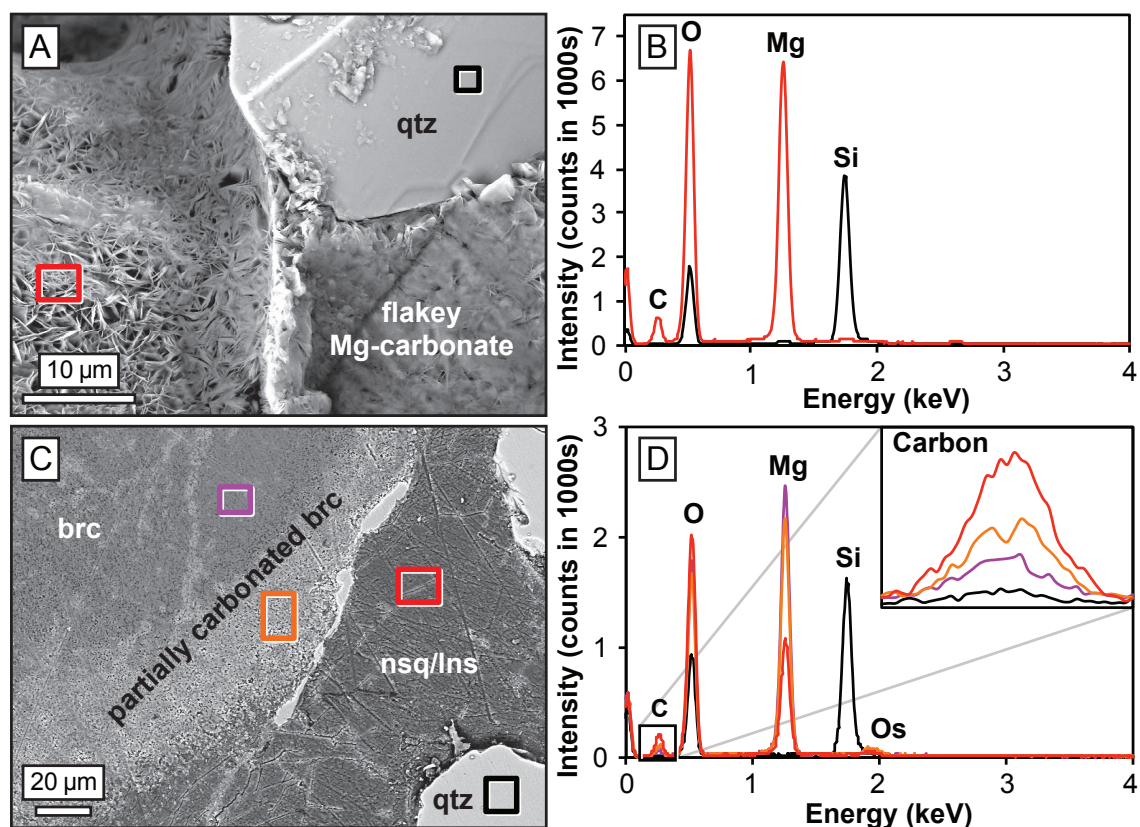


Figure A4.7. Scanning electron micrograph of flakey Mg-carbonate adjacent to a quartz (qtz) grain from 0-10 cm depth in 35% 1 (A) and energy dispersive spectra (EDS) (B) collected from this area. C) Scanning electron micrograph of a thin section showing partially carbonated brucite (brc) surrounded by nesquehonite (nsq) or lansfordite (lns) from 65-70 cm depth in 35% 1 and EDS (D) collected from this area. Rectangles in (A) and (C) indicate the locations from which EDS were collected. The color of the rectangles corresponds to spectra of the same color in (B) and (D). A gradient in the extent of carbonation is evident in (C), as illustrated by the inset in (D).

A4.3.7 Stable carbon isotopic composition

The stable carbon isotopic composition of the solid phase experimental products, the gas phase and the dissolved inorganic carbon are provided in Tables A4.15-A4.17.

Table A4.15. Stable carbon isotopic composition of solid experimental products.

Depth midpoint (cm)	Bulk measurement: $\delta^{13}\text{C}$ (‰ VPDB)			Calculated secondary carbonate: $\delta^{13}\text{C}$ (‰ VPDB)		
	35% saturated 1	35% saturated 2	60% saturated	35% saturated 1	35% saturated 2	60% saturated
5	nd ^a	-20.0	-22.3	nd	-25.3	-27.2
5	nd	-17.5	-21.9	nd	-22.5	-27.5
5	nd	-16.7	-21.7	nd	-20.5	-25.7
15	nd	-19.8	-22.1	nd	-26.6	-25.9
25	nd	-21.6	-22.5	nd	-27.2	-29.0
35	-22.3	-21.7	-23.3	-26.3	-24.7	-26.4
35	-23.9	-22.3	-23.5	-27.6	-27.3	-27.2
35	-23.4	-22.5	-23.9	-27.3	-27.0	-27.2
45	-23.7	-23.1	-26.6	-26.8	-26.0	-31.1
45	nd	nd	-23.4	nd	nd	-26.0
55	-24.8	-23.5	-22.9	-27.6	-25.8	-25.0
55	nd	nd	-21.6	nd	nd	-26.9
65	-23.5	-22.4	-27.7	-25.0	-24.4	-32.9
65	-25.2	-25.3	-24.0	-27.3	-28.0	-24.0
65	nd	-26.1	-26.4	nd	-30.1	-28.6

^ano data

Table A4.16. Stable carbon isotopic composition of gas phase CO₂ and dissolved inorganic carbon (DIC) versus time in 35% 2.

Time (h)	$\delta^{13}\text{C}$ of gaseous CO ₂ (‰ VPDB)		$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	
	Middle	Top	Base	Middle
0	-36.5	-36.5	-12.6	-12.2
3	nd ^a	nd	-30.0	-15.6
4	nd	nd	-30.8	-14.0
6	nd	nd	-30.0	-27.1
8	nd	nd	-29.4	-32.7
12	nd	nd	-28.9	-40.0
16	nd	nd	-28.3	-38.8
24	nd	nd	-29.4	-37.1
32	nd	nd	nd	-34.2
47	nd	nd	-30.2	-34.6
71	nd	nd	-29.6	-34.4
95	nd	nd	-29.4	-32.1
119	-42.4	nd	-27.5	-29.4
143	-40.1	-46.3	-26.3	-28.3
168	-39.1	-42.0	-25.7	-27.0
192	-38.4	-40.8	-25.7	-27.5
215	-38.4	-39.6	-26.5	nd
239	-37.8	-39.0	-25.6	-26.0
288	-37.7	-38.2	-25.6	-26.9
336	-37.1	-37.7	-26.5	-27.5
384	-37.2	-37.9	-26.8	nd
431	-37.4	-38.1	-27.4	-26.4

^ano data

Table A4.17. Stable carbon isotopic composition of gas phase CO₂ and dissolved inorganic carbon (DIC) versus time in the 60% saturated experiment.

Time (h)	$\delta^{13}\text{C}$ of gaseous CO ₂ (‰ VPDB)		$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	
	Middle	Top	Base	Middle
0	-36.7	-36.7	-11.5	-10.1
2	nd ^a	nd	-20.7	-19.9
4	nd	nd	-24.3	-35.6
6	nd	nd	-25.7	-34.7
8	nd	nd	-27.6	-33.0
12	nd	nd	-28.4	-31.9
16	nd	nd	-29.1	-31.8
24	nd	nd	-30.4	-31.4
32	nd	nd	-31	-30.5
47	-43.2	nd	-30.8	-29.8
72	-41.2	nd	-30.9	-29.3
97	-39.6	nd	-30.0	-28.1
121	-38.5	nd	-30.0	-27.4
144	-38.0	-40.8	-29.2	-27.2
168	-37.6	-39.7	-29.5	-27.4
192	-37.7	-39.1	-29.1	-27.1
216	-37.5	-39.5	-28.8	-27.0
240	-37.3	-38.7	-28.1	-26.8
265	-37.5	-39.0	-28.3	-26.6
289	nd	-38.9	nd	nd
313	-36.9	nd	-28.3	-26.8
360	-36.9	-38.7	-28.2	-26.7
408	-37.0	-37.0	nd	-26.5
457	-38.6	-37.0	-28.0	-26.6
504	-38.0	-38.0	-27.7	-26.7

^ano data

A4.3.8 Water film model and modeling results

The threshold brucite volume fractions (i.e., total possible extent of reaction) applied in the MIN3P-DUSTY models are illustrated in Figure A4.8. The carbonate mineral abundance predicted by the base case, dry pore, and water film models in MIN3P-DUSTY are illustrated in Figure A4.9.

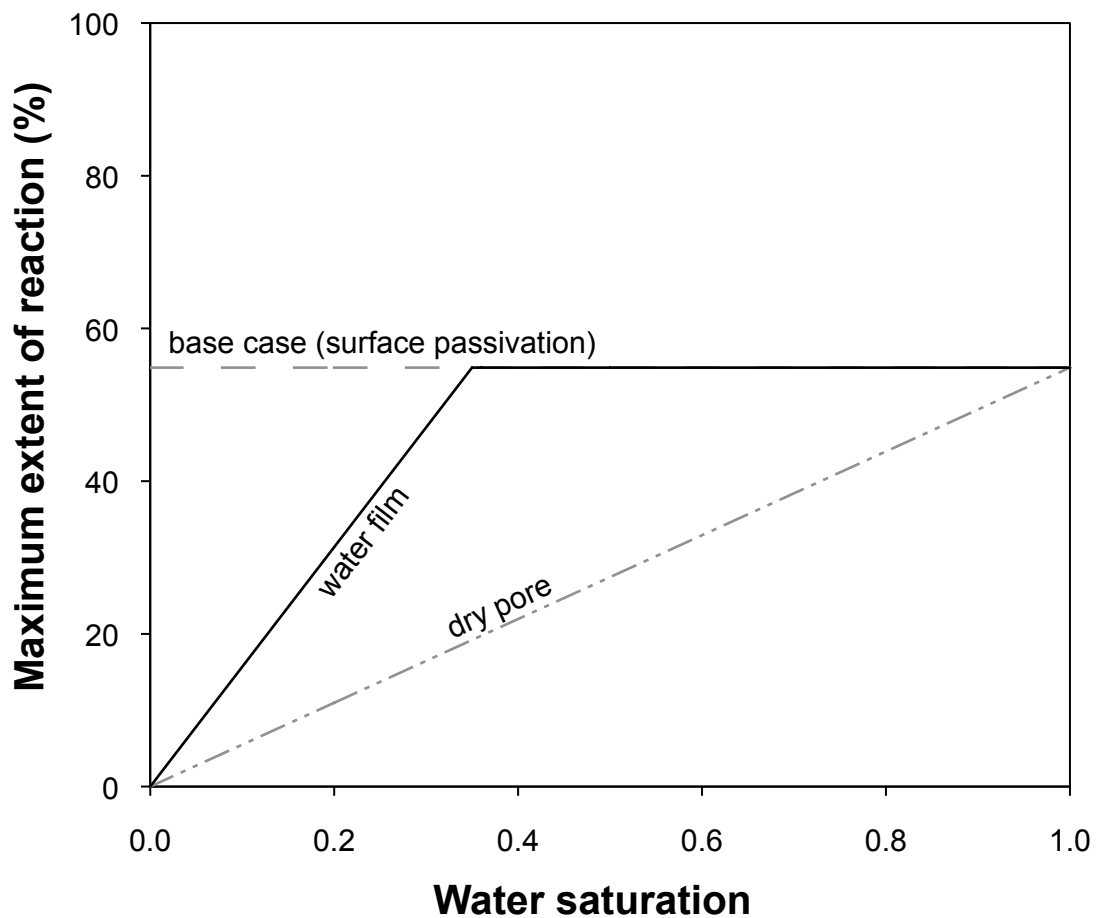


Figure A4.8. The functional relationship between the maximum extent of reaction possible and water saturation as employed in the MIN3P-DUSTY models.

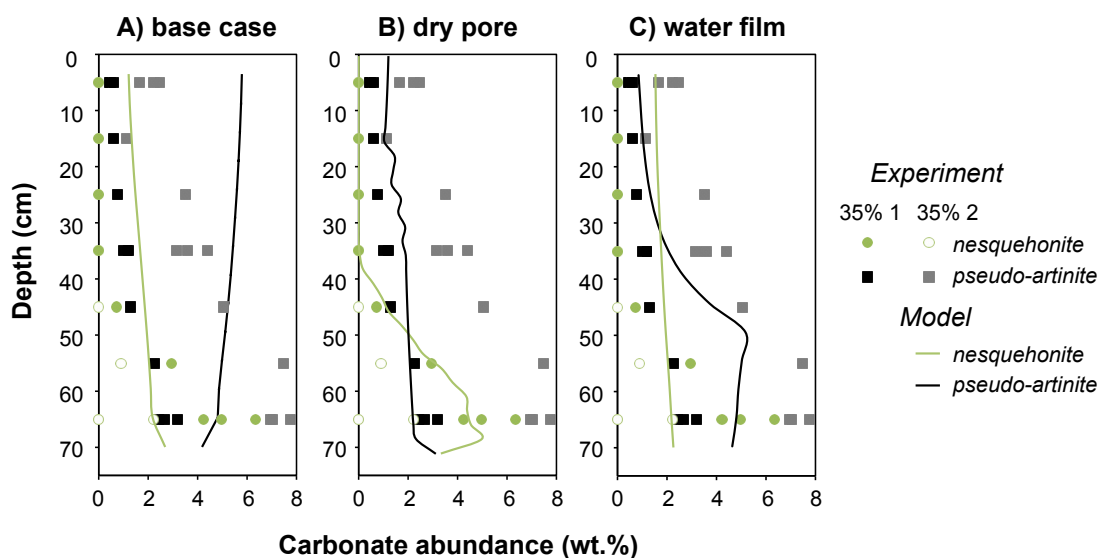


Figure A4.9. Carbonate mineral abundance versus depth in the 35% saturated experiments and predicted by the base case (A), dry pore (B), and water film (C) MIN3P-DUSTY models. Experimental data are represented by points, and model outputs by lines. Filled and open green circles represent measured nesquehonite abundances in 35% 1 and 2, respectively. Black and grey squares represent pseudo-artinite abundances in 35% 1 and 2, respectively. The abundance of pseudo-artinite was calculated by mass balance using the solid phase %CO₂ measurements and the calculated stoichiometry of pseudo-artinite (178.66 g mol⁻¹). The green and black lines represent modeled nesquehonite and pseudo-artinite abundances, respectively. Artinite is used as a proxy for pseudo-artinite in the models.

A4.4 Pore volume change calculations

The total change in solid volume (ΔV_s) during carbonation is calculated as follows:



$$\Delta V_s = \frac{\frac{\nu_B}{\nu_A} (n_{A,i} - n_{A,t}) M_B}{\rho_B} - \frac{(n_{A,i} - n_{A,t}) M_A}{\rho_A} \quad (\text{Eq. A4.4})$$

where $n_{A,i}$ and $n_{A,t}$ are the moles of reactant initially present and at a given time, respectively, M_A and M_B are the molar mass of the reactant and product, respectively, ρ_A and ρ_B are the density of the reactant and product, respectively, and ν_x is the stoichiometric coefficient of a given reactant or product. The net change in water volume in the pores (ΔV_w) can be calculated according to:

$$\Delta V_w = \frac{\frac{\nu_w}{\nu_A} (n_{A,i} - n_{A,t}) M_w}{\rho_w} \quad (\text{Eq. A4.5})$$

where M_w and ρ_w are the molar mass and density of water, respectively. It follows that the net change in gas-filled pore volume (ΔV_p) is:

$$\Delta V_p = \Delta V_w - \Delta V_s \quad (\text{Eq. A4.6})$$

If a decline in porosity is assumed to equate to a decline in permeability, $\Delta V_p > 0$ would provide a positive feedback that amplifies fingers, whereas $\Delta V_p < 0$ would lead to negative feedback that dampens fingers. The ΔV_p was calculated for the common Mg-carbonate products that form during carbonation of Mg-bearing minerals for a porous medium representative of

the column experiments, with 10 wt.% brucite and 90 wt.% quartz and 52% initial porosity. The initial gas filled pore volume was equal to 60% of the total pore volume (~31% of total porous medium volume). In all cases, a net loss in ΔV_p is expected (Fig. A4.10), save for that calculated for pseudo-artinite with its maximum estimated density (i.e., equal to that of magnesite).

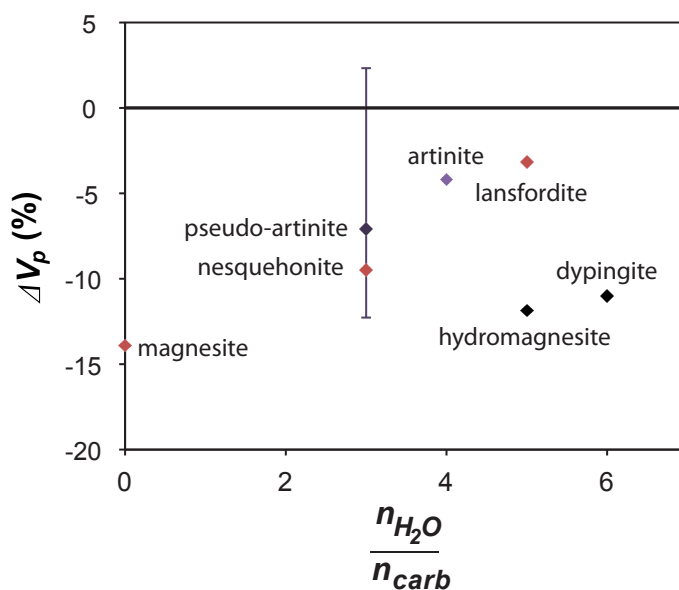


Figure A4.10. Gas filled pore volume change (ΔV_p) versus the molar ratio of water to carbonate ($\frac{n_{H_2O}}{n_{carb}}$) for different Mg-carbonate minerals that are common reaction products during carbonation. A negative value for the change in gas filled pore-volume indicates that it is reduced. Error bars on the pseudo-artinite data point represent the range in pore space changes depending on the density of this phase used in the calculations, as the true density is unknown. Upper and lower limits represent calculations using the highest and lowest density of all Mg-carbonates shown (i.e., magnesite and lansfordite, respectively). The data point is plotted for a density equal to that of artinite.

Appendix 5: Appendix to Chapter 7¹²

Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining

A5.1 Initial and boundary conditions and parameters used in reactive transport models

An atmospheric boundary condition was employed at the surface of a 2.0 m deep section of tailings to capture the effects of evaporation. Sinusoidal functions to represent seasonal fluctuations in relative humidity and temperature were employed for the atmospheric boundary based on data from a nearby weather station, similar to the method employed by Bea et al. (2012) to model the inactive tailings storage facility (TSF) at Mount Keith (TSF1). Temperature and relative humidity varied between 11°C and 37°C, and 19% and 68%, respectively. Rainfall events were applied to the tailings surface, in accordance with weather data recorded at a nearby weather station (Leinster Airport) in 2010, as short duration events that were repeated annually (after Bea et al., 2012; data from the Australian Government Bureau of Meteorology, 2013). Because the atmosphere was deemed to have the most significant influence on the energy balance, a zero energy flux condition was applied at the base of the tailings. A constant head boundary condition (pressure head = 0.0 m) was applied at the base of the tailings to simulate a water table depth at 2.0 mbgs, as is consistent with field observations. Tailings at Mount Keith are deposited as a ~50% slurry of solids and water by mass; therefore, the model

¹²A version of this Appendix is published as the Supporting Information to Wilson et al. (2014). The full version of the Supporting Information can be found in the online version of the paper: doi:10.1016/j.ijggc.2014.04.002. It is partially reproduced here with permission from *International Journal of Greenhouse Gas Control*, 25, Wilson, S. A., Harrison, A. L., Dipple, G. M., Power, I. M., Barker, S. L. L., Mayer, K. U., Fallon, S. J., Raudsepp, M. and Southam, G., Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining, 121-140, Copyright (2014), with permission from Elsevier.

domain was initially saturated. All simulations involved 1-dimensional vertical flow only, as is justified by the low hydraulic conductivity of the fine-grained tailings and low horizontal head gradients, which would cause flow to be primarily vertical.

Primary minerals included in the simulations comprised: serpentine (chrysotile), brucite, magnesite, calcite, and dolomite (Table A5.1). An initial value of 2.5 wt.% brucite was estimated based on its average abundance at depth within TSF2, where it presumably was exposed to the atmosphere for a shorter duration, thereby limiting the extent of its dissolution prior to sampling. Hydrotalcite-group minerals were not included in the simulations owing to the lack of data regarding dissolution rates, and the relatively minor abundance of these phases in tailings. Secondary phases that were allowed to precipitate included: hydromagnesite, halite, chalcedony, gypsum, blödite, epsomite, hexahydrite, and nesquehonite (Table A5.1). Dissolution and precipitation of the primary mineral phases were simulated as kinetically controlled reactions. A far from equilibrium dissolution rate law for chrysotile, a serpentine polymorph, from Thom et al. (2013), was used to describe bulk serpentine dissolution. Although the rate and pH dependence of dissolution for lizardite, antigorite, and chrysotile could differ, the Thom et al. (2013) rate law was used successfully by Bea et al. (2012) to reproduce the observed abundance of serpentine in the inactive TSF1 at Mount Keith. Serpentine dissolution was considered an irreversible reaction whereas brucite dissolution was considered reversible, occurring at a pH-dependent rate prescribed by Pokrovsky and Schott (2004). All other primary phases (calcite, dolomite, and magnesite), were allowed to dissolve only. This is justified by the field-derived mineralogical and isotopic data, which indicate that these phases are unlikely to precipitate in the tailings. Moreover, precipitation of magnesite and dolomite is kinetically inhibited at low temperature (e.g., Hänchen et al., 2008; Kenward et al., 2009), and aragonite precipitation is likely to be favored over calcite due to the high Mg:Ca ratio of the process waters (e.g., De Choudens-Sanchez and Gonzalez, 2009). The kinetic dissolution rate laws, initial mineral abundances, and estimated reactive surface areas for primary phases are summarized in Table A5.1. Precipitation of secondary minerals

was simulated as a quasi-equilibrium process. Table A5.2 provides the composition of the pore water, replenished process water, and boundary (rain water) solution employed in the reactive transport modeling, and Table A5.3 gives the physical and transport parameters that were used.

Table A5.1. Initial mineral abundances, effective reactive surface areas, and dissolution rate laws applied in MIN3P.

	Upper 10 cm ^a	Lower 190 cm		
Phase	Abundance (wt.%)	Abundance (wt.%)	Effective Surface area ^c (m ² g ⁻¹)	Dissolution/precipitation reaction
<i>Initial</i>				
Chrysotile	88.25	87.46	0.6	kinetic (Thom et al., 2013)
Brucite	2.50 ^b	1.34	0.3 ^d	kinetic (Pokrovsky and Schott, 2004)
Dolomite	1.50	1.5	6.9×10^{-5}	kinetic (Chou et al., 1989)
Magnesite	7.50	7.5	6.6×10^{-4}	kinetic (Palandri and Kharaka, 2004)
Calcite	0.25	0.25	3.7×10^{-3} ^e	kinetic (Chou et al., 1989)
Hydromagnesite	0.00 ^b	1.95	n/a	quasi-equilibrium
<i>Secondary only</i>				
Nesquehonite	0.00	0.00	n/a	quasi-equilibrium
Halite	0.00	0.00	n/a	quasi-equilibrium
Chalcedony	0.00	0.00	n/a	quasi-equilibrium
Gypsum	0.00	0.00	n/a	quasi-equilibrium
Bloedite	0.00	0.00	n/a	quasi-equilibrium
Epsomite	0.00	0.00	n/a	quasi-equilibrium
Hexahydrite	0.00	0.00	n/a	quasi-equilibrium

^aApplies to entire domain for process water replenishment model.

^bA linear decline from 1.95 wt.% to 0.00 wt.% is applied in the upper 10 cm of the hydromagnesite burial model with the opposite trend (1.34 - 2.50 wt.% from depth to surface) applied for brucite.

^cEffective surface areas from Bea et al. (2012) unless otherwise specified.

^dEstimated from data from Harrison et al. (2013).

^eEstimated in this study using field observations.

Table A5.2. Water chemistry of initial pore water, replenished process water, and rain water (boundary solution).

	Initial condition (process water and pore water)	Boundary condition (rain water)
Variable	Concentration (M)	Concentration (M)
pH ^a	8.85	6.00
Cl	0.88	0.01
Na	0.78	0.01
K	0.03	1.54×10^{-4}
Mg	0.10	7.41×10^{-4}
Ca	0.01	1.05×10^{-3}
H ₄ SiO ₄	1.51×10^{-4}	1.03×10^{-4}
SO ₄	0.09	1.88×10^{-3}
pCO ₂ ^b	3.50×10^{-4}	3.50×10^{-4}
pO ₂ ^b	0.21	0.21

^aUnitless^bUnit = atm**Table A5.3.** Physical and transport parameters employed for simulations using MIN3P.

Parameter ^a	Value	Reference
Saturated hydraulic conductivity (m s ⁻¹)		
<i>Hydromagnesite burial</i>	4.88×10^{-8} ^b	Stolberg (2005)
<i>Process water replenishment</i>	4.88×10^{-6}	estimated after Stolberg (2005)
Porosity	0.46	(Stolberg, 2005)
Soil-water retention curve		
α (m ⁻¹)	0.80	Bea et al. (2012)
n	1.40	Bea et al. (2012)
S _{ri}	1.00×10^{-3}	Bea et al. (2012)
Gas phase diffusion coefficient (m ² s ⁻¹)	1.65×10^{-5}	Molins and Mayer (2007)
Aqueous phase diffusion coefficient (m ² s ⁻¹)	8.00×10^{-10}	Mayer et al. (2002)
Process water flux (m ³ s ⁻¹)		
<i>Hydromagnesite burial</i>	0.00	n/a
<i>Process water replenishment</i>	3.40×10^{-8}	n/a

^aAll other relevant physical and transport parameters and constants are provided by Bea et al. (2012).^bAverage of two measurements.

A5.2 Detailed CO₂ flux and carbonation rate calculations

In order to evaluate the effect of tailings permeability on brucite carbonation rates, the CO₂ flux that could be achieved at various values of saturated hydraulic conductivity was calculated. Calculations were made under the assumption that the elevation gradient was the driving force for flow, and that water flow was governed by Darcy's law in the saturated zone (Eq. A5.1). In addition, the rate of CO₂ supply was assumed to be rate-limiting for brucite carbonation, as is consistent with field and modeling data. Thus, the CO₂ flux was equated to the brucite carbonation rate, and was calculated according to Equation A5.2 for a 50 cm thick deposit of fresh tailings.

$$Q = \left(AK \left[\frac{dh}{dl} \right] \right) 1000 \quad (\text{Eq. A5.1})$$

Where Q is the volumetric flow rate (m³ s⁻¹), $\frac{dh}{dl}$ is the head gradient across the TSF, K is the saturated hydraulic conductivity (m s⁻¹), A is the cross-sectional area through which the water flows (m²), and '1000' is a conversion factor from m³ to L of water.

$$r_{CO_2} = b \frac{[DIC]}{Q} \quad (\text{Eq. A5.2})$$

Where $[DIC]$ is the concentration of dissolved inorganic carbon (CO₂) in solution at equilibrium with a given CO₂ partial pressure in the gas phase (M), b is a stoichiometric conversion factor to convert the brucite dissolution rate to a CO₂ sequestration rate in hydromagnesite, and r_{CO_2} is the CO₂ sequestration rate in mol s⁻¹.